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# Biorefineries at poultry farms: a perspective for sustainable development

## Leyanet Odales-Bernal,<sup>a</sup> <sup>©</sup> Ralf Kiran Schulz,<sup>b</sup> Lisbet López González<sup>a</sup> <sup>©</sup> and Ernesto L Barrera<sup>a\*</sup> <sup>©</sup>

#### Abstract

Poultry litter (PL) is one of the drier and bulkier manures produced in intensive agriculture. Land spreading is considered the most common treatment option for PL; however, this causes large atmospheric greenhouse emissions and consequently a high negative environmental impact. PL has several factors that limit its sustainable use as an energy source, and thus there is still a need for more studies about sustainable waste management. The paper aims at: (i) proposing sustainable pathways in order to maximise the PL valorisation process, based on previous experiences described in the literature; and (ii) showing the advantages of reforming poultry farms into biorefineries in Cuba. Combinations of techniques are used to increase PL valorisation, but only by modulating the theoretical data has an improvement occurred. In this work, pathways for thermo- and bioconversion processes are proposed which involve four major technologies for converting PL into useful energy and fertiliser, being pyrolysis/gasification, hydrothermal carbonisation and anaerobic digestion as key conversion technologies. Including technologies for nutrient recovery in the proposed pathways would allow better agricultural applications. The treatment of PL in biorefineries in Cuba would have a positive impact on the economy through income generation and savings resulting from reductions in imports (i.e. fossil fuels and agrochemicals), employment creation, improved living conditions and development in rural communities. Future studies should be aimed at evaluating the various proposed pathways in order to maximise the PL valorisation process, in addition to a marketing study of the products generated through the biorefineries at poultry farms. © 2020 Society of Chemical Industry (SCI)

Keywords: poultry litter; biorefineries; technologies; thermoconversion; anaerobic digestion

#### INTRODUCTION

Sustainable development implies the creation of environmental quality, economic prosperity and social equity, to the benefit of current and future generations.<sup>1</sup> The transformation from 'oil refineries' to 'biorefineries' using a combination of biological, physical and chemical processes is essential to contribute to sustainability. A biorefinery is the integration of biomass conversion processes and equipment to produce fuels, power and chemicals, which has three components: feedstock, processing technologies and products (energy and bioproducts). Biorefineries allow the replacement of finite, non-renewable fossil resources with renewable biomass resources for the production of food, feed, fertilisers, fuel, energy, industrial chemicals and other products.<sup>2</sup> Every year 140 billion tons of biomass generated from the agricultural sector is wasted worldwide; this large volume of biomass could be converted into energy, equivalent to 50 billion tons of oil, which can significantly help reduce greenhouse gas (GHG) emissions.<sup>3</sup>

The management and disposal of poultry litter (PL) have become an important issue for farmers, industry and the general public because of the increasing concerns about its negative impact on the environment. Due to the growing demand for chicken production, low ammonia emission in chicken farming systems is urgently needed.<sup>4</sup> Globally, broiler production has grown and consequently its generation of waste. For example, Chinese meat production has been in the first place worldwide for more than 20 years, poultry farming being more than 10 times higher than that of pig farming.<sup>5</sup> According to Dalólio *et al.*,<sup>6</sup> Brazil is considered the world's second largest producer of broilers, generating an annual volume of litter of around 8–10 million tons. In 2018, India was the world's third largest egg producer, the fourth greatest producer of chicken and the fifth for chicken meat production. These producers contribute to 47.05% of the total meat production in India<sup>7</sup> with an annual growth rate of 21% in the broiler sector alone.<sup>8</sup> In Cuba, in the last 30 years the PL volume has risen, to 0.76 tons per year.<sup>9</sup>

This waste is not properly disposed of and, as a consequence, spontaneous leaching occurs due to water leakage and decomposition of organic matter, which ends up in lagoons where methane (CH<sub>4</sub>) and ammonia (NH<sub>3</sub>) emissions arise as a result of the uncontrolled decomposition of the organic matter. Therefore, the absence of an adequate treatment system represents a potential risk for environmental contamination. Land spreading is considered the most common treatment option for PL, because it

<sup>\*</sup> Correspondence to: EL Barrera, Center for Energy and Industrial Processes Studies (CEEPI), University of Sancti Spíritus, Avenida de los Mártires 360, 60100 Sancti Spíritus, Cuba. E-mail: ernestol@uniss.edu.cu

Center for Energy and Industrial Processes Studies (CEEPI), University of Sancti Spíritus, Sancti Spíritus, Cuba

b Institute for Vocational Training at FB 07, Department of Labour Studies, University of Kassel, Kassel, Germany

contains essential nutrients for plant growth, albeit in variable concentrations. Consequently, this causes large atmospheric emissions of CH<sub>4</sub>, NH<sub>3</sub>, nitrogen monoxide (NO), nitrogen dioxide (NO<sub>2</sub>) and dinitrogen oxide (N<sub>2</sub>O), with high environmental impact in the categories terrestrial acidification, particulate matter formation, marine eutrophication and climate change.<sup>10</sup> The higher total ammonia nitrogen concentration in poultry manure is the main reason for the high NH<sub>3</sub> emissions compared to other animal manure such as that of pig and cattle.<sup>11</sup> Wang et al.<sup>4</sup> proposed NH<sub>3</sub> mitigation options for the in-house stage, the outdoor stage and the soil application stage using an acid scrubber and compost biofilter and changing the manure surface application for incorporation into land application, achieving in all cases efficiencies of more than 70% in reducing NH<sub>3</sub> emissions. In spite of that, further advantages would be obtained if the PL was used for power generation. Fuel potential, GHG reduction and the reuse of nutrients to agriculture, such as nitrogen (N), phosphorus (P) and potassium (K), are advantages of the use of PL as biomass for power generation.<sup>12</sup>

