New opportunities for agricultural digestate valorization: current situation and perspectives

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Introduction

Most of the present energy supply derives from fossil fuels, which are the sources of numerous environmental impacts, particularly global warming. Current energy policies are therefore focusing on the use of renewable energy sources for the production of biofuels (*i.e.* bioethanol, biodiesel, biogas, syngas, bio-oil...) in order to reduce greenhouse gas emissions, as well as to improve energy security. In this context, second generation biomasses (*i.e.* agricultural residues, energy crops, catch crops) offer a huge potential for the production of biofuels, mainly due to their availability and low cost. Moreover, their use could contribute to reduce the world's dependency on fossil fuels and diminish global emissions of greenhouse gases (*i.e.* water vapour, CO_2, CH_4, N_2O, O_3 and chlorofluorocarbons).[1,2]

Among biofuels, the production of biogas through anaerobic digestion (AD) of agricultural residues (*i.e.* manure, crop residues) and energy crops presents several advantages compared to other biological processes (*i.e.* biodiesel, bioethanol and biohydrogen fermentation). This is mainly due to its simplicity and capacity to process a wide range of substrates (*i.e.* industrial and municipal wastewaters and sludge, municipal solid wastes, manures, agricultural residues, energy crops) containing high concentrations of readily biodegradable organic matter in the form of carbohydrates, proteins and fats.[3–5] AD processes involve the degradation and stabilization of organic materials under anaerobic conditions by a microbial consortium of microorganisms (*i.e.* hydrolytic-fermentative bacteria, fermentative bacteria, acetogenic bacteria and methanogenic archae), leading to the production of an energy rich biogas. The degradation process takes place in digesters that are designed to provide optimal conditions for microbes (mixing, temperature, pH...). Digesters are classified according to the feeding pattern (*i.e.* batch, continuous, semi-continuous), the number of stages (single stage or two stages, *i.e.* acidogenic and methanogenic) and the temperature of the process (psychrophilic, <30 °C, mesophilic, 30–40 °C, or thermophilic, 50–60 °C conditions[6]), and the fluid-dynamic (*i.e.* plug flow, completely mixed, hybrid), which in turn depends on the feedstock concentration (AD process can operate under wet, $<15\%$ DM, or dry, $>15\%$ DM, conditions).[7] The biogas produced is considered a clean and environmentally friendly biofuel, mainly composed of CH_4 (55–75%) and CO_2 (25–45%), small amounts of water vapour, traces of H_2S, NH_3 and H_2, and possibly other contaminants like siloxanes.[1,8] It can either be valorized as transport biofuel or following a purification step, injected into the public gas grid.

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Another possibility is to convert the biogas into heat and electricity through a combined heat and power (CHP) system, which is at present, the main type of exploitation in European agricultural AD plants. The produced electricity generally feeds the public grid, while the heat can be used for anaerobic digester self-consumption. After digester self-consumption, heat surplus can be provided to the farm installation or to the surrounding district. Nonetheless, a large part of heat produced is generally wasted as it is lost to the atmosphere when the plants are too remote to be able to distribute heat to the surrounding district.

Digestate, in addition to biogas, is a mixture of microbial biomass and undigested material that is also produced in large quantities. To date, digestate is generally mechanically separated into liquid and solid fractions that are stored separately for easy handling and transport. The liquid fraction contains a large part of N and K, whereas the solid fraction is composed of a large amount of residual fibres and phosphorous.[9] For these reasons, the use of digestate as fertilizer or soil improver during the past decades has generated a lot of interest.[10–13] Its utility for agricultural purposes represents economic and environmental benefits, such as the substitution of commercial fertilizers, which is of prime importance in the recycling of limiting nutrients like phosphorous.[14] For instance, Walsh *et al.* (2012) indicated that, contrary to commercial fertilizers, liquid digestate can maintain or improve yields from grassland culture and concurrently reduce nutrient losses to the environment.[15]

However, the use of digestate for land application has also raised certain drawbacks. Firstly, digestate being produced all year round, it therefore has to be stored, as it cannot be used immediately on farm lands. The limitations being mainly due to the growth stages of crops, soil types and stabilization levels.[16] In some AD plants, digestate is stored in uncovered tanks from which different gases (*i.e.* CH_4, CO_2, NH_3 and N_2O) are lost to the atmosphere.[17,18] Greenhouse gases, such as N_2O, CO_2 and CH_4, affect the global environment and climate while NH_3 contributes to general atmospheric pollution. Indeed, recent studies have shown that, in some cases, digestate still contains undigested volatile solids that convert into ammonia and methane during storage and land use. This results in a loss of energy efficiency and in an increase in the environmental impact of the AD plant.[19,20] Furthermore, the increasing number of biogas plants and their densification in certain regions might lead to an oversupply of digestate at a local scale, The excess digestate would therefore have to be transported to distant nutrient-deficient areas.[21] Indeed, farms only receive the amount of digestate which they are allowed to spread in their fields, according to regulations on nutrient loading per hectare, as the application of digestate as fertilizer has to be done according to a specific fertilization plan.[22] Once the costs of transportation and spreading are taken into account, the value of the digestate can be close to zero and it may even become an expense for the farmer.[23] Holm-Nielsen *et al.* (2009) have defined a list of good agricultural practises in order to achieve optimal environmental and economic benefits of using anaerobic digestate.[22] The presence of environmental pollutants (pathogens, heavy metals, pesticides, steroid hormones, organic compounds…) may also represent a drawback for land application.[12,24,25] Before being used as a fertilizer, the chemical composition of digestate has to be accurately assessed in order to avoid soil contamination and subsequent human food chain contamination.[26] Each European state has established specific regulations governing the use of digestate as fertilizer with the aim to protect animal and human health as well as the quality of crops.

All limitations related to the use of digestate and imposed by the European Directive motivate the quest for alternative solutions to ensure a more secure and economically sustainable

exploitation of digestate. The most straightforward solution would be to recover nutrients (N, P, K), typically in the form of high quality, nutrient-rich concentrates that could be placed on the market. To this purpose, technologies such as composting, drying, evaporation, stripping, precipitation, membrane separation and concentration are available. As review papers focusing on these methods already exist, these valorisation alternatives are not within the scope of the present study.[23,27–29]

In this review, promising alternatives for the valorisation of both liquid and solid fractions of digestate are discussed. The first part is a brief description of the biochemical composition of anaerobic digestate. In the second part, a detailed description of the potential alternative routes of digestates, other than land applications, will be presented, including:

- Use of digestate as a culturing media for algae growth;
- Conversion of digestate into energy by biological and thermochemical processes;
- Conversion of digestate into high added value compounds (*i.e.* pyrochar, activated carbons...).

Agricultural digestate composition

Digestate composition is strongly dependent upon the composition of ingestates, the inoculum source, AD operating conditions (*i.e.* pH, temperature, OLR, HRT) and AD configuration (*i.e.* with the presence or not of post-fermenters). Furthermore, the application of a pretreatment step on biomass fed to AD may influence the final composition of the digestate.[30] Table 1 summarizes the main chemical characteristics of agricultural digestates, originating from AD processes and operating under wet conditions (*i.e.* with a dry matter (DM) content lower than 15%).

Table 1 Main chemical characteristics of agricultural digestates produced from wet AD codigesting manure, slurries, energy crops, crops residues and/or agroindustrial wastes

Parameters	Values[a]	Ref.
pH	7.5–8.1	10, 20 and 36
DM (% FM)	1.7–11.5	20, 36 and 38
VS (% DM)	62.1–77	16, 20 and 36
Ash (% DM)	23–37.9	20
TOC (g kg^{-1} DM)	273–374	10
TKN (g kg^{-1} DM)	44–120	10, 20 and 36
NH_4^+ (g kg^{-1} DM)	20–95	10, 20 and 36
NH_4^+/TKN (%)	46.2–79	10, 20 and 36
P (g kg^{-1} DM)	8–42	10 and 39
K (g kg^{-1} DM)	28–95	10 and 39
S (g kg^{-1} DM)	2.9–14.7	10 and 39
Ca (g kg^{-1} DM)	9–65.8	10 and 39
Mg (g kg^{-1} DM)	4.1–24.6	10 and 39
Na (g kg^{-1} DM)	0.68–24.6	10 and 39
Cl (g kg^{-1} DM)	15–57	10
Fe (g kg^{-1} DM)	0.46–7.9	10 and 39
Mn (g kg^{-1} DM)	0.24–1.1	10
Zn (g kg^{-1} DM)	0.072–2.2	10 and 39
Cu (g kg^{-1} DM)	0.014–0.27	10 and 39

[a] In the study of Alburquerque *et al.*,[10] "pig slurries + energy crops" and "cattle slurries + agroindustrial wastes" samples were considered. FM: fresh matter, DM: dry matter, VS: volatil solids, TOC: total organic carbon, TKN: total Kjeldahl nitrogen.

Generally, digestate is characterized by slightly-alkaline pH values (>7.5) caused mainly by the degradation of volatile fatty acids (VFAs) and the production of ammonia (NH_3) during the process as well as the addition of strong bases or carbonates to control both the pH and buffer capacity of the system.[4,13]

Organic matter (OM), total organic carbon (TOC) and ash content are highly variable as shown in Table 1. During AD processes the amounts of OM and TOC decrease through the decomposition of easily degradable carbon compounds in digesters. The efficiency of OM conversion through mesophilic (*i.e.* 35 °C) or thermophilic (*i.e.* 55 °C) AD is generally in the range of 13–65%, and depends on the type of substrate fed to the digester, as well as on anaerobic reactor parameters, such as the organic loading rate (OLR) and the hydraulic retention time (HRT).[3,20] Generally, digestates originating from an AD plant with a high OLR and short HRT still contain a high amount of undigested organic matter.[20] Even after a pretreatment step on the feedstocks, at least 35% of the organic matter remain in the digestate.[17,30]

Digestate N-NH_4^+ content is directly related to the initial TKN content in the feedstock. During AD this TKN content is partially transformed into soluble inorganic nitrogen, mainly ammonium (NH_4^+) and its equilibrium partner ammonia (NH_3). Their equilibrium balance ($pK_a \sim 9.25$ at 25 °C) mainly depends on the temperature and pH of digestate: the higher the pH and temperature, the higher the fraction of free ammonia.[28] A part of N-NH_4^+ is also used by anaerobic microorganisms for growth. Digestates have higher N-NH_4^+/TKN ratios than feedstocks and digestates from highly degradable feedstocks (*i.e.* poultry and pig manure) are characterized by elevated N-NH_4^+/TKN ratios and low C : N ratios, while lignocellulosic feedstocks that are low in N (*i.e.* sorghum, maize silage) lead to a low N-NH_4^+/TKN ratio in digestate.[11]

Other macro-nutrients (*i.e.* P, K, S...) and trace elements (*i.e.* Co, Fe, Se, Ni...) can also be found in digestates. They come from either the feedstock or the supplementation of trace elements for improving digester performance.[31,32] For example, high concentrations in Cu and Zn have been observed in digestates, mainly due to the codigestion of crops and manure. The latter contains these two elements frequently used as additives to stimulate livestock growth and prevent cattle and pig diseases.[10]

Generally, at farm scale, digestate is separated mechanically (belt press, sieve drum, screw press, sieve centrifuge, rotary screen and decanter centrifuge[19,33]) into two fractions (*i.e.* solid and liquid), both stored and handled distinctly.[19,33] Some recent studies reviewed the chemical composition of both liquid and solid fractions of agricultural digestates.[11,33,34] Bauer *et al.* (2008) showed that the average dry matter content of the solid and liquid phases were 19.3% and 4.5%, respectively, after solid/liquid separation.[33] Bauer *et al.* (2008) determined that 61.8% and 58% of dry material and organic matter respectively that were present in the inflow were retrieved in the digestate solid phase.[33] Interestingly, still high amounts of carbohydrates fibers (*i.e.* cellulose and hemicelluloses) were detected in the solid-separated digestate.[35,36]

Nowadays, there are emerging valorisation routes for the utilization of digestate apart from the classical farmland application as fertilizer or soil amendment.[37] Indeed, as mentioned in the introduction, a number of limitations prevent the sole use of digestate as fertilizer and/or soil improver. Moreover the expected future growing production of digestate raises the necessity to find alternative routes. These novel opportunities for the exploitation of agricultural digestate are detailed below.

