

Review

# Reuse and Valorization of Solid Digestate Ashes from Biogas Production

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**Abstract:** Digestate is produced in large quantities by the anaerobic digestion process, which is recognized to be a promising technology for producing bioenergy from biological waste. Digestate is a highly humid by-product containing organic and inorganic substances, including nutrients that make it suitable for soil applications. However, it can be considered a high-risk environmental contaminant if it is not correctly treated. For these reasons, thermochemical treatment is one of the alternatives for valorizing the digestate, leading to a high ash quantity. This review aims to investigate the formation of ash derived from thermochemical valorization treatments of digestate. Furthermore, considering the compositions of the elements present in these ashes, an additional objective is to identify possible prospects for the reuse of these ashes following a circular economy approach.

**Keywords:** ashes from digestate; reuse; valorization of waste; biogas; circular economy

## 1. Introduction

The increase in waste production from human activities and industrial and agricultural processes is a significant issue with adverse socioeconomic effects, endangering sustainable development [1] and irreversibly polluting the environment [2]. Global urbanization and industrial and economic processes produce solid waste that the Earth cannot sustain without suffering irreversible consequences [3,4]. The continuous increase in the formation of solid waste [5], sewage sludge generated from wastewater treatments [6], farming [7], and food residues [8] is an alarming problem. Its resolution should become a universal priority [5]. The global population is predicted to become very nearly 10 billion by 2050, causing a continued raise in the requirement for energy, food, and water [9]. This will cause a growth in waste production. For example, the quantity of the organic fraction of municipal solid waste (OFMSW) generated in 2020 was estimated at about 61 Mt and probably will reach 100–140 Mt by 2040 [10]. Compared to 2016, on average, individual generation of this waste has increased by 29.67%, and the environmental impact of OFMSW is expected to grow by 70 to 148% by 2040, the final result determined by different socioeconomic development paths [10].

This increase in waste production drives the search for strategies and technologies to limit the disposal of and valorize waste reuse according to a circular economy approach. For this reason, in response to the issue of huge organic waste deposits and the necessity of new renewable, low-carbon energy resources, scientific research has begun to investigate the potential of biowaste for energy production [9,11,12].

Compared to established waste discarding approaches in landfill or by incineration, Anaerobic Digestion (AD) is a biological treatment that represents a sustainable energy recovery via biogas (50–75% methane, 25–50% carbon dioxide, and 1–2% hydrogen sulfide, hydrogen, and ammonia) production [8]. AD is particularly advantageous for high-humidity biomasses, such as energy crops, food, and sewage sludge [8,13,14]. The AD process involves four main phases: hydrolysis, acidogenesis, acetogenesis, and methanogenesis [13–15]. The organic biomass is decomposed into biogas by a microbial consortium,



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generating a significant amount of nutrient-rich and partially degraded organic liquid-solid residue called digestate [16,17]. Biogas is a valuable fuel that can be upgraded to biomethane and used to replace fossil natural gas [18].

Biogas production may have various advantages, such as reducing the environmental impact of industrial and agricultural activities, allowing green energy generation, and reducing fossil fuel usage [19]. Moreover, AD allows for the production of biogas from several raw organic materials [5,20–23]. Among these, the best candidates are wastes of agricultural, municipal, or industrial origin: farming, wood, and dairy waste, municipal sewage sludge, dedicated crops, animal manure, algae cultivation, and wastewater treatment sludge from, dairy and palm oil mills [5].

In Europe, energy crops, manure, and agriculture residues are the primary sources of biogas via AD. Additional feedstocks are sludge from wastewater treatment, OFMSW, or solid waste disposed in landfills [24–26].

Modern industrial-scale biogas plants have been realized in Western Europe since the 1980s, though it is only in recent decades that a broad increase in installations was promoted. This effect results from commitments made by EU countries to reduce GHG emissions and promote renewable energy development [5,27–29]. In Europe, the biogas-biomethane sector supplies a quantity of renewable gas greater than  $18 \times 10^9 \text{ m}^3$  [30]. Renewable gas is a fundamental key to the REPowerEU strategy to moderate climate change and enhance the EU's strategic autonomy [30].

In 2013, the number of biogas plants in Europe exceeded 13,000 units, and the corresponding primary energy was 13.4 Mtoe [19]. Among European supply chains, the greatest biogas production was found in Germany, while Italy is currently second after the German supply chain [30,31]. These two countries consume 52% and 11% of the European gross final energy consumption of biogas, respectively [30]. In 2017, the total electric energy produced from biogas was 0.088 GWh, of which 40% was generated in Germany [32]. In Poland, the first biogas plant was activated in 2005. By mid-2020, 310 biogas plants reached a total power capacity of 245  $\text{MW}_e$ , of which only 120 were agricultural biogas plants (128 in 2021) of 101  $\text{MW}_e$  target capacity [5]. The potential biogas production is about  $13\text{--}15 \times 10^9 \text{ m}^3$  per year, with  $7\text{--}8 \times 10^9 \text{ m}^3$  of biomethane yearly, while Poland consumes approximately  $14 \times 10^9 \text{ m}^3$  of natural gas annually [29]. For these reasons, biomethane represents a promising alternative to accelerate the energy transition from fossil fuels to renewable ones, and this is in line with regulations and climate change that support the need to limit (or cast off) fossil fuel consumption [33].

AD represents the most well-known, efficient, and mature technology for OFMSW treatment and is a viable alternative to landfill for different categories of waste (food industry, domestic, and abattoir wastes, etc.). They provide three assets, i.e., safe waste disposal, a sustainable supply for biogas production, and a socially accepted technology [34,35]. On the other hand, a recognized drawback comes in the form of concomitant large production of digestate, leading to a potential environmental problem that requires effective disposal [36]. Digestate contains a low amount of dry matter and has a high nutrient concentration [37], including nitrogen and phosphorus [19]. Its storage, transport, and utilization are not cost-effective [37]. The continuous increase in digestate is directly due to the growing number of biogas plants, based on an estimated  $20 \text{ m}^3/(\text{year kW}_e)$  digestate [19]. It means that a 500  $\text{kW}_e$  AD plant yearly generates more than 10 ktons of solid digestate [16]. According to the circular economy approach, efficiently managing massive amounts of solid digestate, rich in moisture content, has become a challenge for research interests and development of alternative treatment methods [8]. The potential energy recovery of organic matter via thermochemical processes could be a different and valid approach. However, the high water content in the digestate could limit the direct applicability of combustion or pyro-gasification processes. Some tentative solutions are already available in the literature and are considered in this review, but the reusability of digestate ash content remains unexplored. From a circular economy perspective, this aspect is relevant and interesting to evaluate as a further opportunity.