Many reviews have been published concerning the improvement of best management practices of PL in a sustainable way which can be summarised as: soil amendment (compost), animal feed and fuel source.<sup>7,13–15</sup> The alternatives for the use of PL for power generation can be classified into two categories: biochemical methods (anaerobic digestion, AD) and thermal conversion methods (combustion, gasification, pyrolysis and hydrothermal conversion).<sup>15</sup> Previous research has shown successful power conversion of this waste through biorefineries. However, PL has several factors limiting its sustainable use as biomass, such as low carbon-to-nitrogen (C/N) ratio, limited digestibility of bedding material, high moisture content, high pH and high N and K content. Therefore, there is still a need for further studies on sustainable waste management of PL. Available literature on the use of PL as biomass energy at a full scale is still incipient.<sup>6</sup>

This paper aims at: (i) proposing sustainable pathways in order to maximise the PL valorisation process, based on previous experiences described in the literature; and (ii) showing the advantages of reforming poultry farms into biorefineries in Cuba. The paper proceeds via the following scheme: feedstock, technologies and products of the PL sustainable treatment in biorefineries. The next section gives details on the use of PL as feedstock and its physical-chemical characteristics. Then are provided details of the main technologies used for the treatment of PL, including the best experiences of previous research for PL valorisation, potential problems and possible remedies for using PL as an energy source. Also outlined are pathways for the sustainable management of PL using a combination of techniques. After that is a discussion about the main product generated during PL refining and focusing on its application mainly as energy and nutrient source. The necessity for the sustainable management of PL in Cuba is then explored, taking into account the need of energy and nutrients for the country and the advantages of using PL as energy source in rural communities. Conclusions are presented in the final section.

#### PL AS FEEDSTOCK IN BIOREFINERIES

A biorefinery can obtain feedstock from a range of residues such as lignocellulosic materials (i.e. black liquor, wheat, rice straw or bagasse), oils and fats (waste cooking oils, fat from slaughterhouses), others (slaughterhouse trimmings and bones, PL, animal farm wastes and municipal wastes) and dedicated crops (oil, sugar and starch crops). Energy crops are the most controversial because they conflict with food availability for human consumption.<sup>16</sup> Over the years, unlimited confined animal production (i.e. cattle, poultry and swine) has been the major source of manure by-products in many countries, including the USA, Australia and New Zealand.<sup>14</sup> This kind of agricultural waste constitutes a relevant category of livestock source with elevated potential for application in biorefineries which do not compete with food availability. Therefore, due to the large volumes generated, the search for sustainable alternatives for the management of this waste becomes a priority for the agricultural sector.<sup>6</sup>

There are many technologies for handling PL, in order to re-use nutrients and to avoid the risk of contamination. PL has been studied for many years for use in combustion conversion such as direct burning, or by means of gasification, pyrolysis,<sup>17</sup> hydro-thermal conversion<sup>18</sup> and AD, using PL as monosubstrate and in co-digestion.<sup>19</sup>

#### **Characteristics of PL**

PL is one of the drier and bulkier manures produced in intensive agriculture. It consists of a mix of bedding material, excreta, waste feed and feathers.<sup>17</sup> It also contains antimicrobial and antibiotic residues, which are used as growth promoters and for treatment of infections in poultry farms.<sup>20,21</sup> Moreover, PL could contain endocrine disruptors such as chicken metabolic products, and residues of pesticides and herbicides used in cultivation of the grains used for feed production.<sup>22</sup> Many materials can be used as bedding, as long as they have good absorption capacity and are inexpensive, such as wood chips, coffee hulls, peanut hulls, rice hulls, dry grass, chopped corn cobs and others.<sup>23</sup> Therefore, PL is a heterogeneous waste and does not have a standardised composition. The chemical-physical characteristics of PL vary depending on many factors, such as type of bed used and the number of times it is reused, bird feeding, climatic conditions and husbandry practices.<sup>17,23,24</sup> Table 1 presents some chemical-physical parameters of PL and chicken manure (which is the major constituent of PL).