Use of liquid digestate for algae growth

The combination of algal growth and anaerobic digestion dates back to the 1950s and was first proposed by Golueke *et al.* (1957) who suggested that this process would allow the conversion of sunlight into chemical energy.[40] However, this idea remained dormant until very recently. In recent years, various experiments have been performed with the aim to verify the feasibility of using liquor digestates from various origins as a nutrient source in microalgal cultivation. The interest for microalgal cultivation has been essentially driven by the need for alternative feedstocks for reducing the impact of first-generation biofuels (*i.e.* those produced from edible crops) production on the food commodity market. Published studies have pointed out that algal cultivation for biofuel production is nowadays still far from being economically viable since production/extraction costs are still too high. Among the various strategies for cost-reduction, nutrient recovery from waste streams seems very promising and possibly unavoidable.[41–43] As shown in Table 1, agro-waste digestates are rich in both micro and macronutrients which could be used to cover the nutrient requirement for microalgae culturing. In this paragraph, experimental results on the feasibility of growing microalgae on digestate are summarised. The perspectives of this technology will be discussed further on in this paper.

Digestates studied for their potential as a medium for microalgal cultivation typically originate from anaerobic digesters fed with waste sludge in wastewater treatment plants or from farm digesters fed with agrowastes.[44–46] Concerning digestates from agrowaste, Table 2 summarizes the available literature data. First, this data collection suggests that the microalgae most commonly assessed for their ability to grow on digestates belong to the Chlorophyta taxum, even though, a wide range of algal strains was tested, *i.e.* fresh water (such as *Chlorella* sp. and *Scenedesmus* sp.) and marine (such as *Nannochloris* sp.) microalgae, cyanobacteria (such as *Phormidium bohneri* and *Spirulina* sp.) and benthic algae (filamentous green algae). The nature of the digestate also varies significantly, although digestates from dairy and swine manure have been most frequently tested. Experimental results suggest that liquor digestates can be used to support algal growth. Nevertheless, it is important to notice that digestate has been used after pretreatment including solid/liquid separation, macro or micronutrient adjustment/supplementation[47,48] and dilution. The vast majority of available data were obtained by indoor batch tests under controlled (although different among references) temperature, illumination, CO_2 supply and mixing conditions. Differences in culturing conditions, microalgae strains, digestate origin and pretreatment hinder the comparison between the available data on growth kinetics, productivity and nutrient removal.

In general, available data suggest that liquor digestate would be the most suitable nutrient supply for algal culturing although growth rates on media prepared by using pretreated digestate are generally slower (the majority of available data ranging between 0.01–0.8 d^{-1}) than those reached with synthetic culturing media (from 1 to 3 d^{-1} (ref. 49–51)). This lower growth rate has been attributed to the following potential limiting/inhibition factors that have been observed when using digestate as a nutrient source. Turbidity due to dissolved and suspended material has been evidenced as a major drawback in digestates.[52] Microalgal growth is essentially limited by the availability of photosynthetically active radiation (PAR), therefore any suspended or dissolved matter increasing light absorbance between 400 and 700 nm can significantly reduce the microalgal growth yield. For all experiments, chemical precipitation,[53] microfiltration,[47] centrifugation[48,54] or decanting[55–57] were applied to remove solid particles from the digestate. However, there is no information whether the optical characteristics of the digestate were improved after these clarification steps. It is therefore difficult to compare the effect of the various pretreatment techniques on turbidity. A negative linear correlation among turbidity and growth rate has nevertheless been observed.[52]

Ammonia inhibition is another critical issue. Microalgae are known to use ammonium as source of nitrogen, however their tolerance to this form of nitrogen is limited.[58,59] A clear inhibition threshold cannot be easily assessed as it depends upon the algal strain (*Chlorella protothecoides* grows at 80 mg NH_4^+ L^{-1},[60] *Scenedesmus* spp. can tolerate ammonium concentrations as high as 100 mg NH_4^+ L^{-1} (ref. 61)) while adaptation is also likely to occur. Since the ammonium concentration in agro-waste digestate typically ranges between 500 and 1500 mg NH_4^+ L^{-1}, experiments have been carried out on dilute digestates in order to decrease the initial ammonium concentration to about 20–200 mg NH_4^+ L^{-1} thus avoiding significant ammonium inhibition. Nevertheless, the increase in free ammonia from 9 to 34 mg L^{-1} has been observed to strongly slow down the growth rate dominated by *Scenedesmus* sp.[59] Nutrient availability can also affect the algal biomass composition, in certain cases favouring the synthesis of proteins rather than lipids and sugars.[53,62,63] This may play a role in the downstream valorisation pathways of the microalgal biomass. For biogas plants operated in standard conditions, the concentrations in volatile fatty acids in the residual dissolved organic matter of digestates vary between 100 and 1000 mg L^{-1}. These compounds can support the growth of heterotrophic bacteria. However, mixotrophic microalgae are capable of consuming organic matter at low levels.[52] The inevitable bacterial contamination when using bacteria-rich culturing media, such as digestate, could have either positive (symbiotic relationship[64]) or negative interactions

Table 2 Summary of available studies on using agricultural digestates as nutrients source in algal culturing[a]

Algae	Culturing conditions	Digestate origin (pretreatment)	Growth rate μ (d^{-1})	Productivity and/or max biomass concentration	Nutrients removal	Ref.
Mix culture (mainly *Chlorella* and *Scenedesmus*)	Indoor, batch continuous raceway	D–M (S/L separation, dilution)	0.05 0.0155	 6.8 g VS m^{-2} d^{-1} 1.45 g VS L^{-1}	72% on N and 58% on P	53
Spongiochloris sp.	Indoor, batch	Slaughter house (S/L separation, nutrients addition)		1.85 g TS L^{-1} (after 42 d)		47
Mix *Oocystis* sp., *Scenedesmus*, *Chlorella* sp., *Protoderma sp., Chlamydomonas* sp. (mixed with activated sludge)	Indoor continuous; (a) open pond; (b) tubular attached growth PBR	SW–M (S/L separation, dilution)		(a) 0.051–0.332 g TS L^{-1} d^{-1} (b) 0.163 g TS L^{-1} d^{-1}	$N\text{-}NH_4$: (a) 84–99.9%; (b) 80–99.8% P: (a) 54–79%; (b) 73–84%	62 and 63
Scenedesmus sp.	Indoor batch	(a) SW–M (b) codigestion of SW-M and *Nannochloropsis* (c) SW–M with nutrients (d) SW–M with lake water. (S/L separation, dilution)	(a) 1.34(b) 1.62 (c) 0.851.59 (d) 1.66		$N\text{-}NH_3$: (a) 57.7; (b) 99.6; (c) 23–99.9; (d) 100 $P\text{-}PO_4$: (a) 45.5; (b) 92.2; (c) 13.5–83; (d) 99.8	65
Nannochloris spp with bacteria	Indoor batch	Synthetic digestate	0.13–0.72			66
Mixed (*Scenedesmus* sp. dominant)	Indoor batch	Synthetic digestate (dilution)	0.04–0.9			59
Scenedesmus obliquus	Indoor batch	Codigestion C–M and cheese whey (S/L separation, dilution)	0.49–0.64	0.21–0.26 g TS L^{-1} d^{-1}	$N\text{-}NH_4$: 99.9% $P\text{-}PO_4$: 96–97%	54
Neochloris oleoabundans			0.23–0.44	0.22–0.26 g TS L^{-1} d^{-1}	$N\text{-}NH_4$: 84–94% $P\text{-}PO_4$: 97–96%	
Neochloris oleoabundans			0.26–0.37	0.20–0.24 g TS L^{-1} d^{-1}	$N\text{-}NH_4$: 99.9% $P\text{-}PO_4$: 97%	
Chlorella sp.	Indoor batch	D–M (S/L separation, dilution)	0.282–0.409 increasing with the dilution factor		$N\text{-}NH_4$: 100% TKN: 76–82% TP: 62–5% COD: 27–38%	52
Spirulina maxima, mutant strain (short filaments)	Indoor batch high rate oxidation pond	SW–D (S/L separation, dilution)	0.04–0.08 (on TS); 0.12–0.18 (on chlorophyll); 0.09–0.13 (on protein)	0.4–0.6 g TS L^{-1}	$N\text{-}NH_4$ = 100% $P\text{-}PO_4$ = 76% TN = 76%	57
Mixed bacteria and microalgae (mainly: *Scenedesmus* sp., *Chlorella* sp., *Synechocystis* sp.)	Indoor batch	Livestock wastes (S/L separation, dilution, Nutrient correction)	0.78	0.84 g TS L^{-1}		48
Chlorella sp.	Indoor batch	SW–D (dilution)		29–41 mg TS L^{-1} d^{-1}	$N\text{-}NH_4$: 100% $P\text{-}PO_4$: 92–100%	67
Scenedesmus Obliquus				41–57 mg TS L^{-1} d^{-1}	$N\text{-}NH_4$: 100% $P\text{-}PO_4$: 95–100%	
Scenedesmus Obliquus				41–57 mg TS L^{-1} d^{-1}	$N\text{-}NH_4$: 100% $P\text{-}PO_4$: 95–100%	
Phormidium bohneri	Indoor batch	Cheese production (S/L separation, dilution)	0.36–0.58	0.41–0.56 g TS L^{-1}	$N\text{-}NH_4$: 100% $P\text{-}PO_4$: 69%	55 and 56
Micractinium pusillum			0.35	0.14 g TS L^{-1}	$N\text{-}NH_4$: 100% $P\text{-}PO_4$: 33%	

[a] M = manure; SW = swine; D = dairy; C = cattle.