This investigation aims to provide an overview of the digestate treatment methods, focusing on the reuse and valorization of the ash obtained from thermochemical treatments. The research was expanded to other organic substances and the possible reuses of the ashes produced from a specific thermal treatment. The authors glimpsed new opportunities for digestate ash with similar compositions, such as sorbent and catalyst synthesis.

The work is developed from the literature review on digestate by evaluating:

- a. Digestate characteristics, management, and current issues
- b. Ash formation by thermochemical processes of the digestate
  - i. by combustion
  - ii. by pyrolysis
  - iii. by gasification
- c. Prospective reuse of ashes

## 2. Digestate Characteristics and Current Issues

### 2.1. Digestate Characteristics

Digestate is the liquid-solid by-product obtained from the anaerobic digestion of organic waste. This by-product contains macronutrients such as N, P, K, plus Ca, S, and Mg, and micronutrients, including B, Cl, Cu, Fe, Ni, Mo, Mn, and Zn. Generally, the digestate characteristics depend on the incoming feedstock, the AD process operating conditions, and the digestate treatments. The composition of the biogas, the specific methane yield, and the composition of the digestate are, therefore, strongly influenced by the treated raw material [38]. Table 1 shows the characteristics of digestates derived from different raw materials; it can be observed that the composition of the digestate varies considerably as a function of the AD feedstock in terms of proximate and ultimate analyses.

**Table 1.** Characteristics of digestate from different AD feedstock (n.a. = not available; <sup>a</sup> percentage of the ash composition).

Digestate Origin *	Composition											Reference
	Ash	C	N	P	Na	Mg	K	Ca	Fe	Si	Al	
Food waste (wt% dry basis)	25.6	42.1	5.8	2.0	n.a.	0.3	0.6	3.2	0.9	n.a.	n.a.	[39]
Food waste (%)	10.2	43.5	1.9	18.8 <sup>a</sup>	5.7 <sup>a</sup>	2.8 <sup>a</sup>	2.8 <sup>a</sup>	14.9 <sup>a</sup>	4.2 <sup>a</sup>	5.6 <sup>a</sup>	7.1 <sup>a</sup>	[40]
Pig manure (wt%)	40.8	34.1	4.3	4.1	0.2	1.3	0.8	9.9	0.8	1.1	0.3	[41]
Swine manure (wt%)	23.0	37.2	4.6	11.5	0.1	0.9	0.1	26.3	0.5	0.7	0.2	[42]
Quinoa residue and wastewater sludge (wt%)	15.9	37.0	2.8	1.7	0.2	0.4	1.3	1.7	0.5	n.a.	n.a.	[43]
Kitchen waste and domestic waste (% dry basis)	42.1	23.1	3.6	1.1 <sup>a</sup>	0.7 <sup>a</sup>	n.a.	1.0 <sup>a</sup>	28.6 <sup>a</sup>	3.0 <sup>a</sup>	3.3 <sup>a</sup>	1.2 <sup>a</sup>	[44]
Corn silage and small proportion of cattle slurry (wt% TS)	20.5	40.2	3.2	0.9	0.4	0.8	4.8	2.1	n.a.	1.9	0.1	[45]
Maize silage, grass and grass silage, Potatoes (% dry basis)	18.3	45.3	2.9	1.3	n.a.	n.a.	1.2	n.a.	n.a.	n.a.	n.a.	[46]
Maize silage, sugar sorghum/sudan grass silage, poultry manure and Corn cob mix (% dry basis)	14.6	43.2	1.5	1.1	n.a.	n.a.	1.1	n.a.	n.a.	n.a.	n.a.	[46]
Energy crop and cow manure (wt% dry basis)	29.2	40.0	1.9	3.1 <sup>a</sup>	0.4 <sup>a</sup>	2.2 <sup>a</sup>	13.2 <sup>a</sup>	6.5 <sup>a</sup>	0.8	19.6 <sup>a</sup>	1.2 <sup>a</sup>	[47]
Agricultural residue (% dry basis)	16.0	44.1	3.2	1.2	0.3	0.7	1.6	1.3	2.3	1.8	n.a.	[48]
Residual municipal solid waste (% dry basis)	55.5	24.1	1.5	0.7	0.9	1.4	1.6	10.4	3.2	10.2	n.a.	[48]
Sewage sludge (% dry basis)	46.9	28.6	3.4	2.7	0.5	0.9	0.7	4.6	3.3	7.6	n.a.	[48]
Vegetable, garden and fruit waste (% dry basis)	43.8	29.5	2.0	2.6	0.5	0.8	0.7	4.3	3.0	7.1	n.a.	[48]
Maize silage, liquid cattle manure, grass silage (% dry basis)	27.7	50.5	3.6	1.4	n.a.	0.9	5.2	2.0	0.3	6.7	0.5	[49]

\* Reported units are those of original literature references.

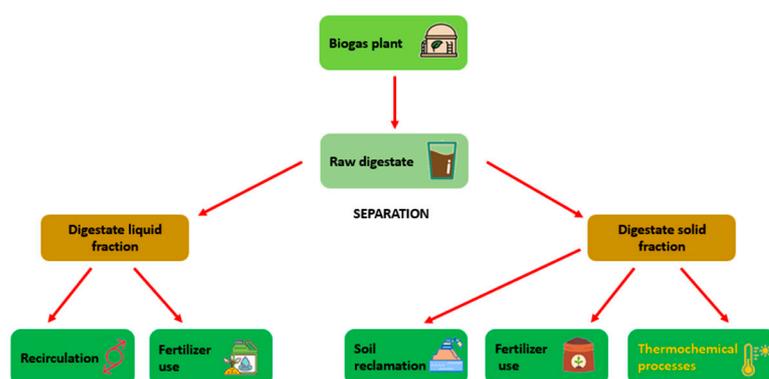
It is possible to point out that the highest value of ash reported in Table 1 reaches 55.5% for residual municipal solid waste (% dry basis) [48]. The lowest ash content found

in digestate from food waste (10.21%) can be explained by the high amount of organic substances in food waste, especially cellulose, proteins, and fats. [40].