Volatile solids (VS) refer to the part of total solids (TS) that is volatilised during incineration at temperatures above 500 °C. High VS (63.5-88.3%: Table 1), seen in PL, means a higher organic content which is desirable for using PL as fuel biomass.<sup>17</sup> Moisture plays a key role for the composition of biomass, among other factors, because of variable total mineralisation of water (dissolved solid matter).<sup>29</sup> Lynch et al.<sup>17</sup> reported the moisture content of PL ranged from 18.7% to 51.8%, with 40% as average using wood shavings as bedding material. Regardless of the material used as a bed, moisture absorption increases as the substrates become denser due to the deposition of faecal solids.<sup>23</sup> Atmospheric conditions and collection forms also have an influence on moisture; litter stored outdoors in a waste pile had more than double the moisture content of litter collected from within the poultry house.<sup>30</sup> The ash content of PL is higher (10.9-21.7%) compared with other biomass such as woody biomass, the ash content of which is 2.2%.<sup>31</sup> Both ash components and chemical composition of biomass are highly variable due to the high variations of moisture and different genetic types of inorganic matter in biomass.<sup>29</sup>

Alkalinity is often related with buffer capacity, which is the equilibrium of carbon dioxide and bicarbonate ions that provides resistance to significant and rapid changes in pH, and the buffering capacity is therefore proportional to the concentration of bicarbonate.<sup>32</sup> According to Callaghan *et al.*,<sup>33</sup> total alkalinity (TA) together with total volatile fatty acids (VFA) can be used to

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Table 1. Chemical and physicochemical characterisation of PL								
Parameter	Unit	PL <sup>a</sup>	PL <sup>b</sup>	PL <sup>c</sup>	Chicken manure <sup>d</sup>			
TS	%	74.9	_	81.2-82.6	29.9			
VS	%TS	70.9	_	78.3-88.3	63.5			
Moisture	% wb	25.1	48.7	_	_			
Ash	%	_	_	11.7–21.7	10.9			
ТА	g CaCO <sub>3</sub> L <sup><math>-1</math></sup>	_	_	_	9.2			
TN	% TS	_	3.6	1.9–2.2	_			
Cellulose	% TS	_	_	26.5-28.5	20.0			
Hemicellulose	% TS	19.8	_	_	23.2			
Lignin	% TS	4.6	_	4.1-7.5	1.6			
$P_2O_5$	% TS	_	0.7	0.4–0.6	_			
K <sub>2</sub> O	% TS	_	3.8	0.8-1.1	_			
рН		7.3	8.8	7.8-8.0	9.0			

TS, total solids; VS, volatile solids; TA, total alkalinity; TN, total nitrogen; wb, wet basis.

<sup>a</sup> From Zhu *et al.*<sup>2</sup>

<sup>b</sup> From Guerra-Rodríguez *et al.*<sup>26</sup>

<sup>c</sup> From Ortiz *et al.*<sup>2</sup>

<sup>d</sup> From Li *et al*.<sup>2</sup>

judge the stability of digestion by biochemical methods such as AD, with up to 0.4 being the optimal ratio (VFA/TA). The buffer capacity in animal manure is higher than in other waste; for example TA in chicken manure is 9.2 g  $CaCO_3 L^{-1}$  (Table 1) and 1.2 g  $CaCO_3 L^{-1}$  for kitchen waste.<sup>28</sup> The high TA means the reduction of the VFA/TA ratio and support for microbial growth for efficient digestion. Buffering capacity would help maintain the stability of digestion.

Furthermore, the contents of cellulose, hemicellulose and lignin are part of the organic matter in the form of non-crystalline solids.<sup>29</sup> Cellulose and hemicellulose can be transformed into glucose or into other sugars such as pentoses (xylose or arabinose) or hexoses (glucose, mannose or galactose). Lignin is a complex polymer that contains considerable amounts of mono-aromatic hydrocarbons.<sup>34</sup> The lignocellulosic feedstock hinders the digestion process because of the low solubility of lignin in water, due to the lignin structure being mainly hydrophobic. The lignin provides resistance to microbial attack and oxidative stress.<sup>35</sup> PL has similar content of cellulose (20-28.5% TS) and hemicellulose (19.85-23.2% TS) and less content of lignin (1.6-7.5) (Table 1). Although the low lignin content means better accessibility of microorganisms to cellulose, others factors like the cellulose crystallinity influence the hydrolysis, the main step for the digestion of lignocellulosic biomass.

Chickens consume vast amounts of protein and other Ncontaining substances in their diets. The dietary conversion of N is relatively inefficient, where 50–80% of N is excreted.<sup>36</sup> Hence, chicken manure is rich in N-containing compounds. N can be present in several forms, which depend on microbial activity, temperature, pH, humidity and oxygen concentration. Guerra-Rodríguez *et al.*<sup>26</sup> reported a 3.56% TS of total nitrogen (TN) in PL (Table 1), a high level (60–80%) being organic N due to the high content of urea, proteins and amino acids.<sup>13,37</sup> TN contents are closely related with the kind of material used as bedding. For example, Garces *et al.*<sup>23</sup> found a high concentration of TN (1.38% TS) in PL using coconut husk as bedding material. In contrast, TN contents also depend of the age of the manure, its content being higher when the manure is more fresh.<sup>30</sup> The presence of K in ashes is also dependent on the type of bedding material used. K content is very high, around 4-6% TS, when straw is employed, while wood shavings reduce the level of K to around 1.5% TS.<sup>12</sup> The high content of K in PL (0.8-3.8%TS; Table 1) could be marketed as 'extra K', and could be reused in soils with lower K, silage or where extra K is required. P in PL is present at about two-thirds as solidphase organic P (in the form of phytic acid salts)<sup>38</sup> and one-third as inorganic P (in the form of dibasic calcium phosphate, amorphous calcium phosphate and weakly bound water-soluble phosphates).<sup>39,40</sup> A large proportion of P in PL is in acid-soluble fraction, indicating low bioavailability.<sup>41</sup> The amount of total P varies with the diet and bedding material. Guerra-Rodríguez et al.<sup>26</sup> reported 0.7% TS of  $P_2O_5$  (Table 1) in PL and Bolan et al.<sup>14</sup> reported values from 0.3 to 2.4% TS. The pH of PL fluctuates from 7.3 to 9.0. These high values are due to the levelling effect of faecal and water accumulation over time,<sup>42</sup> which favours the formation of ammonium salts, from the hydrolysis of uric acid excreted by chickens.<sup>27</sup>