(*i.e.* competition for nutrients or micronutrients) that still need to be fully elucidated. Bacterial growth is certainly expected to modify the turbidity, pH, dissolved oxygen, nutrient apportioning (mineral or organic) and chemical nature (oxidation state). Finally, bacterial contamination may induce sanitary issues for downstream biomass valorisation.

Digestate conversion into energy

Digestate recirculation for methane production

Maximal substrate utilization and a minimal residual methane potential[68,69] should be targeted in order to develop an efficient and environmentally-friendly biogas process. Methane emissions from the digestate are an issue if it is stored in open-air tanks. These emissions depend on the digestate composition but also on the storage time and temperature. Some authors have recently developed models predicting the amount of methane emissions in the storage tanks of biogas plants.[70,71] Muha *et al.* studied 21 full-scale biogas plants operated with energy crops and cow manure.[71] The energy crops contained maize silage as the main substrate and smaller proportions of grass silage and grain, representing 56% to 100% of the feedstocks. Their model showed that a high ($\approx$95%) degradation of the substrate could be obtained if the hydraulic retention time (HRT) was at least 90 days for energy crops and at least 200 days for cattle manure. Noneless, HRT reported in the studied biogas plants ranged from 40 to 172 days. Presently, the main objective for full scale plants is energy production (*i.e.* biogas). Digesters are therefore operated at a low residence time (above which energy efficiency begins to decline), resulting in a digestate that is not completely depleted in terms of biodegradable organic compounds.[10]

The recirculation of the digestate in the biogas plant is an interesting option to reduce methane emissions and to produce more biogas from feedstocks.[20,36,39,71–73] Several studies have determined the residual methane potentials of digestate, and results show a very high range of values; for example, in the case of pig slurry (87%) and energy crop (13%) co-digestion with 51 days of HRT, Menardo *et al.*[5] obtained a residual methane potential as low as 3 NmL CH_4 g^{-1} VS[5]. On the contrary, Thygesen *et al.* measured 240 NmL CH_4 g^{-1} VS as a residual methane potential of the digestate from pig manure (85%) and fish mucus (15%).[73] Such high variations in residual methane potential can be explained by the methane potential (BMP) test conditions and by the quality of the digestate. In addition to temperature, BMP test period is expected to have a high impact on the results as digestate is composed of slowly biodegradable material. The BMP periods in literature range from 22 days[93] to 125–136 days.[31] Methane potentials of digestates are also dependent on the HRT and OLR of digesters but also on the nature of the feedstock. Thygesen *et al.* (2014) studied the residual methane yield of seven digestates from mesophilic full-scale digesters with low HRT (16–25 days), operated with manure (mainly pig manure or cattle manure in two cases) and foodwaste. Residual methane yields varied between 156 and 240 NmL CH_4 g^{-1} VS.[73] In another study, Ruile *et al.* (2014) investigated the residual methane potentials of digestates from 21-full scale anaerobic digesters operated with manure (cattle manure as the main one, but also horse and poultry manure in a few cases) and energy crops (maize silage as the main one but also grass silage and grain silage). They reported values ranging from 24 to 126 NmL CH_4 g^{-1} VS[69] and a significant negative correlation between residual digestate BMP and HRT ($r = -0.73$). The authors also concluded that the feedstock characteristics have the largest impact on the degradation time. As discussed above, the manure/crop ratio[20,69] should have a strong effect on the residual methane potential, with a higher residual BMP corresponding to the higher manure fraction in the feedstock.[74] For example, Seppala *et al.*[31] studied the increase of the maize/liquid cow manure ratio (from 30/70 to 40/60) in the influent of a lab-scale digester, while maintaining OLR (2 g VS L^{-1} d^{-1}) and HRT (28–30 d) constant. This resulted in a decrease of the residual BMP of digestate from 99 to 75 NmL CH_4 g^{-1} VS_{feed}.[31] Additionally, the nature of manure (pig manure or slurry, cattle manure or slurry, poultry manure) or energy crops (maize, sorghum or grass silage) may affect the digestate residual methane potential, concurrently with the digester HRT. Indeed, the lowest residual methane yield (3.5 NmL CH_4 kg^{-1} VS) was reported after the digestion of a feedstock containing 87% pig slurry[5]. The reason for this low value can be the high ammonia concentration N-NH_4^+ = 8.7% (g g^{-1} TS), corresponding to 78% of total nitrogen in the digestate which had a pH value of 8.1. This resulted in an ammonia N-NH_4^+ concentration of 2.7 g L^{-1}, a value greater than the 2.5 g L^{-1} threshold, above which methanogenic archae are known to be inhibited.[20,75] In summary, the residual methane potentials of digestate vary across a wide range of values, essentially depending on the nature of the feedstock and on the hydraulic retention time in the digester. Some studies have shown how their recirculation in a biogas plant can be beneficial to mitigate methane emissions during land spreading or uncovered storage and to increase biogas yield. Moreover, with the reintroduction of washed out microorganisms, the microbial population can be enhanced, thus improving reactor performance.[6] Nonetheless, the high ammonia concentration in digestate can also lead to failure of the process, resulting in a low methane production. This point is particularly relevant because digestate pH is generally alkaline and favours the presence of free ammonia. To avoid ammonia inhibition, recent studies have investigated technologies for ammonia reductions before the recirculation of the digestate liquor.[76,77] In contrast, for feedstocks with low nutrient contents (*i.e.* energy crops, crop residues), the recirculation of digestate liquor could become a viable technology. Indeed it would contribute to lower operational costs by reducing nutrient and water addition as well as the volume of digestate to dispose of.

Optimal economic benefits can be ensured by post-treatment of the entire digestate or solid digestate prior to their recirculation in the AD plant. The role of the post-treatment is to enhance the biodegradability of refractory digested compounds present in solid digestate.[68] Some authors have investigated the application of post-treatment (*i.e.* mechanical, thermal, thermochemical, enzymatic) to enhance the methane production of digestate (Table 3). The digestate post-treatment option presents two major economic benefits: (i) an increase in the recovery of methane per ton of feedstock and (ii) the cost of post-treating digestates is significantly lower than for the pre-treatment of raw substrates.[78] Lindner *et al.* (2014) applied ball-milling post-treatment on solid-separated digestate. After ten minutes of ball-milling, a higher methane potential

Table 3 Comparison of BMP data related to untreated and post-treated digestates[a]

AD plant characteristics	Digestate sample	Post-treatment conditions	BMP test conditions	Methane yield (NmL CH_4/g VS)	Ref.
Batch test Duration: 30–50 days Solid fraction from swine manure	DIG	— Aqueous ammonia soaking 22 °C, 3 days, 32% (w/w) ammonia	37 °C, 35–50 d	111 ± 11 200 ± 7	81
Full-scale digester HRT = 36 days; OLR = 3.4 kg m^{-3} d^{-1} Feed: maize silage (25%); sorghum silage (11%) Olive waste (11%); cow manure (8%) Pig manure (18%); turkey poultry manure on Coconut chips (26%)	DIG	— 80 °C, 1 h Enzymes (cellulases and xylanase), 40 °C, 24 h, pH 5 NaOH (1% w/w), 40 °C, 24 h	35 °C, 65 d	66 57 ± 2 106 ± 4 42 ± 12	36
	SS-DIG (screw press separator)	— 80 °C, 1 h Enzymes (cellulases and xylanase), 40 °C, 24 h, pH 5 NaOH (1% w/w), 40 °C, 24 h		85 176 ± 5 98 ± 5 154 ± 21	
Full-scale digester HRT = 160 days; OLR = 5.1 kg m^{-3} d^{-1} Feed: liquid manure (43.9%); solid manure (9%); maize silage (19%); grass silage (21.4%); grain (6.8%).	SS-DIG (screw separator)	— Ball milling: 10 min, eight ball of 30 mm diameter	37 °C, 35 d	117 ± 10 321 ± 25	72
Full-scale digester (150 m^3) cow manure (100%)	SS-DIG (sieve separation)	— 80 °C, 3 h NaOH (4% w/w), 20 °C, 48 h Freezing (−20 °C; 24 h) Mechanical maceration <1 mm	35 °C, 30 d	61 ± 4.7 48 ± 1.5 61 ± 0.9 47 ± 1.2 51 ± 1.6	79
Full-scale digester Feed: manure (90%); agricultural residues (5%); industrial waste (5%)	SS-DIG (decanter centrifuge)	— Wet explosion (180 °C, 10 min) Wet explosion (165 °C, 10 min, 6 bar O_2)	38 °C, 50 d	80 209 224	78
Full-scale digester HRT = 150 days; Feed: cattle slurry (35%); cattle manure (24%); triticale and sorghum silage (35%); separated solid fraction (6%)	SS-DIG (screw press separator)	— 120 °C, 30 min	40 °C, 56 d	157 ± 7 79 ± 7	80
Full-scale digester HRT = 100 days Feed: cattle slurry (33%); cattle manure (23%); chaff rice (7%); maize silage (33%); separated solid fraction (4%)	SS-DIG (compression roller separation)	— 120 °C, 30 min		117 ± 11 102 ± 6	
Full-scale digester HRT = 40 days Feed: swine slurry (76%); grass silage (8%): maize silage (16%)	SS-DIG (compression roller separation)	— 120 °C, 30 min		71 ± 5 81 ± 3	

[a] BMP: biochemical methane potential, AD: anaerobic digestion; SS-DIG: solid digestate; HRT: hydrolytic retention time; OLR: organic loading rate; d: days.