## 2.2. Digestate Management and Current Issues

One of the digestate problems is that it has a high water content and consequently occupies a large volume, leading to high transport costs. Therefore, a large amount of space is required for storage facilities. Before use, the digestate is stored and various factors directly influence the needed storage period: environmental limitations and directive constrains, its stabilization, geographical position, type of soil and crop, and seasonal digestate demand [19].

Digestate is rich in elements such as N, K, and P, but it also contains some heavy metals [50], medicines [51], organic impurities [52], or pathogens that can restrict its use [53]. As shown in Figure 1, there are different methods of reusing digestate depending on the quality and the origin of the raw material used for AD; this determines the type and main characteristics of the digestate [19]. Digestate from agricultural, agroindustry by-products, and source-separated biowaste (OFMSW) is mainly used as fertilizer and as a soil conditioner in agriculture horticulture and gardening. Conversely, digestates from sewage sludge and digestate derived by OFMSW are incinerated or landfilled [54]. Overall, 95% of digestate in Europe is used in farming [55].



**Figure 1.** Production and management of the solid fraction of digestate (inspired by [56]).

Thanks to the high nitrogen, phosphorus, and potassium content, the most common and natural use of digestate is soil application as a fertilizer and soil conditioner [57]. In particular, digestate is recognized as a biofertilizer, as it advances the soil's properties with its high nutrients. The slightly alkaline nature is helpful for immobilizing contaminants in degraded agricultural soils, thus representing an added value for the digestate as soil amendment and remediation [8]. Although digestate potentially closes the nutrient cycle in agronomy by reducing the external demand for mineral fertilizers, the application of digestate on agricultural land raises possible problems [58]. The uncontrolled spreading of digestate on the ground can cause the runoff of nutrients [59], especially for digestates derived from the AD of protein-rich biomasses, in which the concentration of TAN (total ammoniacal nitrogen) increases. This limits the use of digestate in areas vulnerable to nutrient pollution of the soil and water [60]. The high phosphorus content of digestate is also worrying because it is responsible for eutrophication pollution (Water Framework Directive, 2000/60/EC). The application of digestates rich in these substances through traditional methods such as spray irrigation causes emissions of ammonia, odor [61], carbon dioxide, and nitrous oxide, posing phytotoxic risks for plants and inducing environmental drawbacks such as acidification in addition to the already mentioned eutrophication phenomena [62–65].

In Europe, various pieces of national legislation establish the maximum nitrogen loads applicable on fields and, consequently, the compulsory minimum capacity required for digestate storage [60]. Depending on the raw material that undergoes the AD process, the

digestate contains the contaminants mentioned above [19]. The digestate obtained from sewage sludge accumulates typical wastewater, often characterized by relevant concentrations of heavy metals (0.5–2%, up to 4% on dry basis) [66], which can restrict its direct agricultural reuse considering the legislation in force [67]. The origin of heavy metals trackable in sewage sludge derives mainly from the contribution of household chemicals, industrial wastewater, and heavy metals present in foods, which are concentrated in the sludge and could make it impossible to apply it to the ground [68]. Moreover, the digestate obtained from manure contains, in addition to heavy metals, pharmaceutical products such as antibiotics, extensively used in livestock farming activities [69]. The environmental regulations regarding pathogens (EU Regulation no. 142/2011 of the Commission) and heavy metals (Directive 86/278/EEC) must be applied to evaluate the quality of the digestate. In addition, national legislatures (Austrian, Swiss, Danish, etc.) have imposed severe standards on quality parameters, especially organic pollutants such as polychlorinated dibenzodioxins (PCDDs), adsorbable organic halogens (AOX), linear alkylbenzene sulfonates (LAS), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs); these are substances known as persistent, bio-accumulative, and toxic (PBT) or very persistent and very bio-accumulative (vPvB), which are of concern since they are persistent and toxic to living organisms [70]. The accumulation of emerging medical contaminants (antibiotics, anti-inflammatory drugs, and antibiotic-resistant genes) in digestate is alarming. It requires additional light to be shed on the safety of the soil [71]. Since digestate is a very wet by-product, transport distances become crucial in the economic feasibility of spreading digestate in land applications [72]. Considering the critical problems in the direct agricultural storage and reuse of digestate, it is necessary to study alternatives that minimize environmental pollution and lead to implementing the integrated biorefinery concept, in line with the European zero-waste strategy [73]. The first necessary treatment is drying this by-product for reuse and transport. Dehydration of digestate overcomes logistical and environmental problems in common digestate management techniques, but an integrated approach inspired by a circular economy perspective would be desirable to contribute to the achievement of decarbonization targets and the containment of environmental and climate damage, i.e., energy production, use of second-generation solid fuel and biochar production [74], and reuse of ashes.

Alternative processes for valorizing and reusing these by-products that have attracted interest at both the academic and industrial levels are thermal treatments, including hydrothermal carbonization (HTC), torrefaction, pyrolysis, and gasification. These thermochemical conversion processes are gaining importance due to the variety of applications for the liquid, solid (chars), and gaseous products obtained, not only from an energy point of view as biofuels or for increasing the CHP efficiency of a biogas power plant but also for the recycling and recovery of secondary raw material promoting circular economy principle [60]. The biochar produced by thermochemical processes of digestate are considered carbon sinks, capable of removing carbon dioxide from the atmosphere and sequestering it long-term [75].

The need to implement thermochemical conversion processes is also given by the accumulation of biogas plants in some regions; this could lead to an oversupply of digestate, especially in areas with intensive livestock farms or where there are several digesters of biological residues and waste. This situation can be more problematic if the agricultural area available is very small; then, for adequate use of the digestate, the excess material must be transported to regions with nutrient deficits, but other solutions must be found more sustainable from an environmental point of view and in line with European regulations [76]. The integration of the AD process with thermochemical treatments can reduce the problems related to the disposal of digested sludge [77] and encourage virtuous circular economies [78]. This review aims at a specific excursus on the formation of ash and the actual uses implemented while also giving space to hypotheses of solutions not yet explored.