Sugarcane bagasse, coffee husk and rice husk are used as bedding materials in Cuba because they are wastes generated in large amounts and have been good materials to guarantee better health for chickens and productive yield.<sup>27</sup> The variation of the parameters observed in PL reported by Ortiz *et al.*<sup>27</sup> were due to bedding materials used. However, PL generated in Cuba has characteristics similar to others (Table 1). Typically, PL is removed once the production cycle is finished (every 6 months). In order to eliminate odours, calcium carbonate or other substances are added. This is the reason of the high calcium (Ca) content in PL generated in Cuban poultry farming (0.9–1.8% TS), while other authors such as Bolan *et al.*<sup>41</sup> reported 0.16–0.19% TS.

#### MAIN BIOREFINERY PROCESSES OF PL

The main processes for the energy conversion of PL in biorefineries are discussed in this section, focusing on the use of PL as biomass. The conversion process for utilising biomass as an energy resource can be separated into three basic categories: direct combustion, thermochemical process and biochemical process.<sup>6</sup>

#### **Direct combustion**

Combustion is widely used at different scales to convert biomass to heat and/or electricity, with the assistance of a steam cycle such as power plant, stove and boilers,<sup>43</sup> in which occurs the complete oxidation of biomass in the presence of stoichiometric or excess atmospheric oxygen.<sup>16</sup> Modern systems are efficient combustion facilities with advanced gas clean-up, which produce energy and reduce the waste to an inert residue (ashes) with lower pollution in terms of GHGs. The relevant parameters to be investigated in this process for the efficient running of a combustion facility are: (i) moisture content, (ii) air mixture and (iii) combustion temperature.<sup>12</sup> Also evaluated have been energy density, calorific value, amount of volatile material generated during combustion, volume of ash at the end of the process, fixed carbon content, chemical analysis and elemental content.<sup>44</sup>

Combustion facilities may be distinguished between: (i) massburn incineration and (ii) other types which include fluidised bed. Mass-burn incineration is a large-scale incineration of mass combustion (10 and 50 tons per hour) in a single-stage chamber unit in which complete combustion takes place.<sup>13</sup> However, the fluidised bed is the most popular for the treatment of PL, which involves small-scale volumes (1 and 2 tons per hour). Among the technologies that can be used for biomass combustion, the fluidised bed is emerging as an interesting alternative due to its flexibility and high efficiency.<sup>44</sup>

#### Fluidised bed combustion

Fluidised bed combustion is an alternative method of direct combustion. There are three main types of fluidised beds: bubbling, turbulent and circulating bed types. All designs include a bed of solid particles (usually silica sand) in a refractory-lined chamber through which primary combustion air is blown from below which is supplied through a nozzle distributor plate.<sup>13</sup> Bubbling and circulating beds are considered for small-scale operation, as mature technologies. In bubbling fluidised bed combustion (BFBC), the bed particles are kept in suspension by the primary air at lower fluidisation velocities (*ca* 1.0–3.0 m s<sup>-1</sup>), while in circulating fluidised bed combustion (CFBC) higher gas velocities (*ca* 3.0–6.0 m s<sup>-1</sup>) are employed.<sup>44</sup> Figure 1 shows schematics of simple CFBC and BFBC systems. The fluidised bed reactor allows the dispersion of incoming fuel, where it is quickly heated to ignition temperature, and there is sufficient residence time in the reactor for complete combustion. In addition to combustion, a fluidised bed reactor can be used for other thermochemical processes, and offers advantages over a fixed bed reactor, such as reduction of PL treatment duration.<sup>18</sup> Compact fluidised beds facilitate high heat storage and heat transfer rates and thus allow faster ignition of less combustible waste.<sup>13</sup>

Billen et al.<sup>10</sup> considered the environmental impact of two treatment options for poultry manure: direct land spreading for agriculture and BFBC with subsequent recycling of the ashes, BFBC being the best option because of the energy recovered to produce electricity which reduces the impact on climate change and depletion of fossil resources, in addition to the generation of zero waste and wastewater. In addition, a sterile and easily transportable ash is generated, with a composition similar to that of a commercial mineral fertiliser, rich in P and K; this also contributes to the reported environmental benefits. Table 2 presents the temperature range of the reactor and the low heating value or high heating value, being an expression of the energy content of PL. Secondary air at a temperature above 900 °C is used as a combustion aid, considering the difficult fuel properties and the range of heating values. Lynch et al.<sup>17</sup> also used BFBC to reduce waste to 10% of the original mass of PL.