(321 NmL CH_4 kg^{-1} VS) than that of raw solid digestate (117 NmL CH_4 kg^{-1} VS), was obtained.[72] Mild thermal post-treatment (80 °C, 1–3 h) did not affect the methane potential of digestate[36,79] whereas thermal post-treatment at higher temperature (120 °C, 30 min) had contrasted effect in enhancing the methane potential of only two digestates out of the three investigated.[80] On the contrary, Biswas *et al.* (2012) reported a methane potential enhancement of 61% after wet explosion post-treatment (180 °C, 10 min) on solid digestate.[78] Thermo-alkaline post-treatments (20–40 °C, 24–48 h, 1–4% w/w NaOH) did not enhance the methane potential of digestate[36,79] whereas aqueous ammonia soaking (22 °C, 3 days, 32% w/w ammonia) resulted with an increase in 45% of the methane potential.[81] Finally, Sambusiti *et al.* (2015) found that enzymatic post-treatment enhanced methane production by 13% and 51% for solid separated-digestate and whole digestate, respectively.[36]

So far, few studies have focussed on the effect of digestate post-treatment at the scale of a continuous reactor.[78,82] Biswas *et al.* (2012) investigated the recirculation of post-treated (wet explosion, 180 °C, 10 min) solid digestate (originating from pig manure (>95% volume) codigested with agricultural residues) in CSTR experiments with an HRT of 20 days and an OLR of 3.5 kg VS m^{-3} d^{-1}. Post-treated solid digestate was codigested with filtered manure (1 : 1 (w/w, as VS content)) and a methane production of 194 mL g^{-1} VS_{added} was reached which was 8% higher than the control reactor using fresh fibres.[81] Similarly,

Jagadabhi *et al.* (2008) studied the recirculation of alkali-treated solid digestate in a continuous stirring-tank reactor (CSTR).[82] In this case, the control reactor was fed with a mixture of grass silage and cow manure (0.43 : 1 w/w, as VS content) at an OLR of 2 kg VS m^{-3} day^{-1} and an HRT of 20 days. The control reactor using raw biomass exhibited a methane potential of 182 L CH_4 kg^{-1} VS which was higher than reactor operated by both raw biomass and alkali treated solid digestate (161 L CH_4 kg^{-1} VS) as well as the reactor operated by both raw biomass and untreated solid digestate (143 L CH_4 kg^{-1} VS).[82] Even though data on continuous mode are scarce, these two studies clearly demonstrated the feasibility and stability of solid digestate recirculation. Nonetheless, recirculation of digestate with or without a post-treatment step resulted in methane potentials that were similar or slightly lower than for reactors operated with the initial biomass. Consequently, if the energy produced per volume of digester should be considered, the recirculation of digestate does not seem worthwhile, as digestate recirculation leads to a reduction of the initial feedstock loading. Nonetheless, recirculation of solid digestate increases the energy recovery for a same amount of initial biomass, thus reducing the necessary arable land for digester feeding in cases of crop energy. All these parameters should positively contribute to reduce the environmental impact of present-day AD plants.

Bioethanol production

Bioethanol production through biological fermentation is another promising alternative route towards valorisation of both solid and liquid digestates. Indeed, due to its high content in cellulose fibres, solid digestate has also recently attracted attention for bioethanol production.[83–85] However, digested fibres can present physicochemical barriers such as the presence of lignin that can limit carbohydrate availability and degradation. For this purpose, a treatment step should be applied prior to enzymatic hydrolysis and fermentation to overcome these natural barriers.[83] As a general rule, dilute-alkali treatments are applied to solubilize lignin from the lignocellulosic matrix and increase the cellulose content in the remaining solid fraction.[83,84] Yue *et al.* (2011) observed the bioethanol production in digestates from two types of anaerobic digester, a CSTR and a plug flow reactor (PFR). Ethanol production of 105 g kg^{-1} dry digestate and 85 g kg^{-1} dry digestate were obtained respectively, for the CSTR and the PFR.[86] A higher ethanol production from the CSTR digestate was due to a higher cellulose content than in the PFR digestate.[86] Finally, Yue *et al.*, (2010) reported an ethanol production of 51 g L^{-1} and an ethanol yield of 72% during fermentation of digested animal manure fibres.[87] These results were similar to those obtained during switchgrass bioethanol fermentation.[87] Finally, MacLellan *et al.* (2013) investigated bioethanol production from solid digestate obtained from the digestion of a mixture of corn-stover and swine-manure (40 and 60% fresh material, respectively). They reported that 152 g CH_4 and 50 g ethanol kg^{-1} DM were obtained by coupling AD and bioethanol production.[83]

In general rules, it has been shown that digestate produced from AD process present several advantages for bioethanol production, as the digestate obtained is generally enriched in cellulose which is easily accessible.[84,86,87] Indeed, AD process with low HRT seems to act as a biological pretreatment changing the composition of AD fiber, making it suitable as a cellulosic feedstock for ethanol production,[87] even if such approach is a relatively new concept still controversy in the literature.[88] For instance, Yue *et al.* (2011) showed that anaerobically digested manure contains less hemicelluloses (11%) and more cellulose (32%) than raw manure, and it presented better enzymatic digestibility than switch-grass.[87] On the other hand, the classical bioethanol process comprises a mechanical fractionation and/or thermo-chemical pretreatment followed by an enzymatic hydrolysis-ethanolic fermentation. Recently, Motte *et al.* (2015) observed that anaerobic biological degradation prior to mechanical fractionation could significantly reduce the energy requirement of the milling step (142 kW h t^{-1} for initial feedstock to 95 kW h t^{-1} for digestate).[89] Consequently, besides enriching the initial feedstock in cellulose, the AD process could also improve the energy efficiency of the mechanical fractionation process which is an important step in current bioethanol production methods.[90]

Furthermore, to improve the overall economic aspect of the bioethanol production process, the liquor fraction of digestate can also be used as culture medium to replace freshwater and nutrients.[32,91,92] Gao and Li (2010) investigated the bioethanol production from wheat using a thermophilic digestate liquor as culture media.[91] Nutrients like nitrogen, phosphorous and potassium as well as minerals (*i.e.* magnesium, zinc, copper) were concentrated in the digestate liquor. Such compounds are essential for the enzymatic functionality and yeast growth. Interestingly, Gao and Li (2010) reported similar bioethanol productions from media supplemented by the AD liquor (85.9 $g_{ethanol}$ L^{-1}) and synthetic nutrient media (82.8 $g_{ethanol}$ L^{-1}).[91] In addition, an advantage in using AD liquor effluents as culture media is that they contain reduced amounts of potential inhibitory compounds (*i.e.* furans and phenolics) thanks to the capacity of AD processes in degrading them.[5,93,94] Such compounds have been found to be inhibitory for various processes, such as enzymatic hydrolysis,[95,96] ethanol fermentation,[97,98] xylitol and butanol production,[99,100] biohydrogen production using pure cultures or mixed cultures[101,102] and microbial fuel cells.[103] The threshold inhibition levels depend on the type of microorganisms but it is generally around 1 g L^{-1} for most biological processes.[5,102,104]

Thermal conversion processes

Thermal conversion (*i.e.* combustion, hydrothermal carbonization process, pyrolysis) has been investigated on agricultural anaerobic digestate to produce energy and improve the overall energy efficiency of AD processes.[105–107]

Hydrothermal carbonization (HTC) usually occurs at temperatures lower than 250 °C, leading to carbonization reactions of biomass, that produce char as a primary product.[105,108,109] HTC is a thermochemical process used for converting wet organic feedstocks into carbon rich products called "hydrochars" with chemical characteristics comparable to those of fossil coals.[109] Vapothermal carbonization (VTC) has been also investigated for

the production of carbon rich solid fuel. In the case of VTC, the biomass is saturated in vapour instead of being submerged in water in the case of HTC.[103]

The physicochemical properties of hydrochar, close to fossil coal, would allow it to be used as solid fuel. Recent studies have investigated the production of hydrochar from solid digestate for energy purposes.[109–111] As shown in Table 4, the yield of hydrochar produced from anaerobic digestate varied from 66 to 74 g 100 g^{-1} DM when hydrothermal temperatures around 180–190 °C were applied. Interestingly, Funke *et al.* (2013) highlighted, that at a temperature of 190 °C during 6 hours the hydrochar yield was 57% and 66% for wheat straw and anaerobic digested wheat straw (ADWS), respectively.[110] They hypothesized that the lower hydrochar yield observed for straw could be due to its lower content in lignin than found in ADWS.[110] Indeed, carbohydrates are known to yield less hydrochar compared to rich lignin biomass.[112] Toufiq-Reza *et al.* (2015) investigated HTC process on wheat straw digestate at 180–260 °C.[113] Up to a process temperature of 220 °C, digestate derived hydrochar contained primarily crystalline cellulose and lignin. At 260 °C, crystalline cellulose was degraded and more aliphatic carbon and lignin-rich hydrochars were produced. In general rules, elemental carbon and oxygen concentrations are related to the quality of hydrochar as fuel. For this purpose, higher carbon content and lower oxygen content are desirable.[113]

At various operational parameters of HTC, the heating value of hydrochar produced from anaerobically digested maize silage varied from 25.4 to 35.7 MJ kg^{-1} DM.[109] Similarly, Oliveira *et al.* (2013) evaluated the digestate hydrochar heating value (23.5 MJ kg^{-1} DM) after HTC at 180 °C for 4 hours.[111] Funke *et al.* (2012) estimated that the energy recovery from initial biomass could be nearly doubled with a cascaded AD–HTC process,

Table 4 Products appartioning for various whole and solid anaerobic digestates submitted to thermal conversion processes[a]

		Products distribution (% DM)				
Solid digestate origin	Thermal process parameters	Gas	Bio-oil	Gas + bio-oil	Pyrochar	Ref.
Separated anaerobic solid digestate	HTC realized in a custom-built autoclave at 180 °C for 4 h	8.3	17.4	25.7	74.3	111
Whole anaerobic digestate from wheat straw digested in upflow anaerobic solid-state continuous reactors at 55 °C	HTC realized in 1 L stirred pressure reactor at 190 °C for 6 h	nd	nd	nd	66	110
Whole anaerobic digestate from mesophilic anaerobic plant treating 70% corn stillage and 30% cow manure	HTC realized in 18.75 L stainless reactor at 230 °C for 6 h. Solid loading: 5%	nd	nd	nd	53.5	115
Whole anaerobic digestate from mesophilic anaerobic plant treating 70% corn stillage and 30% cow manure	VTC realized in 18.75 L stainless reactor at 230 °C for 6 h. Solid loading: 25%	nd	nd	nd	64.5	115
Whole anaerobic digestate from maize silage digested in a two-stage solid state reactors at 55 °C	HTC realized in 1 L stirred pressure reactor at 190 °C for 6 h	nd	nd	nd	70.1	109
Sugar beet tailings digested in anaerobic two-stage reactor at 55 °C	Bench-scale slow pyrolyzer. Temperature of 600 °C, heating rape of 10 °C min^{-1} and residence time of 2 h	42	12.5	54.5	45.5	140
Sugarcane bagasse digested in anaerobic batch at 55 °C	Laboratory mini tubular pyrolyzer reactor. Temperature of 600 °C, heating rape of 10 °C min^{-1} and residence time of 1.5 h	nd	nd	82	18	141
Chicken manure and corn stover digested in CSTR reactor at mesophilic temperature	Laboratory pyrolysis tube reactor. Temperature of 800 °C, heating rape of 50 °C min^{-1} and residence time of 3 h	40	32	72	28	106
Mix of slurry and energy crops	Thermo catalytic reforming plant: pyrolysis reactor connected to a reformer. Temperature from 150 °C to 500 °C in the pyrolysis reactor. Temperature of 600 °C in the reformer	34	33	67	33	122
Pig manure digested in real anaerobic plant operating at mesophilic conditions and HRT of 20–30 days	Laboratory scale pyrolysis reactor Temperature of 600 °C and residence time of 15 min	45	12	57	43	128
Mix of manure and agricultural residues digested in real anaerobic plant operating at 45 °C and HRT of 62 days	Laboratory Rotary Kiln pyrolysis reactor. Temperature of 500 °C, heating rape of 20 °C min^{-1} and residence time of 10 min	9	58	67	33	119