### 3. Ash Formation by Thermochemical Processes of the Digestate

Methods of thermochemical valorization of the digestate inevitably lead to ash production [74]. The ash quantities can be very significant due to the initial composition of digestate and, even before, of AD raw materials. Among the recent studies on the thermochemical valorization of digestate, the following stand out: the combustion process [47,79,80], torrefaction process [74,81], pyrolysis and gasification processes [74,82], and HTC processes [83–86]. During thermochemical processes such as combustion, the nitrogen in the digestate is converted into  $\text{NO}_x$ . In contrast, during partial oxidation processes such as gasification, nitrogen can be converted into ammonia and HCN, causing greenhouse gas emissions. Instead, co-gasification and catalytic gasification help reduce the nitrogen compounds in the digestate and recycle them into  $\text{N}_2$ . [87]. Among thermochemical conversion processes, combustion, pyrolysis, and gasification are those that produce ash as the primary solid by-product.

Generally, the ash derived from thermochemical treatment is mainly characterized by oxidated species such as oxides of Si, Al, Fe, Ca, Mg, Na, K, Ti, P, S, and insoluble carbonate, sulfate, and aluminosilicate compounds (each of them can range from 0.1 wt% up to about 100 wt%), as well as trace elements (multiple oxides of V, Cr, Mn, Co, Ni, Cu, Zn, Sr, Mo, and B), frequently <0.1 wt% and rarely up to 1 wt%. The solid by-product composition changes as a function of the treatment temperature because the elements present in the matrix, such as Na, K, Cl, S, and C, showed a relevant gas phase transfer behavior [88–96]. An example emerged in the literature for a significant percentage of ash production from the pyrolysis process of food waste digestate obtained at a temperature range between 300 and 900 °C, reaching 88.1% of dry matter. For this reason, the study of their potential reuse is a fundamental aspect [60].

#### 3.1. Ash Formation by Combustion Process

The combustion process consists of the oxidation of the fed raw material (digestate) in the presence of more oxygen than the stoichiometric one; this is needed for the complete oxidation reactions. Excess oxygen oxidizes all the carbon and volatile compounds at temperatures above 1000 °C [87]. In addition to the heat of combustion (combustion is a highly exothermic process) and the exhaust gases containing  $\text{NO}_x$  from the oxidation of the nitrogen coming from the digestate [87], combustion produces ash as a solid residue [97].

The dried digestate can be used as solid fuel, a valid alternative to classic disposal treatments. Wet digestate must be dried close to the biogas plant, and this solution would reduce transportation and storage costs. The combustion heat and the thermal waste can be spent drying the digestate to dry matter, losing up to approximately 80–90% of its original weight [46].

In 2010, Kratzeisen et al. tested the applicability of biogas digestate as a solid fuel and inferred that, due to the high ash content, which was in their case between 15 and 20%, and the characteristic smell of the digestate, the use of digestate as a fuel is especially suitable near the production point. Two types of digestate, named Digestate A and Digestate B, were derived from the AD treatment of the mixture of feedstock components shown in Table 2 [46] and were tested. These studies determined that the total energy demand of the combustion process of the two investigated digestates is 3.24 kWh/kg. The water content negatively interferes with the energy balance of the process, given that for the decantation treatment (which removes 25% of water) and for the drying treatment (which dehydrates the digestate to the final content of 80–85% of dry matter), 0.12 kWh<sub>e</sub>/kg and 2.97 kWh<sub>th</sub>/kg are required, respectively [46]. From these studies, Kratzeisen et al. have concluded that the examined digestates are recommended as fuel for combustion. The net heating value of Digestate A and B fuel pellets are 15.8 and 15.0 MJ/kg, respectively; this is comparable to the net heating value of wood (pinewood with bark = 16.3 MJ/kg) [46].

**Table 2.** Feedstock composition of digestates used as combustion fuels (wt% of fresh matter) (reproduced from [46]).

Digestate	Feedstock Components	(%)
A	Maize silage	50
	Grass and grass silage	40
	Potatoes	10
B	Maize silage	81
	Sugar sorghum/sudan grass silage	9
	Poultry manure	7
	Corn cob mix	3

Subsequently, the composition of the obtained combustion ash was analyzed; the results of these studies are reported in Table 3. The results compare the ashes from the combustion of the two digestates, A and B, and pine wood with bark ash and energy crop [46].

**Table 3.** Characteristics of digestate ash derived from two mixing of feedstocks compared to pinewood with bark ash.

Digestate	P	K	Mg	Na	Ca	Si	S	Fe	Al	As	Cr	Ni	Reference
	(%)						(mg/kg)						
A	20.4	8.5	2.7	3.1	17.0	18.0	3.2	22.5	3.1	0.8	76	36	[46]
B	26.7	15.5	8.4	0.8	13.6	30.4	0.9	1.8	1.2	1.1	184	285	[46]
Energy crop	3.09	13.15	2.23	0.41	6.53	19.6	0.91	0.80	1.23	n.a.	n.a.	n.a.	[47,98]
Pinewood with bark	2.6	6.4	6.0	0.7	41.7	25.0	1.9	2.3	4.6	4.1	325.5	66	[46,99]

n.a. = not available.

These results show that the ash from the digestates has a higher percentage of P, K, and Ca nutrients than the ash from the pinewood pellets, making these ashes potentially usable on agricultural land. On the other hand, Digestate B and pinewood with bark have an Fe content of about 2%, whereas Digestate A has a Fe percentage ten times higher (22.5%). The explanation for this is that the Fe accumulation in the digestate and then in the related ash of Fe results from the addition of iron chloride for desulphurization during the digestion phases to produce biogas [46]. Comparing these values with the German fertilizer regulation Düngemittelverordnung [100], heavy metal elements such as As, Pb, Cd, Hg, and Tl concentrations in the ash are at acceptable levels, being lower than the threshold values [46]. Due to the characteristics observed, the ash derived from the combustion process is suitable for application as a fertilizer on farming land. Nevertheless, Ni and Cr content higher than the threshold values has been found, and it must therefore be reduced with appropriate methods such as leaching or additional thermal treatments of the ashes [46,101]. Given the presence of these transition metals and elements such as Al and Si, a possible alternative reuse of ashes is as catalysts, catalyst supports [102,103], or sorbent materials for the capture of CO<sub>2</sub> in practical local applications such as biogas upgrading via pressure swing adsorption (PSA) techniques [104]. In the referenced work, the authors synthesized zeolites from combustion ashes.