Abelha *et al.*<sup>12</sup> investigated the direct combustion in a CFBC system of PL mixed in equal amounts with peat to minimise the problems with high moisture content, achieving stable and sustainable combustion of PL. Although the sustainability of incineration is questionable, the interest as an appropriate treatment technology is growing as a method to eliminate pathogens and microorganisms from PL and to generate energy and ash. Li *et al.*<sup>48</sup> also investigated co-combustion in the BFBC of PL, mixed with coal, considering this an opportunity to address the energy supply issues and aid in the control of air pollution. That investigation concluded that high volatile matter contained in PL induces: (i) the bed temperature to decrease and the temperature in the freeboard region to increase; (ii) the CO emission to increase (in contrast, sulfur dioxide (SO<sub>2</sub>) emissions are reduced due to

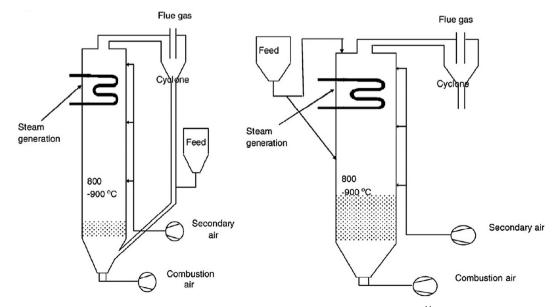


Figure 1. (a) Circulating fluidised bed combustor; (b) bubbling fluidised bed combustor. Source: Khan et al.44

ltems	Combustion <sup>a</sup>	Gasification <sup>b</sup>	Fast pyrolysis <sup>c</sup>	Torrefaction <sup>d</sup>	HTC <sup>d</sup>
Reactor type	Bubbling fluidised bed	Bubbling fluidised bed	Bubbling fluidised bed	Fluidised bed	Steel reactor
Temperature (°C)	750–765	700	450-550	300	180–210
Feed rate (g h <sup>-1</sup> )		660	200	_	_
TN flow rate (L min <sup><math>-1</math></sup> )	_	6	18	5	_
Heating value (MJ kg <sup>-1</sup> )	6–8 (LHV)	13.5 (LHV)	26–29 (HHV)	18.8 (LHV)	19.7 (LHV)

<sup>a</sup> From Billen *et al.*<sup>10</sup>

<sup>b</sup> From Pandey et al.<sup>45</sup>

<sup>c</sup> From Agblevor et al.<sup>46</sup>

<sup>d</sup> From Isemin *et al.*<sup>47</sup>

fuel-S dilution and PL ash derived from natural desulfurisation, where a strong reducing atmosphere is created that suppresses the oxidation of  $H_2S$ ; and (iii) a larger amount of released volatile matter, suppressing the formation of NO.

#### Thermochemical process

Apart from combustion, thermochemical conversion technologies are capable of converting PL into transportation fuels and fertilisers. Among them, gasification pyrolysis and hydrothermal conversion are promising technologies.

#### Gasification

Gasification is a complex thermochemical process involving drying, devolatilisation, partial oxidation and reforming of both gaseous and solid carbon compounds. Gasification can be undertaken in fixed/moving bed (updraft and downdraft configurations or some variation of these), fluidised bed or entrained flow reactors.<sup>49</sup> The use of poultry manure in biomass gasification facilities is currently underdeveloped.<sup>50</sup> In spite of that, some advantages and greater flexibility over direct combustion are achieved through thermochemical gasification, such a higher energy conversion efficiency and solid by-products (biochar and ash) from the gasifier can be used on agricultural lands.<sup>45</sup>

For the treatment of PL, due to the high content of minerals and ashes, it is usually used as a co-feed (e.g. pine wood, timber residues, coal).<sup>6</sup> Pandey *et al.*<sup>45</sup> studied, on a laboratory scale, air and air–steam gasification of PL and limestone as bedding material, using a bubbling fluidised bed gasifier. The parameters of the experimental setting are presented in Table 2. Using 0.08 kg of limestone per kg of PL, fluidisation problems caused by the mineral composition of PL ash (high K and P content) were overcome. A gaseous product with 4.5 MJ Nm<sup>-3</sup> as average heating value was obtained, which can be used in gas engines or boilers. A gaseous product with lower energy content was obtained by Katsaros *et al.*<sup>51</sup> (3.3 MJ Nm<sup>-3</sup>) through gasification of PL in a bubbling fluidised bed reactor. In this case those authors used PL only, and worked at low operating temperature for avoiding problems related to agglomeration, conducting the experiment successfully.