[a] HTC: hydrothermal carbonization; VTC: vapothermal carbonization; nd: not determined.

instead of an AD process alone.[110] Similarly, Reza *et al.* (2014) showed that the combination of AD and HTC processes yielded 13.2 MJ kg^{-1} DM initial feedstock, representing at least 20% and 60.2% more than for HTC and AD alone, respectively.[114]

Recently, Funke *et al.* (2013) compared the performance of vapothermal carbonization (VTC) and traditional HTC processes on anaerobic digestate.[115] VTC was carried out with a higher initial solid content (25%) compared to HTC (5%), as the biomass was subjected to saturated steam instead of liquid water. When the quantity of hydrochar produced by VTC (66.8 g 100 g^{-1} TS) was higher than HTC (53.5 g 100 g^{-1} TS), the carbon content of the hydrochar reached 64.5% and 70.4% for VTC and HTC processes, respectively.[115] The heating capacities of produced hydrochar were 16.4 and 17.7 MJ kg^{-1} DM for HTC and VTC processes, respectively. Finally, certain studies referring to a biorefinery concept have investigated the possible recirculation of the liquid produced from HTC processes into a methane-producing anaerobic digester.[111,116] Such liquid is generally composed of VFAs, phenols, furans and its derivatives.[117]

Contrarily to hydrothermal processes, other thermal conversion processes found in literature (*i.e.* pyrolysis and combustion) require a solid digestate with a low moisture content, and thus a severe drying-up pretreatment, for efficient operation.[118] At farm scales, heat recovery from the CHP system can be used efficiently for the drying of solid digestate. For this purpose, Monlau *et al.* (2015) have recently suggested that the energy balance of a real agricultural anaerobic digester plant could allow to assess whether heat surplus (13 351 kW h_{th} day^{-1}) produced from CHP after self-consumption of the digester would be sufficient to ensure a complete drying of solid anaerobic digestate.[119] Interestingly, they demonstrated that the generated heat surplus, which was estimated at 13 249 kW h_{th} day^{-1}, is capable of totally drying the solid digestate fraction.

After the drying step, solid digestates can be converted into pellets for combustion.[107,120] Combustion is a thermochemical process based on the complete oxidation of organic wastes to produce energy in the form of heat.[121] Net calorific values of digestate pellets varying between 16.5 and 17.3 MJ kg^{-1} DM have previously been reported.[120] The calorific value of digestate pellets was found to be similar to the calorific value of wood.[120] Kratzeisen *et al.* (2010) have drawn energy balances of digestate pellet combustion by calculating the energy input to energy output ratio. Their calculation considered the separation phase of digestate, the drying step and the pelletizing step as energy inputs, Indeed, a pelletized form of substrate with homogenous properties has been recommended for optimal storage and transport conditions.[120] Interestingly, these authors estimated the ratios between energy inputs and outputs to be 0.74 and 0.78 for the two digestates. These values, being less than 1, suggest a positive energy balance of the overall system. Thus, the use of digestate pellets is a promising approach, as they can be burnt with market-available combustion technologies while the emission of flue gas remains within the defined limits for biofuels.[120] Nonetheless, the use of solid digestate as feedstock for a combustion furnace can show certain limitations due to its high ash content.[107] Pedrazzi *et al.* (2015) have shown that ashes create agglomerates, which obstruct the brazier holes and partially choke the combustion after few minutes.[107]

Pyrolysis process is another promising technology that can make use of solid digestate.[119,122] Pyrolysis is an endothermic thermo-chemical process which can recover energy from organics, regardless whether the organic matter is biodegradable or not.[123] Pyrolysis heats dry digestate under an oxygen-free atmosphere, breaking down organics within the feedstock into biochar, and vapour phase.[124] By cooling the vapour, polar and high molecular weight compounds condense out as liquid (bio-oil) while low-molecular-weight volatile compounds remain in the gas phase (syngas).[124] According to operational conditions, pyrolysis can be classified either as "slow" or "fast" pyrolysis.[125] Generally, slow pyrolysis occurs at low heating rates (<10 °C min^{-1}) and residence times of minutes or hours, whereas fast pyrolysis occurs at high heating rates (≈ 1000 °C min^{-1}) during seconds or a few minutes. Desired products obtained by slow pyrolysis are generally char ($\approx 35\%$) and syngas ($\approx 35\%$), whereas bio-oil is mainly produced through fast pyrolysis ($\approx 70\%$).[125] Syngas is essentially a mixture of H_2 and CO, but also typically contains CH_4, CO_2, H_2O, and several low-molecular-weight volatile organic compounds.[126] Bio-oil generally contains an aqueous phase and an organic phase, the latter being considered for energy production. Bio-oil is generally composed of a large range of compounds including mainly sugars, acids, ketones, phenols and furans compounds.[127]

Pyrolysis processes have been applied recently on solid digestate for energy production and improve the energy balances of current AD plants.[106,119,128] The appartioning of char, bio-oil and syngas for the various studies is mentioned in Table 4. The amount of potentially valuable products as energy sources (*i.e.* syngas, bio-oil) ranges from 54.5 to 82 g 100 g^{-1} DM (Table 4). Recently, Liang *et al.* (2015) have shown that the quality of bio-oil and the selectivity of pyrolytic products could be obviously improved by AD process. Bio-oil obtained from AD residues presented more phenols compounds (*i.e.* mainly 4-vinyl phenol) than bio-oil obtained by original feedstock, due to higher content of lignin in digestate.[35,127]

Currently, considering farm scale implementation, the most promising issue is syngas and bio-oil conversion through a combined heat and power (CHP) system using gas or oil engines.[129,130] Syngas has also been investigated for production of biofuels (*i.e.* bioethanol, butanol, biohydrogen...) and chemicals through syngas fermenting microorganisms.[131–134] Although not currently suitable as a basic transportation fuel, bio-oil can however be upgraded into synthetic transportation fuels or chemicals.[124,135] Finally, in an integrated process, conversion of bio-oil and syngas through recirculation into an AD process for biogas production have been proposed.[136–138] Hubner and Mumme (2015) recently investigated the conversion of the aqueous phase of pyrolysis bio-oil through an AD process for methane production. Pyrolysis was initially carried out at three temperatures (*i.e.* 300, 400 and 500 °C) on anaerobic digestate (*i.e.* issue from an AD plant digesting cow manure and maize at a ratio of 4 : 3). Methane production was tested on the liquid aqueous phase of the produced bio-oil that was rich in water soluble substances but also

in slightly soluble substances (*i.e.* phenol, furans). Methane yields showed similar means of 199 and 194 mL CH_4 g_{COD}^{-1} respectively for 330 °C and 430 °C pyrolysis temperature. However it dropped to 129 mL CH_4 g_{COD}^{-1} at 530 °C due to a lower soluble COD degradation, probably due to inhibition by recalcitrant compounds like phenols and furans at 530 °C.[137] Torri and Fabbri (2014) have also observed a similar inhibition phenomenon during the AD processing of the aqueous phase of bio-oil. They suggested that inhibition can be overcome by the use of pyrochars, which adsorb the problematic substances.[139]

Preliminary energy balances using anaerobic digestate as potential feedstock for energy recovery through pyrolysis have been drawn.[106,119,128] Li *et al.* (2013) concluded that pyrolysis of digestate provided an additional energy yield of 6.1 MJ kg^{-1} $VS_{initial}$ compared with the AD process alone. Nonetheless, in this study only syngas was valorized as energy without considering the bio-oil upgrade into energy.[106] In their energy balance, Monlau *et al.* (2015) were careful to distinguish electrical and heat inputs/outputs. Indeed, electrical energy can be provided to the public grid, providing extra income for the farmer, whereas thermal energy, after the self-consumption of the AD plant, is generally lost. Interestingly, Monlau *et al.* (2015) showed that coupling AD with a pyrolysis process at 500 °C increased the electricity yield by 59% compared with the AD process alone.[119]

Until now, few studies have reported the environmental impact of coupling AD with thermochemical processes.[121] Fernandez-Lopez *et al.*, (2015) investigated the environmental impact of coupling manure AD processes with subsequent digestate valorization by combustion or pyrolysis.[121] They found that the dual AD/pyrolysis system presented the best environmental performances.

Generation of value-added products

Pyrochar as soil amenders

As previously mentioned, pyrochar is a charcoal-like residue obtained after a pyrolysis process. Pyrochar production has recently been in the limelight worldwide for climate change mitigation as it could play a major role in sequestering atmospheric carbon dioxide.[142] Indeed, biomass conversion into pyrochar can stabilize the carbon captured by plants in the form of charcoal, which is highly resistant to biological degradation.[124,142] Due to their physicochemical properties, pyrochars have also attracted attention as soil improvers in order to preserve the fragile quality of soils; this practice is in line with the principles of ecology and sustainable agriculture. Spreading of charcoal for improving soil fertility is an ancient process, used by indigenous civilizations of the Amazon basin centuries ago.[143] Pyrochars are extremely porous and thus have a very large surface area and porosity available for adsorption or chemical reaction and exchange capacity.[144] Due to their high accessible surface area and porosity, pyrochars can improve the water-holding capacity of the soil and attenuate the drought stress of certain region of the world.[145] Their porous structure should provide shelter for beneficial soil micro-organisms like mycorrhizae and bacteria. Moreover they can affect the binding between important nutritive cations and anions.[146] Pyrochar application on soil should also reduce the dispersal of pesticides and the leaching of heavy metals with their subsequent accumulation into plants.[124,147] From an environmental point of view, the disposal of biochars into the soil should decrease CO_2 emissions due to high charcoal stability, but can also reduce the release of N_2O and CH_4.[145] The benefits and environmental implications of using biochar in agricultural soils have been well reviewed by Xu *et al.*[145]

Table 5 summarizes the main physico-chemical characteristics collected from recently published studies on pyrochars derived from digestate. Inyang *et al.* (2012) activated the production of pyrochar by converting digested dairy waste (DAWC) and digested whole sugar beet (DWSBC) through slow pyrolysis at 600 °C for 2 h. The authors reported a BET surface area and total pore volume of 161.2 m^2 g^{-1} and 0.147 cm^3 g^{-1} for DAWC, and 48.6 m^2 g^{-1} and 0.034 cm^3 g^{-1} for DWSBC.[148] Yao *et al.* (2011) have shown that pyrochar obtained from anaerobically digested biomass presented a higher accessible surface (336 m^2 g^{-1}) compared to pyrochar produced from raw feedstock (2.6 m^2 g^{-1}).[140] Furthermore, pyrochars generally have an alkaline pH, which is crucial for the reequilibration of acidic soils in area with low pH soil.[124,149] Finally, Pituello *et al.* (2014) have demonstrated that pyrochars derived from cattle manure and silage digestate exhibit a higher P concentration than the initial feedstock suggesting that they can be used for low nutrient release, P being an important element for plant growth.[150] Inyang *et al.* (2010) compared the characteristics of pyrochars from anaerobically digested sugarcane bagasse (DBC) and raw sugarcane bagasse. Compared to pyrochars produced directly from raw sugarcane bagasse, DBC showed a higher surface area, a higher cation exchange capacity (14.3 cmol kg^{-1}) and a more negative surface charge (−61.7 mV).[141] All these properties are beneficial for soil amendment applications. Anaerobic digestion seems to play a "biological activation" role by producing better quality pyrochars with higher accessible surface area.