In 2021, Cao et al. studied the characteristics of ash derived from energy crop digestate; the results are reported in Table 3. The feedstock composition by weight is approximately 42% cattle manure, 20% corn, 28% grass, 9% whole plant silage, and 1% cereals. This feed undergoes wet fermentation at a biogas plant (43 °C) [98]. The produced digestate has an ash content equal to 29.2% by weight, and the reported composition of the ash is obtained at 550 °C. By comparing the characteristics of the energy crop ash with other combustion ashes (see Table 3), the percentages of nutrients such as P and Ca are much lower than those of the digestate ash A and B, whereas the K content is comparable to the other values. Percentages of Al, Si, and Mg are similar to the values present in the ashes of digestates A

and B; therefore, the appreciable presence of elements such as Al, Si, and Mg in these ashes could make these materials suitable for synthesis of sorbent materials [47].

Pedrazzi et al. studied the application of AD digestate pellets of a feedstock composed of manure, corn flour, and straw as biofuels in a domestic furnace. In their study, the average ash content obtained increased from 11.4 wt% at 105 °C to 20.7 wt% at 200 °C. Furthermore, the authors reached the maximum digestate higher heating value of 16.6 MJ/kg at 150 °C. However, to prevent the ash sintering phenomenon, digestate pellets were prepared by mixing 50% of “digestate 1” and 50% of wood [105].

### 3.2. Ash Formation by Pyrolysis Process

Pyrolysis is a thermochemical process that thermally decomposes organic substances in an oxygen-free atmosphere at a temperature range between 300 and 900 °C. Pyrolysis heats the feed (digestate) in an inert atmosphere, releasing organic matter [106]. Among the digestates processed through pyrolysis treatment, digestates from food waste and OFMSW [107–110], digestates from animal manure and agricultural waste [78,83,111], and digestates obtained from sewage sludge and a mixture of different feedstocks [77,112,113] have emerged as case studies. This treatment appears to be less polluting than conventional incineration or combustion methods, as it concentrates the mineral elements in a solid carbonaceous residue. Therefore, its leaching is not as crucial as that which occurs with incineration ash [114]. The involved reactions are mostly thermal decomposition and condensation. Conversely to the highly exothermic combustion process, pyrolysis is an endothermic process of about 100 kJ/kg [107]. Generally, the products of pyrolysis are an incondensable gaseous phase, mainly composed of H<sub>2</sub>, CH<sub>4</sub>, CO, and CO<sub>2</sub>, a liquid fraction made up of a bio-oil containing acetic acid, acetone, and methanol, as well as heavy hydrocarbons, and a solid fraction known as biochar, which in most cases consists of carbon and ash [106]. As shown by the results obtained by Liu et al., it is possible to observe that as the pyrolysis temperature increases, the weight percentage of volatile substances decreases, and consequently, the ash content increases [40].

#### 3.2.1. Ash Formation by Pyrolysis from Food Waste and OFMSW Digestate

Table 4 shows the content of the ash and the relative compositions obtained from the pyrolysis process of the digestate of food waste (FWD) and OFMSW.

In 2016, Opatokun et al. characterized food waste and its digestate as a raw material for the thermochemical process of pyrolysis in a lab-scale apparatus. They found that the ash content obtained from raw food waste ranged from 12 wt% at 300 °C up to 18.1 wt% on a dry basis at a temperature of 700 °C, whereas the food waste digestate biochar (FWD) has an initial ash content of 25 wt% and reaches 60.2 wt% on a dry basis at a temperature of 700 °C. This significant percentage of ash containing inorganic substances and heavy metals should be valorized from a circular economy perspective [39,115]. Opatokun et al. have also studied the lab-scale pyrolysis of the FWD from industrial food waste treatments for biochar production, addressed to its direct application as a biofertilizer or soil improver. The authors observed that the presence of Ni, Cu, and Fe in the ashes limits its application for soil spreading but could allow the reuse in the catalyst synthesis [39].

Buss et al. investigated the application of biochar (BC) obtained in a lab-scale pyrolysis process of FWD sourced from the UK and other types of digestates for soil application. They demonstrated that under typical biochar production conditions, the average ash content at 550 °C is 26.85 wt% on a dry basis and contains various Potential Toxic Elements such as As, Al, and Zn. In contrast, the nutrient content, including Ca and Mg, was partially reduced. Furthermore, Cr and Ni contaminated biochar and its ashes; the average concentrations of these elements are presented in Table 4. Al, Cr, and Ni are dangerous for soil applications; however, these elements make the ash suitable for synthesizing catalysts and sorbent materials [116].