Multiple advantages of PL gasification, such as the reduction of the impact on the environment by more than 90% such as global of warming potential, fossil and ozone layer depletion, freshwater eutrophication, ecotoxicity, human toxicity (no cancer), ionising radiation and particulate matter formation were obtained by Jeswani *et al.*<sup>50</sup> through a life cycle analysis. The same investigation revealed that gasification of PL could supply 0.6% of the national

electricity and heat demand, saving 1.7 Mt of GHG emissions per year in the UK.

#### **Pyrolysis**

Pyrolysis occurs when biomass is heated to high temperatures (400 to 600 °C) in an oxygen-free atmosphere to produce a solid (biochar), a liquid (tars and oils) and a gaseous (syngas/methane) fraction.<sup>52</sup> The high fertiliser value of the biochar could offset the large amounts of energy required to process the PL.<sup>53</sup> The fraction of nutrients recovered in biochar is about five times higher than that in incineration ashes with better plant availability, especially for P.<sup>54</sup> Pyrolysis is considered a technically feasible and environmentally friendly alternative method for poultry waste management.<sup>55,56</sup>

Fast and slow pyrolysis processes are distinguished by the residence reaction time and the heating rate. Fast pyrolysis has a short residence time and a high heating rate, which favour a high yield of liquid product. In contrast, the long residence time of slow pyrolysis produces a high yield of solid product.<sup>57</sup> Elements like N, H and O decrease in the biochar with an increase in pyrolysis 1, while the C content increases.<sup>56</sup>

Agblevor *et al.*<sup>46</sup> used PL from broiler chicken and turkey houses, as well as bedding material (hardwood shavings) to convert into biocrude oil in a fast pyrolysis fluidised bed reactor. The conditions for the reaction are presented in Table 2. The main results of the investigation were: biocrude oil and biochar yields depended on the age and bedding material content of the PL; the viscosities of the oils were a function of source of PL and the pyrolysis temperature; and the biochar ash was very rich in K and P. Pandey *et al.*<sup>56</sup> also studied the formation of products (gases, biochar and bio-oil) during the fast pyrolysis of PL in a laboratory-scale bubbling fluidised bed reactor. The bio-oil yield was over 27 wt% and the heating value was 32.17 MJ kg<sup>-1</sup> (dry basis). In agreement with Agblevor *et al.*<sup>46</sup> the bio-oil had high N content (>7 wt%), which is higher compared to that of bio-oil produced from wood (0.1 wt%).

#### Hydrothermal conversion

In accordance with the phase diagram of water and its various regions above the vapour pressure and critical temperature, hydrothermal conversion can be classified as hydrothermal gasification (HTG), hydrothermal liquefaction (HTL) and hydrothermal carbonisation (HTC).<sup>58,59</sup> Hydrothermal conversion is a successful technology for treating animal waste.<sup>60,61</sup> Biocrude, gas phase and aqueous phase (hydrochar) are generated during hydrothermal conversion. The HTG process occurs at a relatively high

temperature of more than 215 °C, and causes a release of H<sub>2</sub> and CH<sub>4</sub>.<sup>62</sup> Liquefaction is a catalytic process in the presence of water, CO and hydrogen.<sup>16</sup> HTL can be operated at temperature and pressure near and below the critical point of water (374 °C and 22.09 MPa). It has advantages over the other thermochemical processes, due to the fact that it does not need drying pre-treatments because it is carried out in the aqueous phase, which also allows a high conversion of raw material to biocrude.<sup>63</sup> HTC is similar to HTL, but occurs at a lower temperature (less than 300 °C). Both techniques are more sustainable than pyrolysis due to the energy saving, high energy efficiency and low tar yield.<sup>61,64</sup>

Hydrothermal conversion has become a good technique as an alternative for optimising biomass valorisation; however, to our best knowledge, few researchers have made use of PL treatment using this technology. Isemin et al.<sup>47</sup> carried out an assay where they showed the results of comparative experiments between the low-temperature pyrolysis method (torrefaction) and HTC. Table 2 presents the operating parameters for both processes. The main advantage of fluidised bed torrefaction over HTC is that it requires shorter processing time (360-480 s). Also Mau and Gross<sup>65</sup> studied PL through HTC and slow pyrolysis and concluded that HTC is more energy-efficient because one can generate more net energy (24% higher) due to it involving heating the litter to lower temperatures, and it is done under pressure, avoiding the need to evaporate water. In addition, hydrochar has a higher caloric value and mass yield than biochar, leading to higher energy generation during combustion.

There are several factors limiting the sustainable use of biomass using combustion or thermochemical treatment, such as humidity, ash content and chemical elemental composition.<sup>6,44,66</sup> The high moisture and ash content in biowaste fuels can cause ignition and combustion problems.<sup>67</sup> The calorific value of PL decreases with increasing moisture content, air-dried samples having a typical value of 13.5 GJ per ton, which is about half that of coal.<sup>13</sup> Both pyrolysis and gasification processes require a pretreatment of dehydration. Thermal drying could be a method used for this purpose.<sup>15</sup> This may make the process of bioconversion of PL more expensive. More than 25% moisture content can need more energy to dry the biomass<sup>6</sup> and cause incomplete combustion and the consequent release of CO into the environment.<sup>68</sup> Kelleher et al.<sup>13</sup> considered dietary manipulation, as long as it does not adversely affect other physiological parameters of the chicken, as a method to reduce the moisture content of poultry manure. In spite of that, it is recommended that biomass with a high moisture content (more than 25%) be treated using a wet conversion process, such as AD.<sup>69</sup>