Nonetheless, during land application an important issue needs to be considered related to toxic compounds (*i.e.* heavy metals, PAHs...) and their possible leachability into the soil. Indeed, as pyrochar is produced from incomplete combustion, PAHs and dioxins are likely formed whereas heavy metals content is originating from the original feedstocks.[151] However, the bioavailability of such compounds has been found to be limited by the sorption capacity of pyrochar.[151] Effectively, pyrochars in the soil only act as a contaminant reservoir (*i.e.* heavy metals, pesticides, aromatic hydrocarbons...), without the capacity to remove or eliminate them. Contaminants thus still prevail in the soil, even if they have become hardly bioavailable. For instance, for pyrochar produced from digested manure at 600 °C, Hale *et al.* (2012) reported a total concentration of 0.189 μg PAHs g^{-1} pyrochar in which only 0.830 ng g^{-1} were available. However, data on the bioavailable fraction of such toxic compounds are clearly missing in the literature especially

Table 5 Physicochemical characteristics of pyrochars deriving from solid agricultural digestate

Pyrolysis conditions/feedstocks	Elemental composition (%)					Physicochemicals characteristics						
	C	H	O	N	S	N_2 surface area (m^2 g^{-1})	CO_2 surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Surface-zeta potential (mV)	Cation exchange capacity (cmol kg^{-1})	pH	Ref.
Pyrolysis at 600 °C of digested sugar beet tailings	30.8	1.4	39.9	2.7	0.46	336	449	—	−18.11	—	9.9	140
Pyrolysis at 600 °C of digested dairy waste residues	65.4	0.68	—	3.6	—	161.2	555	0.147	−29.18	—	10	148
Pyrolysis at 600 °C of digested whole sugar beet residues	20.2	1.07	—	0.43	—	48.6	128.5	0.034	−15.85	—	9	148
Pyrolysis at 600 °C of anaerobically digested sugarcane bagasse	73.5	2.41	24.1	—	—	17.7	—	—	−61.7	14.3	10.9	141
Pyrolysis at 600 °C of anaerobically digested pig manure	33.8	1	—	3.8	—	17	—	—	—	—	—	128
Pyrolysis at 400 °C of anaerobically co digested food waste and silver grass	63.5	5.28	18.1	0.94	0.065	7.6	—	0.013	—	—	8.8	152
Pyrolysis at 550 °C of cattle manure and silage digestate	65.9	—	—	2.2	0.5	58.6	254	0.065	—	—	10.3	150
Pyrolysis at 750 °C of corn digestate	52	—	—	0.9	—	448	—	0.28	—	—	10.5	153

from biochar produced after AD process. Before soil application, potential negative side effects associated to these compounds should be carefully addressed. Furthermore, the mechanisms explaining the interaction between pyrochars and soil properties have not been fully understood.[144] The effect of long term field applications of pyrochars is also necessary to provide a better understanding of the long term effect on soil and crop quality.

Pyrochars as bio-adsorbents

Another advantage of pyrochars is that they have an excellent sorptivity towards environmental contaminants (Xu *et al.*, 2012). Today, most environmental problems derive from a rapid industrialization producing and discharging wastes containing heavy metals, pesticides, herbicides and other toxic organic molecules into the environment.[140,153,154] Heavy metals and certain organic molecules cannot be biodegraded and represent toxic compounds that can accumulate in living tissues causing various diseases and human health disorders.[155] Due to their chemical properties, high accessible surface area and porosity, the use of pyrochars from digestate could be an efficient solution to bio-adsorb these contaminants as shown in Table 6. Recently, Sun *et al.* (2013) prepared pyrochars from AD residues which were used as a bio-adsorbent for the removal of cationic methylene blue dye (MB).[152] The efficiency of MB removal in the samples with initial concentrations of 5 mg L^{-1} at pH 7.0 and 40 °C after 2 h of contact time was 99.5%. In another study, Inyang *et al.* (2011) examined the ability of pyrochars derived from raw and digested sugarcane bagasse to remove lead from water.[156] The sorption of lead by pyrochars produced from raw (BC) and digested sugarcane bagasse (DBC) was compared with a commercial activated carbon (AC) using batch sorption experiments. Pyrochar from DBC proved to be a more effective sorbent of lead from water than AC, and was far more effective than BC. The maximum lead sorption capacity of DBC (653.9 μmol g^{-1}) was double of that of AC (395.3 μmol g^{-1}) and about twenty times higher than that of BC (31.3 μmol g^{-1}).[156] Yao *et al.* (2011) investigated the removal of phosphate from an aqueous solution by biochars derived from digested sugar beet tailings (DSTC).[140] The phosphate adsorption capacity of the DSTC was close to 133 mg kg^{-1}. The authors suggested that biochars produced from digested sugar beet tailings is a promising alternative adsorbent, which can be used to reclaim phosphate from water or reduce phosphate leaching from fertilized soils.[140] In another study, Eibisch *et al.* (2015) investigated the use of pyrochars from corn digestate for the sorption of herbicides (*i.e.* isoproturon) in loamy sand soil.[153] Finally, Monlau *et al.* (2015) have recently investigated the use of pyrochar from digestate for the detoxification of lignocellulosic hydrolyzate. Indeed, lignocellulosic hydrolyzate may contain furan compounds (*i.e.* furfural, 5-HMF) that can affect the majority of sugar-fermenting microorganisms.[157] In their study, Monlau *et al.* (2015) demonstrated that pyrochars from digestate were efficient for furans adsorption (≈49 mg g^{-1} pyrochar) without affecting the sugar concentration. According the results of this paragraph, it is obvious that pyrochars produced from digestates could be effective alternative and low-cost bio-adsorbents for organic and inorganic contaminants.[157]

ACs derived from pyrochars as bio-adsorbents

For a better adsorption capacity, pyrochars can be converted into activated carbons (ACs). Activated carbons (ACs) are produced in

Table 6 Summary of selected recently reported studies utilizing pyrochars or activated carbons from digestate for organic and inorganic pollutants adsorption

Nature of pyrochar or activated carbon (AC)	Contaminants	Adsorption capacity	Ref.
Pyrochar produced from digested residues (400 °C)	Heavy metals in acidic wastewater: Cu^{2+}, Zn^{2+} and Mn^{2+}	Cu^{2+} (182 μmol g^{-1}) Zn^{2+} (35.3 μmol g^{-1}) Mn^{2+} (60.7 μmol g^{-1})	165
Pyrochar produced from digested dairy waste (600 °C)	Heavy metals in aqueous solution: Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}	High removal efficiency for Pb^{2+}(99%) and Cu^{2+} (98%) Low removal efficiency for Ni^{2+} (26%), Cd^{2+} (57%)	148
Pyrochar produced from digested whole sugar beet residues (600 °C)	Heavy metals in aqueous solution: Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}	Removal efficiency higher than 97% for the four metals	148
Pyrochar produced from digested sugarcane bagasse (600 °C)	Lead in water	654 μmol g^{-1} pyrochar 395 μmol g^{-1} commercial AC 31 μmol g^{-1} sugarcane bagasse	156
Pyrochar produced from digested sugar beet tailings (600 °C)	Phosphate in aqueous solution	0.13 mg g^{-1} (Langmuir model)	140
Pyrochar produced from anaerobic digestate (600 °C)	Furans in aqueous solution	49 mg_{furans} g^{-1}	157
Pyrochar produced from digestate (400 °C)	Cationic methylene blue dye in aqueous solution	9.5 mg g^{-1} (Langmuir model)	152
Activated carbon prepared from digested Spartina alterniflora (H_3PO_4 activation at 700 °C)	Cadmium(II) in aqueous solution	39 mg g^{-1} (Langmuir model)	160
Activated carbon prepared from digestate (H_3PO_4 activation at 500 °C)	Methylene blue (MB) in aqueous solution	Maximum adsorption of MB = 344.8 mg g^{-1} (Langmuir model)	159
Activated carbon prepared from digested dairy manure (steam activation at 850 °C)	H_2S in biogas	177–470 mg H_2S g^{-1}	161

two stages, the first being the pyrolysis of the carbon at a temperature below 800 °C, followed by either a chemical, physical or steam activation process.[158]

ACs exhibit a much higher accessible surface area and porosity than pyrochars. For instance, activated carbons derived from digestate (*i.e.* anaerobic digester processing dairy manure) exhibited a high accessible surface area of 1950 m^2 g^{-1} and a pore volume of 1.232 cm^3 g^{-1}.[159] Due to emerging environmental pollution problems, the world consumption of activated carbons has dramatically increased these past decades. However, for many countries, the commercially available activated carbons are still considered as expensive materials due to the use of non-renewable and expensive raw materials such as coal.[159] Unused digestates can offer an ideal source for the production of low cost value added ACs.[159] Until present, very few studies have yet investigated the production of activated carbons from solid anaerobic digestates for adsorption purposes.[159,160] ACs prepared from digested *Spartina alterniflora* showed a cadmium adsorption from an aqueous solution of 39 mg g^{-1} at 25 °C.[160] Similarly, Yuan *et al.* (2010) showed that ACs prepared from digestates exhibit an adsorption capacity of MB in an aqueous solution of 345 mg g^{-1} at 25 °C.[159]

Regarding possible biorefinery integration, ACs generated by digestates can also be used to improve the performance of a biogas plant. For this purpose, White *et al.* (2010) studied the development of ACs from an anaerobic digestion by-product to remove H_2S from biogas.[161] Indeed, H_2S in biogas, at levels higher than 300–500 ppm, damage energy conversion techniques like the CHP system.[22] Under optimal conditions, AC produced by steam activation was efficient in removing H_2S up to 470 mg H_2S g^{-1} carbon. Furthermore, besides adsorbing H_2S, ACs also allow the surface oxidation of hydrogen sulfide into elemental sulfur and sulfate. Since the sulfur has a beneficial form as a fertilizer, the recycled sulfur-containing carbon can be spread on farmland, thus eliminating any costs related to used carbon disposal.[161]

Other value-added products

Other value-added products (*i.e.* particleboard, nanocellulose or bio-adsorbents) from solid digestates have been also investigated as valorization alternatives.[162–164] Winandy and Cai (2008) explored the possibility of substituting wood in particleboard manufacturing by digested bovine biofibers (ADBF). It was found that a mixture of 50%/50% of ADBF and wood fiber has similar characteristics to standards of wood particleboard.[164] Recently, Henniges *et al.* (2014) investigated the feasibility of the isolation of micro fibrillated cellulose (MFC) from the residual fibers of digested miscanthus straw. The diameter of MFC produced from miscanthus digested fibers was found to be comparable to the reference (*i.e.* cellulose extracted from raw miscanthus). They were also free from non-fibril deposits occasionally found in the reference.[162] In another study, Wang *et al.* (2013) examined the potential use of anaerobic digested corn stover as a bio-adsorbent to remove heavy metals

(Cu^{2+}, Cd^{2+}) from aqueous solutions.[163] Results indicated that anaerobic digested corn stover was efficient in removing heavy metals with a higher affinity for the Cu^{2+} than Cd^{2+}. The maximum adsorption capacities of anaerobic digested corn stover were 83.3 mg g^{-1} and 50 mg g^{-1} for Cu^{2+} and Cd^{2+} respectively.