**Table 4.** Comparison of biochar compositions and ash content obtained from pyrolysis processes.

Biochar *	Ash	P	K	Mg	Na	Ca	Si	Fe	Al	As	Cr	Ni	Cu	Reference
	(%)													
FWD 300 °C	35.7	2.92	0.87	0.37	n.a.	4.55	n.a.	1.37	n.a.	$9.1 \times 10^{-5}$	0.004	0.002	0.007	[39]
FWD 400 °C	49.2	4.13	1.24	0.50	n.a.	6.53	n.a.	1.97	n.a.	$1.1 \times 10^{-4}$	0.004	0.003	0.004	[39]
FWD 500 °C	55.1	4.54	1.39	0.53	n.a.	7.26	n.a.	2.18	n.a.	$9.8 \times 10^{-5}$	0.004	0.005	0.01	[39]
FWD 700 °C	60.2	4.78	1.53	0.55	n.a.	7.76	n.a.	2.22	n.a.	N.D.	0.002	0.004	0.011	[39]
BC 400 °C	34.27	18.02	2.71	2.66	5.57	15.03	5.78	4.22	7.20	n.a.	n.a.	n.a.	n.a.	[40]
BC 500 °C	36.31	18.88	2.33	2.96	5.51	15.37	5.27	4.06	7.29	n.a.	n.a.	n.a.	n.a.	[40]
BC 600 °C	36.94	17.70	2.58	2.78	5.31	16.15	5.85	4.34	7.19	n.a.	n.a.	n.a.	n.a.	[40]
BC 700 °C	37.66	19.28	2.50	2.85	5.42	14.98	5.51	4.37	7.18	n.a.	n.a.	n.a.	n.a.	[40]
BC 800 °C	37.92	18.42	2.83	2.71	5.36	15.12	5.39	4.15	7.31	n.a.	n.a.	n.a.	n.a.	[40]
DSD 300 °C	~55	3.48	0.58	1.02	0.92	22.30	n.a.	0.67	0.36	n.a.	n.a.	n.a.	n.a.	[110]
DSD 400 °C	~60	4.12	0.64	1.16	0.99	26.94	n.a.	0.71	0.40	n.a.	n.a.	n.a.	n.a.	[110]
DSD 500 °C	~65	3.96	0.63	1.11	0.95	25.00	n.a.	0.65	0.37	n.a.	n.a.	n.a.	n.a.	[110]
DSD 600 °C	~65	4.58	0.73	1.30	1.10	29.36	n.a.	0.76	0.44	n.a.	n.a.	n.a.	n.a.	[110]
DSD 700 °C	~90	6.25	1.02	1.71	1.48	41.01	n.a.	1.04	0.61	n.a.	n.a.	n.a.	n.a.	[110]
DSD 800 °C	~90	6.79	1.00	1.81	1.50	40.24	n.a.	1.15	0.63	n.a.	n.a.	n.a.	n.a.	[110]
DSD 900 °C	~85	6.72	0.67	1.83	1.20	41.79	n.a.	1.09	0.62	n.a.	n.a.	n.a.	n.a.	[110]
PSD 300 °C	~50	2.77	1.07	0.43	1.36	15.70	n.a.	0.88	1.45	n.a.	n.a.	n.a.	n.a.	[110]
PSD 400 °C	~60	3.17	1.24	0.50	1.57	17.19	n.a.	0.82	1.67	n.a.	n.a.	n.a.	n.a.	[110]
PSD 500 °C	~65	3.31	1.29	0.51	1.63	18.24	n.a.	0.91	1.72	n.a.	n.a.	n.a.	n.a.	[110]
PSD 600 °C	~65	3.45	1.37	0.53	1.69	19.18	n.a.	1.02	1.81	n.a.	n.a.	n.a.	n.a.	[110]
PSD 700 °C	~80	3.93	1.48	0.64	1.89	21.42	n.a.	1.43	1.98	n.a.	n.a.	n.a.	n.a.	[110]
PSD 800 °C	~80	4.07	1.48	0.62	1.81	21.40	n.a.	1.26	2.11	n.a.	n.a.	n.a.	n.a.	[110]
PSD 900 °C	~80	4.36	1.10	0.67	1.23	23.72	n.a.	1.23	2.21	n.a.	n.a.	n.a.	n.a.	[110]

n.a. = not available. N.D. = below the detectable limit. \* The names and units reported are those of the original literature references.

Liu et al. analyzed the properties of the biochar produced in the lab-scale pyrolysis plant of the FWD and determined that the ash content ranged from 34.27 wt% at 400 °C to 37.92 wt% at 800 °C. As shown in Table 4, Al, Si, and P contents are approximately 7%, 5%, and 18% P, respectively. The biochar and related ash obtained at this temperature could be suitable for synthesizing CO<sub>2</sub> sorbent materials, upgrading biogas to biomethane, or for land applications [40].

Li et al. treated waste from the anaerobic digestion of food residues from the Xiang'an plant (Fujian Province, China) for recovering energy and producing biochar. They tested the pyrolysis process from the laboratory to the pilot scale. The proximal analysis of the biochar obtained via pyrolysis of hydrothermally pretreated FWD exhibited an ash content of 73 wt%. Environmentally harmful elements, such as Cr, Ni, and Cu, were also identified, but they could direct the reuse of the ash for the synthesis of catalysts and catalyst supports [102,103,117].

Peng et al. explored the potential adsorption of phosphate using carbons produced from the solid fraction of digestate collected from a large-scale biogas plant treating food waste and OFMSW. Two types of raw materials, namely dried and pelletized solid digestate (hereinafter DSD and PSD, respectively), have been tested and used to produce chars through lab-scale pyrolysis at a temperature range of 300–900 °C. An ash content greater than 40% was obtained for both DSD and PSD, reaching a maximum ash content of approximately 90% in the char obtained at 700 and 800 °C from DSD; in this case, a percentage of Fe and Al was also identified within the ash [110].

Recently, Yang et al. carried out the pyrolysis of food waste digestate (FWD) and observed the percentage of ash production at various process temperatures at 500, 600, 700, 800, 900, and 1000 °C, starting from 31.3% and increasing to 73% in the solid fraction obtained from the process carried out at 1000 °C [118]. Inorganic components present in FWD have a strong influence on the formation of the molecular structure and the surface properties of biochar, and this could further influence its performance as an adsorbent [119],

or for both pollutant capture and CO<sub>2</sub> capture in a process for upgrading biogas to biomethane. Definitely, the FWD seems to be an ideal raw material for the preparation of ash-biochar composites. Recent experiments concluded that a high ash content could improve the wastewater purification capacity of biochar [119,120], i.e., the actual performance of these materials for removing water contaminants. The CO<sub>2</sub> adsorption needs to be further explored.

### 3.2.2. Ash Formation by Pyrolysis from Animal Manure and Agricultural Waste Digestate

Chao-Yi Hung et al. evaluated the biogas digestate quality obtained from the anaerobic treatment of swine manure as a potential raw material for the production of biochar in a lab-scale pyrolysis apparatus at a temperature range of 300 to 900 °C. The results of the proximate analysis showed that the solid fraction of the untreated digestate has an average ash content of 23.03%. Traces of inorganic elements and metals such as Al, Cu, Fe, K, Mg, Mn, Na, Si, Sr, Ti, and Zinc were also reported. Furthermore, high values of the macronutrients were detected in the analyzed solid digestate sample, including the high Ca content, which reacts with carbonate or phosphate [42,121].

Tsai et al. characterized the biochar obtained by laboratory-scale pyrolysis from fresh biogas digestate obtained from an anaerobic digester processing pig manure. The untreated digestate has a high ash content (40.81 wt%). The biochar with ashes obtained at 800 °C contains approximately 10% P, 2% Fe, 1% Al, and 4% Mg; therefore, it enters the threshold values imposed by the regulations for soil application [41].

Zuo et al. studied the effects of pyrolysis temperature at lab scale (350, 450, and 550 °C) on the properties of the biochar obtained from chicken manure and dairy waste digestates. They observed that the ash content in the pyrolyzed digestates reached maximum values of approximately 80% at a temperature of 550 °C [122].