The high content of K<sub>2</sub>O and sodium oxide (Na<sub>2</sub>O) in PL leads to agglomeration in the fluidised bed, as well as the formation of scale, and corrosion of heat transfer surfaces.<sup>70,71</sup> The high content of organic N (60–90%) has a direct influence on thermochemical processes, due to the release into the atmosphere of GHGs (NO<sub>x</sub>, N<sub>2</sub>O) after reaction with oxygen.<sup>71</sup> For better results in the management of PL, many authors used co-combustion in the thermochemical process, to improve parameters such as humidity and emission of pollutant gases.<sup>12,13,72</sup>

In general, pyrolysis and gasification have an advantage over direct combustion due to better energy recovery and the possibility of using biochar as a soil amendment. However, the use of this thermochemical conversion for the treatment of PL is hampered due to high moisture content (25–49%) and other factors. Whereas, hydrothermal conversion is a more sustainable alternative to thermal treatment at high temperatures, such as gasification and pyrolysis, due to it being an energy-saving process, and drying pre-treatments are not necessary.

#### **Biochemical process: AD**

Recent studies report that AD is an efficient alternative technology that combines biofuel production with sustainable waste management.<sup>35</sup> The biogas resulting from the digestion of PL can have several uses such as electricity generation giving heat to the poultry house in cold countries, which is one of the main operational costs for producers,<sup>30</sup> or for electricity and fuel. The digester effluent contains mineralised nutrients, such as N, K and P.<sup>13</sup> Possible uses for the biosolids include fertiliser and feed supplement<sup>39</sup> and the liquid can be used for fertirrigation of traditional crops and also for the cultivation of algae rich in proteins and lipids, which can be subsequently used for biofuel production and as a feed amendment for fish and livestock.<sup>30</sup>

Previous studies have reported that among the four microbial groups involved in AD, methanogens are those with the slowest growth rate and are the most sensitive to changes in process conditions such as pH, temperature, redox and inhibitors. Hence, methanogenesis is the key pathway for biogas production and is generally considered the rate-limiting step of the entire process.<sup>73</sup> In order to achieve cost-effective biogas production, it is necessary to optimise the combination of technical and economic parameters, such as the species of microorganisms, pre-treatment and purification technologies, substrate properties and optimal reactor conditions. These are considered current issues and prospective research and development efforts should address the main research gaps.<sup>35</sup> While, research and development of novel AD products should relate to biofertiliser.<sup>74</sup>

The high content of TN in PL (3.6% TS) has a negative impact on biochemical processes, due to the inhibition of the microbial community in the AD process.<sup>73</sup> Wittmann *et al.*<sup>75</sup> found that an excess of NH<sub>3</sub>-N can cause inhibition of the AD process due to change in the intracellular pH, increase of maintenance energy requirement and inhibition of a specific enzymatic reaction. While a concentration of up to 200 mg L<sup>-1</sup> is considered beneficial because N is an essential nutrient for microorganisms,<sup>76</sup> values of NH<sub>3</sub>-N above 1.7 g L<sup>-1</sup> can cause a 50% reduction of CH<sub>4</sub> production.<sup>73</sup>

PL has high pH value in the range of 7.3–9 (Table 1). By comparison, the optimum pH for AD is generally in the range 6.5 to 8.0.<sup>77,78</sup> It has been probed that if this parameter is regulated before and during AD, the methanogenesis process could be improved and better biogas production could be achieved.<sup>79</sup> The problem represented by the high pH of PL is closely related to the inhibition by N. During AD at high pH there is a shift of the equilibrium from free NH<sub>3</sub> to ionised (NH<sub>4</sub><sup>+</sup>) ammonia, which is identified as the main cause of inhibition.<sup>80</sup>

In order to minimise NH<sub>3</sub> inhibition, the use of treatments such as ammonia stripping<sup>81,82</sup> and dilution of the material to 0.5–3.0% TS have been recommended,<sup>83</sup> to increase the CH<sub>4</sub> yield of this residue. In addition, to reduce NH<sub>3</sub> content in AD, trace elements such as Se, Co and W or a combination of these could be added which can stabilise the AD process and biogas production.<sup>84</sup> Also used have been ion exchange,<sup>85</sup> zeolite adsorption<sup>86</sup> and struvite precipitation.<sup>87</sup> In addition, a better use of PL as biomass can be obtained using co-digestion. This allows optimum parameters such as pH, C/N ratio and NH<sub>3</sub> concentration.<sup>73</sup>

#### PL in co-digestion

PL is not well suited to AD because of its physical and chemical characteristics, but a great number of researchers have reported

the successful operation of digestion systems. Co-digestion of Nrich substrates with C-rich substrates has been proposed as a solution to unfavourable C/N ratios. PL has a C/N ratio in the range 6–12.<sup>19,88</sup> However, the optimum C/N ratio is within the range 20:1 to 30:1.<sup>89,90</sup> Carbon is consumed at a faster rate; therefore, a high C content is required to operate at optimum conditions.<sup>91</sup> The importance of co-digestion is that, in addition to achieving an optimum C/N ratio, it allows one to stabilise conditions in the digestion process, such as macro- and micronutrients, pH, inhibitors or contaminated compounds and dry material.<sup>77</sup>