Discussions

The AD process is an attractive biological process which permits to convert a large range of feedstocks into energy. Nonetheless, to improve the efficiency of current AD plants, the output effluents (*i.e.* CO_2 stream, liquid digestate and solid digestate) need to be fully valorized according to a biorefinery approach. Notably, liquid digestate has been shown to be a low cost culture media for microalgae, whereas whole and solid digestates can be converted into energy and/or value added molecules through biological or thermo-chemical processes.

Microalgae cultivated on liquid digestate can be further used as feedstocks for AD, in order to counterbalance the high C/N ratio of lignocellulosic biomasses.[166–168] Furthermore, the carbon dioxide present in biogas can be used for microalgal growth, thus promoting the interesting possibility of closing the flux of the AD residues.[167,169,170] Even the effluent subsequent to algae production can be recycled for operating the anaerobic digester.[37] Moreover, the residual microalgae after oil extraction[171] can be further converted into biogas, thus improving the energy balance of a combined biodiesel–AD process.[167,172,173]

Some drawbacks should however be pointed out concerning microalgae cultivation on liquid digestate. In particular, the long term culturing stability and inhibition by organic trace elements of heavy metals need to be investigated. The large dilution factors applied in most of the studies and their batch nature leave many open questions such as long term culturing stability and inhibition by turbidity, organic trace elements of heavy metals. The lack of long-term data from continuously operated microalgal culturing, together with the above discussed potential inhibition/limitation factors make this alternative for digestate valorization still in its infancy and require supplementary research works.

Furthermore, the claim that the productivity of microalgae is significantly higher than for commonly grown crops, stated in some press releases has been questioned. Indeed studies suggest that similar production rates are more likely to occur.[174] By considering stoichiometric and thermodynamic constraints, the maximum theoretical energy conversion of the full spectrum of sunlight into biomass is around 10%, while outdoor cultures show much lower yields as observed by Williams and Laurens.[43] These authors reviewed the productivity of various literature data from different culturing systems. They demonstrated that present average areal productivities lie between 10 and 20 g m^{-2} d^{-1}, corresponding to 10–30% of the maximum theoretical energy conversion. Even though these data do not refer to cultivation of microalgae on digestate, similar values have been found by culturing benthic algae on dairy and swine effluents (11–21 g m^{-2} d^{-1} [175,176]). The economic viability of algae-based biofuel production, even when integrated with the AD process, has been questioned by a number of authors[43,177,178] However, as quoted by Williams and Laurens (2011) these evaluations depend on a set of hypotheses based on efficiencies, production costs, and revenues that need to be corroborated.[43] These uncertainties comprise: microalgal production costs (depending on productivity which in turn depends on latitude, algal species, reactor type, technical solutions, and nutrient sources), biofuel conversion costs (depending on the harvesting and extraction technologies), the energy market as well as local environmental constraints and legislation (including government eco-incentive, subsidies and environmental credits). Although these analyses have acknowledged that microalgae had been optimistically overvalued as potential feedstock for a third generation biofuel production, their integration into existing AD plants remains a noteworthy and potentially beneficial solution. The improved use of resources such as low-grade heat streams, CO_2 rich off-gasses, and nutrients are not even valued by economic analyses. In this view, promising results have been published, suggesting the feasibility of a decrease in biomass production costs, close to a threshold value of 0.5 $ per kg. This has been recognized as a target limit for biofuel production from microalgae to be profitable.[41] Similar beneficial effects are expected to reflect of the overall life cycle energy assessments. Both Lardon *et al.* (2009) and Clarens *et al.* (2010) performed life cycle assessments on biofuel production process from microalgae in comparison with other biofuels and fossil fuels production processes, agreeing on the conclusion that, to date, algal-based biofuel processes have a positive energy balance, although they are lower if compared to other types of biofuels.[179,180] Clarens *et al.* (2010) suggested that a major factor driving the low environmental impact of algal biofuels was the demand for CO_2 and fertilizer as a nutrient source. Integration in AD plants is therefore expected to reduce these costs by using recycled nutrients and CO_2.[179] In agreement with the Nitrate Directive (91/676/EEC) enforcing the requirement for nutrient recovery technologies, the need for nitrogen load reduction in nitrate sensitive areas can be another driving force for integrating microalgal-based technologies into agro-industrial biogas-plants. In this context, microalgal culturing would be seen as a biotechnology targeting both solar energy recovery and nutrient removal and recovery, and would potentially improve the biogas plant environmental footprint. Nitrogen removal by conventional biological treatment costs approximately 2.5 $ per kg N removed.[181] Therefore, assuming a 10% N content in the microalgal biomass, such production would allow to save 0.25 $ per kg for the associated N recovery from digestate, thus contributing to the sustainability of the overall process.

Concerning solid digestate, the most investigated alternative route focused on energy production through biological (*i.e.* bioethanol, AD) and/or thermo-chemical (*i.e.* pyrolysis, combustion, HTC) processes. By comparing the various processes, energy recoveries of 2.5–4.3 MJ kg^{-1} DM were estimated for bioethanol considering a heating value of 29.6 MJ kg^{-1} ethanol.[182] For methane production, values ranging from 1.75–6.4 MJ kg^{-1} DM were reported. It is important to note that for these estimations

the energy consumptions of each process were not taken into account. Furthermore, such values should only be regarded as rough estimations, as the initial solid digestates used were from different origins. Low energy recoveries for bioethanol fermentation are mainly due to the fact that only the cellulosic fraction is converted into ethanol using *S. Cerevisiae* strains. The present development and optimization to obtain new cost effective strains that are able to convert both C_5 and C_6 sugars will contribute to the increase in energy recovery.[183] In certain cases, high-energy recovery was obtained after AD of solid digestate (6.4 MJ kg^{-1} DM) suggesting that a large part of the matter is not degraded during AD. To overcome this limit, the application of post-treatments to enhance digestate conversion and energy recovery through AD process seems to be an interesting option but such technologies have to be tested in large scale application to assess their real environmental and energy impact.

Energy yields obtained from thermo-chemical conversions were in general higher than those from biological process conversions (Fig. 1). Indeed, contrarily to biological processes, thermo-chemical ones are able to convert both crystalline cellulose and lignin into energy. For instance HTC and VTC lead to 8.7–18.2 MJ kg^{-1} DM and pyrolysis process provides 8.6–10.8 MJ kg^{-1} DM. Hydrochar produced from HTC or VTC is commonly used as solid fuel for heat generation.[117] Therefore, HTC or VTC processes that do not require a drying step of digestate appear the best option, when the heat produced from the AD plant is integrated into the heat district. On the contrary, in the case where the heat is not valorized, the surplus of heat generated from the AD plant can be used to dry digestate before a pyrolysis process.

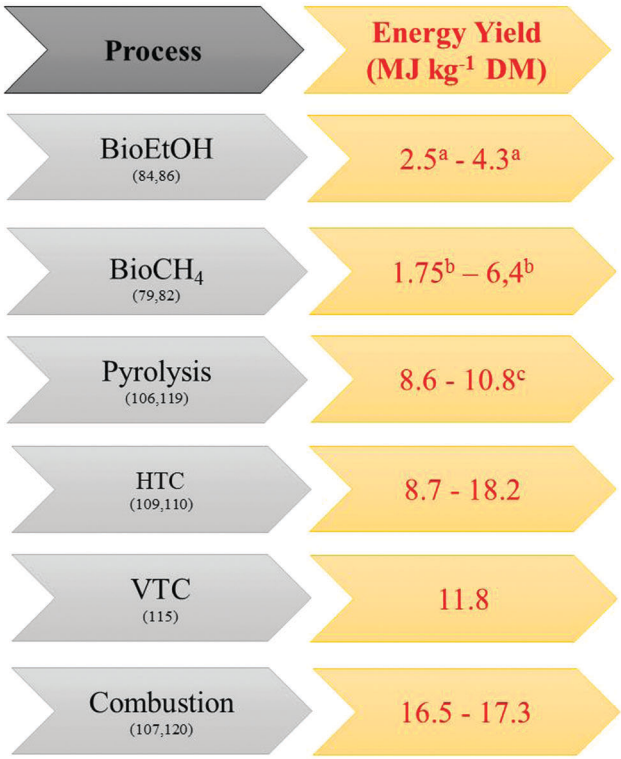

Fig. 1 Comparison of energy yields (MJ kg^{-1} DM) obtained by biological or thermochemical conversion processes of anaerobic solid digestate.

Concerning HTC process, the liquid produced from such processes can also be fermented by AD.[111,116] Nonetheless, even if AD process has been shown to be able to degrade furans and phenolic compounds present in such liquid, few studies report the synergic effect of such compounds on AD performances and supplementary data are needed to state on this valorization route.[5] Furthermore, hydrochar produced from HTC or VTC, besides being used as solid fuel, can also be used for application similar than pyrochar (*i.e.* as soil amendment and/or bio-adsorbents). Although there are a lot of literature data about using pyrochar as soil amenders, only few of these deal with hydrochars as soil amendments.[117] If HTC or VTC processes seem to be promising pathways especially for heat recovery, no industrial-scale HTC plants are yet in operation making difficult to evaluate such technologies. Until yet, most of promising works are currently focused on pyrolysis digestate processing. Interestingly, strong complementarities between AD and thermochemical processes, especially pyrolysis, were highlighted. First of all, it was highlighted that both bio-oil and syngas can be sent back to the AD process for increasing methane production from recalcitrant biomass. Besides, to maximize energy recovery, pyrolysis of solid digestate can also produce value-added products (*i.e.* pyrochar, activated carbon) that are potentially beneficial to the AD process. These present or prospective complementarities that may lead to promising research topics are listed below and represented in Fig. 2.

(1) The excess heat produced in AD can be used efficiently for the drying step of the solid digestate for further application in pyrolysis process.[119]

(2) Activated carbon (ACs) derived from digested biomass can be used as bio-adsorbents for removing H_2S in biogas.

(3) Pyrochars can also be used for soil amendment to improve carbon sequestration in the soil and water and nutrient retention.[124,141]

(4) Recently, pyrochars or ACs from lignocellulosic biomass have been used efficiently for the detoxification of hydrolyzates by removing furans compounds that might further inhibit biological processes.[184–186] To our knowledge, no research papers have investigated the use of pyrochars derived from solid digestate for detoxification.