### 3.2.3. Ash Formation by Pyrolysis Digestates Obtained from Sewage Sludge and a Mixture of Different Feedstocks

Ambaye et al. studied the lab-scale pyrolysis of sewage sludge digestate at temperatures of 350 and 550 °C, obtaining an average ash content of the treated digestate ranging from 41.2 wt% at 350 °C to 59.3 wt% at 550 °C [123].

Rodríguez Alberto conducted lab scale pyrolysis at different temperatures (500, 800, and 1000 °C) to produce biochar from cow manure and industrial food waste digestate [124]. The obtained ash content ranges from 12.4 at 500 °C to 14.4 wt% at 1000 °C on dry basis. Furthermore, the iron content in the biochar with the ash deriving from the digestate is relatively high (10,760–11,805 mg/kg) compared to commercial wood biochar and other similar materials, such as dairy manure biochar (2290 mg/kg, for biochar produced at 700 °C) [125].

Taybi et al. produced biochar from sewage sludge and digested quinoa residues and observed that the biochar had an average ash quantity of 38.2 wt% compared to 15.9 wt% in the solid digestate [43]. Macronutrient (N, P, K, Mg, and Ca) content was measured in the solid digestate and the biochar and, except for N, all macronutrients were enhanced in the biochar, in agreement with previous studies of biochar production from solid digestate [78,126].

## 3.3. Ash Formation by Gasification Process

Gasification in the presence of sub-stoichiometric air has greater advantages than pyrolysis [127]. Thermochemical gasification mainly allows the production of syngas (a gaseous fuel). Syngas is primarily a mixture of H<sub>2</sub> and CO, and also contains CO<sub>2</sub>, CH<sub>4</sub>, light hydrocarbons, tar (polycyclic aromatic hydrocarbons—PAHs), and water [87,127]. Gasification reactions are usually carried out at temperatures above 800–900 °C, preventing the sintering phenomenon of the ash. Commonly, air is the gasifying agent; nevertheless, many studies have reported using oxygen, steam, carbon dioxide, air-steam, oxygen-steam, and steam-carbon dioxide mixtures as gasifying agents in different gasification applications.

Gasifying agents play an exceptional role in the composition of the final syngas product, albeit characterized by the intrinsic properties of the fed substrate. Gasification involves four phases: drying, pyrolysis, oxidation, and reduction [128,129]. In addition to syngas, the final by-product of gasification is ash, which may contain mineral matter and heavy metals originally present in the feedstock [87]. Unlike pyrolysis, partial oxidation of organic matter provides the energy for an autothermic process [130,131]. As recognized by Giuliano et al., few research works are available in the literature regarding the gasification of digestate [127,132,133].

Chen et al. investigated the air gasification of biogas provided by digestate in a lab scale downdraft fixed bed gasifier. The digestate comes from a Chinese biogas plant located in Shandong Province. A mixture of manure and fresh-weight straw with a ponderal ratio of 1:0.3 is the raw feedstock of the AD plant [134]. These studies have determined a high ash percentage (approximately 50%). Furthermore, the authors also compared the concentrations of the elements present in the ash of the gasified digestate with the threshold values of the German regulation for fertilizers *Düngemittelverordnung* [100]; they inferred that despite the quantities of nutrients such as P, K, and Ca present, these ashes are potentially applicable to agricultural land. The concentration of Cr (close to 300 mg/kg) exceeds the threshold value by approximately two times. For this reason, it should be necessary to reduce its concentration through leaching or thermal treatments [46]. On the contrary, the concentration of heavy metals such as Cd, As, Pb, and Hg in digestate gasification ash is low and does not exceed any prescribed threshold values [134].

Antoniou et al. explored the lab scale gasification of the digestate provided by an Italian AD plant feed with a mixture of pig and cow manure (43% and 20%, respectively), maize and triticale silages (25%), and cereal bran (12%). The average content of ash obtained from the gasification product is equal to 38.2% of total solid, and the presence of main nutrients such as calcium (311 g/kg), phosphorus (54.4 g/kg), and potassium (34.7 g/kg) were detected, which make char a promising candidate for soil application. Finally, a high concentration of Al was estimated (3418 mg/kg total solid), which agrees with the results obtained by [135] on the char resulting from the gasification of rice husk [136]. The studies of Antonious et al. have demonstrated that a carbonaceous material rich in macronutrients (P, K, Ca, Mg) is suitable for carbon sequestration. This work represents a clear example of a closed-loop approach to converting AD digestate into energy and soil fertilizer and gives new suggestions for sustainable business.

#### 4. Prospectives for the Reuse of Ashes

As extensively reported, a high quantity of ash is produced by the thermochemical processes of valorization of the digestate, and some suggestions for its innovative uses have been mentioned. Since digestate is a biogas by-product whose composition is very variable and depends on the type of raw material that undergoes the AD treatment, the composition of the ash derived from the thermochemical valorization treatments of digestate is just as variable. The nutrient elements in the ash are P, K, and Ca, but metals such as Cr and Ni also limit the application of this by-product to the soil. For this reason and finding a limited presence in the literature on the reuse of digestate ash, this review suggests possible prospectives for reusing digestate ash by comparing analogous works on reuses of different ashes following the circular economy approach.

A relevant example is featured the study by Sharma et al., where the authors studied the application of wood ash (WA) as a potential heterogeneous catalyst for biodiesel synthesis. They tested uncalcined wood ash and calcined wood ash-based catalysts ( $WAC_x$ , where  $x$  represents the calcination temperature) at different calcination temperatures between 500 and 1200 °C [137]. Table 5 compares the compositions of the elements present in the WA and the respective calcined ( $WAC$ ) and activated and calcined catalysts ( $A_yWAC_z$ , where  $y$  represents the carbonate cation used for activation K, Ca, and  $z$  represents the mass fraction percentage of  $K_2CO_3$  or  $CaCO_3$  in wood ash), with the compositions of ash derived from pyrolysis and digestate gasification processes.

**Table 5.** The elemental compositions of ashes obtained from gasification and pyrolysis of digestates compared to wood ashes (WA)-based catalysts (C: calcined, A: activated).

Ash *	P	K	Mg	Na	Ca	Si	Al	Reference
(wt%)								
Digestate gasification	26.96	4.29	8.45	0.57	19.85	24.11	3.09	[134]
Digestate pyrolysis	17.70	2.58	2.78	5.31	16.15	5.85	7.19	[40]
WA	1.15	7.3	2.9	0.6	14.7	17.6	9.0	[137]
WAC500 °C	0.80	6.7	2.7	0.6	13.3	15.7	8.3	[137]
WAC800 °C	0.50	5.7	4.5	5.7	17.8	21.5	1.2	[137]
WAC1000 °C	0.50	7.0	3.1	5.6	22.3	22.9	1.3	[137]
WAC1200 °C	0.50	2.5	0.5	-	36.6	20.1	0.2	[137]
A <sub>K</sub> WAC <sub>1</sub>	0.55	36.8	3.0	8.5	10.5	31.9	1.1	[137]
A <sub>K</sub> WAC <sub>0.5</sub>	0.47	10.8	2.6	8.3	8.5	31.9	1.3	[137]
A <sub>Ca</sub> WAC <sub>0.5</sub>	0.40	3.0	2.7	1.0	44.5	30.5	1.5	[137]

\* Reported units are those of original literature references.

From the compositions presented in Table 5, it is possible to observe that some element contents of the digestate ashes are comparable with their concentrations in the WA and the respective synthesized calcined and activated catalysts. This rough evaluation may open up the outlook of using digestate ash to synthesize heterogeneous catalysts exploitable for, e.g., vegetable oil conversions, lubricant production, and their regenerations. Sharma et al. observed that catalysts obtained from wood ash showed good catalytic activity in biodiesel production via transesterification of *Jatropha* oil, reaching an ester conversion of between 97 and 99% [137].

Ferella et al. studied carbon dioxide sequestration from dry CO<sub>2</sub>/CH<sub>4</sub> mixtures using a lab scale pressure swing adsorption (PSA) plant with zeolites synthesized from fly ash provided by an Indian coal-fired power plant. Table 6 compares the ash compositions of digestates produced via thermochemical gasification and pyrolysis processes with the elemental composition of the fly ash used for the synthesis of sorbent materials and the respective synthesized zeolites (named A1, A2, A3, A4, B1, and B2). The authors also compared the performance and the compositions of commercial zeolite 13X [104] with their original materials, concluding that no significant difference was detectable.

**Table 6.** Comparison of the elemental composition of the ash obtained from the pyrolysis of digestate and fly ashes from the biomass combustion process with the elemental composition of the synthesized (A1, A2, A3, B1, B2) and commercial (13X) zeolites.

Material *	K	Mg	Na	Ca	Fe	Si	Al	Reference
(wt%)								
Digestate ash pyrolysis	2.33	2.96	5.51	15.37	4.06	5.27	7.29	[40]
Original fly ash	3.37	0.24	n.a.	0.25	1.96	20.36	13.45	[104]
Washed fly ash	3.39	0.23	n.a.	0.19	1.83	18.74	12.78	[104]
A1	1.02	0.15	6.35	0.17	1.53	11.10	7.76	[104]
A2	0.81	0.18	6.90	0.20	1.52	11.34	7.83	[104]
A3	1.13	0.17	6.67	0.22	1.60	12.05	8.12	[104]
A4	0.92	0.066	7.10	0.21	1.48	13.81	9.75	[104]
B1	0.81	0.0072	6.91	0.097	1.02	12.19	9.03	[104]
B2	0.68	0.18	7.45	0.21	1.65	12.58	9.44	[104]
Zeolite 13X	0.11	0.72	5.07	0.32	0.35	11.68	6.16	[104]

n.a. = not available. \* Reported units are those of original literature references.

Table 6 shows that the Si content in the ash of the digestate from the pyrolysis process is much lower than that of the other investigated materials, whereas the Al content is comparable with the content in zeolites A and B. The Si/Al ratio for A zeolites is always approximately 1.45 by weight. On the contrary, this ratio decreases to about 1.35

for the B zeolites. Although the Si/Al ratio in commercial 13X zeolite (target reference) is approximately 1.90, the Si/Al ratio in the pyrolysis digestate ash observed is below 1 (approximately 0.72). This low ratio could not be a relevant issue since the higher amount of aluminum is expected to lead to greater availability of alkaline ions [138]. The tests conducted by Ferella et al. have shown that the best results were obtained with zeolite A2 at an operating pressure of 2 bar, a value compatible with industrial biogas plants; 98.1% of the CO<sub>2</sub> entering the biogas mixture was recovered (99.6 vol% purity); 95.2% of the CH<sub>4</sub> has been separated with a purity of 98% by volume and is suitable for injection in the natural gas distribution network or could be used as fuel for transportation. Furthermore, the best zeolites were subjected to five adsorption-desorption cycles, demonstrating a stable capture capacity of zeolites that can be regenerated by a pressure swing adsorption technique [104]. From the first qualitative observations made, the ashes deriving from the thermochemical processes of the digestate, despite having a very variable composition, seem to be suitable for the synthesis of zeolites for the capture of CO<sub>2</sub> to upgrade biogas to biomethane, integrating the AD, thermal treatments and ash reuse according to a process intensification and circular economy approach.

## 5. Conclusions

This review aimed to investigate the formation and prospects of possible reuses of the ash obtained from thermochemical valorization treatments of the solid fraction of the digestate. Despite being simple, cost-effective, and widely available, direct reuse of the solid fraction of nutrient-rich digestate as a fertilizer or soil improver is limited because it can lead to severe problems of environmental impact. One of the possible alternatives to spreading digestate on land is an integrated thermochemical valorization with biogas plants. Combustion, pyrolysis, and gasification processes lead to the formation of ash in which the inorganic substances and heavy metals, already present in the digestate solid fraction, are concentrated. From the analysis of the literature, not many works were found regarding the reuse of these ashes derived from the thermochemical treatments of the digestate, but by carrying out comparisons with possible reuses of the different ashes, it was inferred that the ashes from digestate could be exploited as catalysts for the production of biofuels, as sorbent materials for the sequestration of CO<sub>2</sub> in the biogas upgrading to biomethane, as agent for wastewater remediation. Therefore, the application of a thermochemical process at the point where the AD is carried out, combined with the reuse of the ash of the solid fraction of the digestate produced for the synthesis of materials for the upgrading of biogas to biomethane, could improve the energy efficiency of CHP plant and increase the biofuel production, solve the environmental and related problems to the management and transport of the digestate by-product using a holistic strategy based on the circular economy approach.

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