(5) Solid acid carbon catalysts synthetized from pyrochar derived from lignocellulosic biomass have been used for lignocellulosic biomass hydrolysis by replacing a homogenous acid catalyst like H_2SO_4.[187,188] In a closed cycle, pyrochars derived from digestate could be further converted into acid carbon catalysts or catalyst support for hydrolyzing biomass and improving anaerobic performances, as hydrolysis remains the limiting step in such a process.

(6) Even though few literature data are available on the topic, produced pyrochars or ACs could be supplemented in a digester as a biofilm support for microbial colonization and further

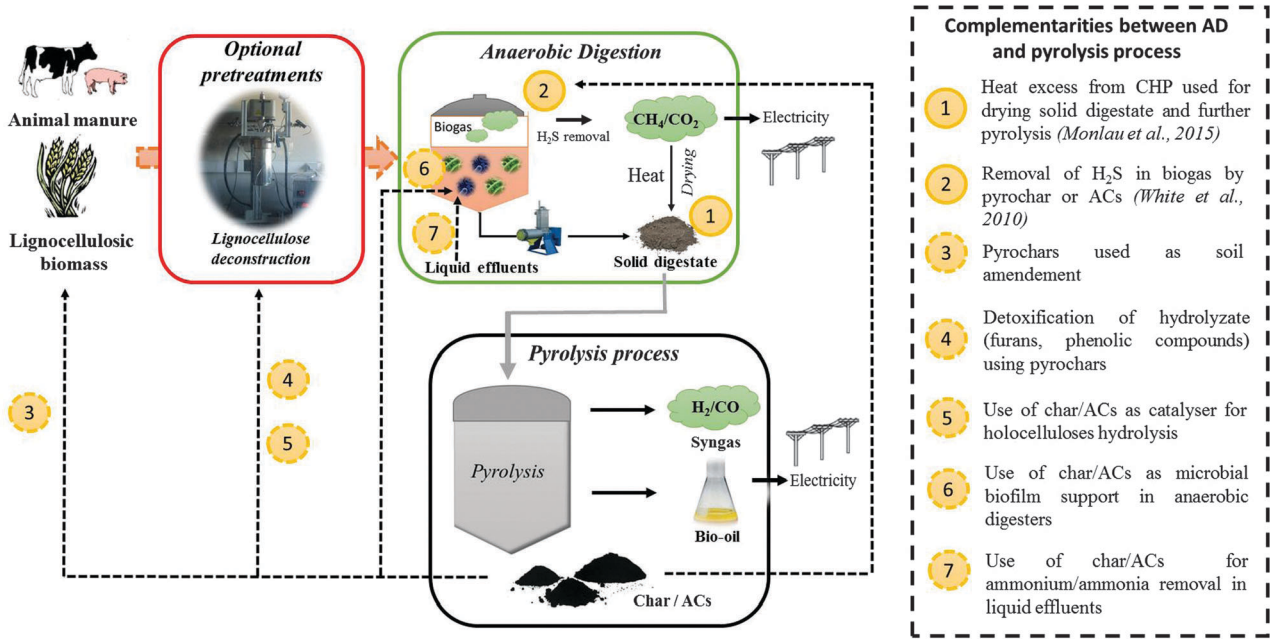

Fig. 2 Flux of materials from coupling AD/pyrolysis processes: present and potentials complementarities between AD and pyrolysis process.

increased performances.[189–192] Until present, no studies have yet reported the use of pyrochars derived from anaerobic digestate.

(7) Pyrochars deriving from lignocellulosic biomasses or digested biomasses can be used to remove ammonium or ammonia nitrogen in anaerobic digestate slurry. Further recirculation of the liquid part in the digester can thus avoid inhibition.[193] Indeed, excessive ammonia concentration can lead to the failure of the anaerobic digester.[75]

Research outlooks

In the future, digestate valorization should reach out to new horizons by considering energy production through novel biological and/or thermochemical pathways. Indeed, up to now, biofuels production from digestate is mainly restricted to biomethane and bioethanol. Data relative to other biological processes (*i.e.* dark fermentation, lipid fermentation, microbial fuel cells…) are still scarce in literature. For instance, in a recent study, Zhong *et al.*, (2015) investigated the production of sustainable biodiesel by combining AD and aerobic fungal fermentation of solid digestate for biogas and lipids production.[194] Similarly, few studies focused on solid digestate conversion through other thermo-chemical processes, like gasification, but these mainly concern digestate from wastewater sludge.[195,196] Hoffman *et al.* (2013) modelled an integrative-cascade process by combining AD and hydrothermal liquefaction.[105] Like HTC processes, hydrothermal liquefaction does not require the dehydration of solid digestate and thus could present a promising solution for the valorisation of anaerobic digestate into bio-oil, principally used as combined heat and power (CHP) production.[105]

Finally, to create a sustainable biorefinery scheme around AD, a step-change is required to alter the perception of "waste" from agricultural digestate, to a product with a real economical, energetic and environmental benefit.[197] Until yet, most of studies dealing with digestate valorization have focussed on separated valorization of liquid or solid digestate without considering a fully integrated system. Consequently, to answer to these challenging outlooks, digestate valorization has to be fully integrated in a cascaded biorefinery scheme where co-products at each stage being used as the starting point for a new stage of biomass upgrading, thus maximizing the energy, economic and environmental benefits (Fig. 3). In such approach, AD is considered as the core of the integrated process, this allows benefiting from the existing AD plants. AD process could play the role of entry and exit point of this agro-energy closed loop system. At the entry, AD process could act as a "biological pretreatment" improving the accessibility, fractionation and grindability of the remaining solid digestate for further biological processes.[86,87,89] Furthermore, outputs generated could be further fully integrated with AD plant as previously described. Nonetheless, most of these points are still in their infancy and further researches are needed to confirm their real potentials.

Furthermore, it is important to note that in fields of research, thermochemical approaches are often viewed as parallel or competing with the biological ones.[139] Interestingly, strong complementarities, previously cited, underline the synergy between the dual biological/thermochemical systems. As the level of process integration in the biorefinery scheme should contribute to their energetic and economical sustainability, it is important to admit that these technologies, until now considered as competitors, could be applied in series to improve the biomass conversion efficiency and further the overall energy and economic balances.[139,198] Here, the biorefinery approach proposed is based on the literature survey of existing digestate valorization routes. Nonetheless, such valorization routes

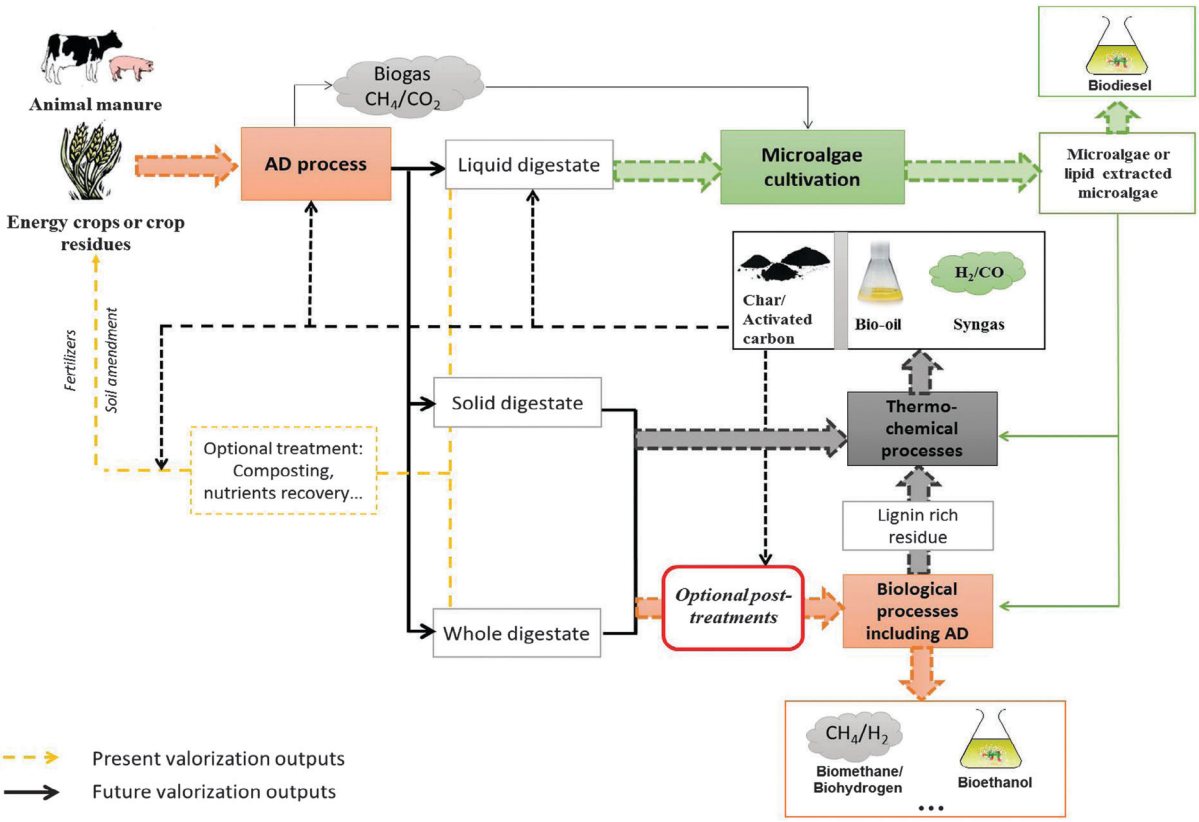

Fig. 3 Integrated biorefinery approach to ensure an optimal digestate valorization different from fertilizers and/or soil amendment.

are not exhaustive and news horizons have to be investigated and considered.

In view of current findings and state-of-the-art, digestate valorization and its integration in a sustainable biorefinery concept will become an important research field in the coming years due to the growing number of AD plants. For sure, such integrative approach will require skills from various research horizons including agronomy, process, economy and environmental science. Until yet, most of these alternative valorization routes have still been undergoing laboratory research development. For this purpose, authors consider that a comprehensive environmental and economic analysis is premature. In the future, we should redouble our efforts in promoting pilot-scale implementations to assess the real energy, economic and environmental benefits and to decide on the combinations of processes that would be most suitable from an industrial point of view.

Conclusion

Currently, the number of anaerobic digesters is increasing worldwide and consequently a huge amount of digestate is being produced. Hence, the necessity to determine innovative alternative solutions to integrate digestate and AD plants in a sustainable biorefinery scheme should become a major research issue in the future. In an integrative approach liquid digestate can be devoted to microalgae culture whereas solid digestate is converted onto energy through biological and/or thermochemical pathway. In this review, strong complementarities that can coexist between biological and thermochemical processes have been also highlighted. Authors are convinced that such dual-system will show a growing worldwide interest in the future to ensure optimal lignocellulosic conversion and energy recovery.

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