The suitability of PL in co-digestion with different substrates has been addressed by many researchers. Some recent research includes wheat straw,<sup>25</sup> yoghurt whey, municipal solid waste, hay grass and wheat straw at different ratios,<sup>92</sup> food waste, wheat straw and hay grass,<sup>93,94</sup> cow dung,<sup>79</sup> municipal solid waste,<sup>91</sup> corn stover or apple pulp,<sup>95</sup> sugar beet pulp<sup>96</sup> and microalgae.<sup>97</sup> In all cases, CH<sub>4</sub> yield was greater than 300 mL g<sup>-1</sup> VS<sub>added</sub>. Codigestion of PL yielded roughly double the CH<sub>4</sub> production compared to the digestion of PL as monosubstrate (150–-160 mL g<sup>-1</sup> VS).<sup>30</sup>

The co-digestion of PL with substrates, fundamentally agroindustrial wastes, is the most cost-effective technique to reduce NH<sub>3</sub> inhibition and is less difficult to implement.<sup>19</sup> However, if a suitable carbon-rich co-substrate is not available nearby, codigestion will not be feasible due to high waste transport cost. Thus, nutrient removal technologies to extract N are a trend in the management of PL as monosubstrate for AD.

#### PL as monosubstrate in AD

Some of the more recent reports include the treatment of chicken manure as monosubstrate. Most of these systems were designed combining AD with membrane-based ammonia separation,<sup>4,98,99</sup> stripping ammonia<sup>81,82</sup> and AD via two stages,<sup>4,100</sup> to avoid NH<sub>3</sub> inhibition and minimise NH<sub>3</sub> in the digestate.

Bayrakdar et al.<sup>98</sup> used batch experiments with AD of egg-laying hen manure combined with membrane-based NH<sub>3</sub> separation. Two types of membranes were used to remove NH<sub>3</sub> from the continuously fed anaerobic digester. The first was a hydrophobic hollow-fibre polypropylene membrane (ACCUREL®) PP 300/1200) and was used after day 68. After day 95 a tubular hydrophobic polypropylene membrane (ACCUREL® PP V8/2HF) was used, to overcome the acid leakage problem. The main advantages were a  $CH_4$  yield of 300 mL  $g^{-1}$  VS with high OLR (6.0 kg VS  $m^{-3}~d^{-1})$  and high influent TKN concentration (15 g L<sup>-1</sup>) without incurring any process failure. Furthermore, NH<sub>3</sub> removed from the digester was recovered as ammonium sulfate, which can be used as fertiliser. Monofermentation of chicken manure was also successfully carried out by Bayrakdar et al.98 using membrane ammonia separation in a single-stage methanogenic leach bed reactor, which allowed a  $CH_4$  yield of 272 mL  $g^{-1}$ VS, while Wang *et al.*<sup>4</sup> achieved better CH<sub>4</sub> yield (470 mL  $g^{-1}$  VS) using membrane contractor as intermediate in two-stage AD.

Dalkılıc and Ugurlu<sup>100</sup> used PL as monosubstrate at TS loadings higher than 5%, in a two-stage mesophilic acidogenicthermophilic methanogenic AD system. With the stage separation, biogas yields of 426–554 mL g<sup>-1</sup> VS<sub>feed</sub> were obtained at shorter hydraulic retention time (12 days), with 74% as average for the CH<sub>4</sub> content. However, although the separation of the AD process into two stages can increase the conversion rate of biomass into CH<sub>4</sub>, the cost of such a complex system is a disadvantage.<sup>101</sup>

Stripping–scrubbing systems are coupled to an anaerobic digester to reduce potential  $NH_3$  inhibition during AD. Different

pathways can be implemented: after mechanical separation of the digestate, the liquid fraction is stripped and recirculated into the digester, or the raw digestate is stripped using biogas as a stripping agent, then the NH<sub>3</sub>-rich biogas is scrubbed and the stripped digestate is recirculated into the digester.<sup>102</sup> Nie *et al.*<sup>82</sup> designed an experiment in which the entire liquid digestate from chicken manure was recirculated into the digester after the stripping–scrubbing process. A stable process was realised at high loading rates (6 g L<sup>-1</sup>), with specific biogas yield of 270 mL g<sup>-1</sup> VS and an average free NH<sub>3</sub>-N concentration of 0.86 g L<sup>-1</sup>.

### Sustainable pathways combining thermo- and bioconversion processes

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A closed-loop system is an important concept for PL management in which the outputs from one industry become inputs for another. Therefore, pollution could be reduced because waste as a raw material is reused, which could be transformed into another useful product.<sup>15</sup> A better valorisation of PL can be achieved by combining different techniques. At the moment the realisation is incipient, but there are investigations that model and optimise technological superstructures aimed at increasing yield in the recycling of nutrients and obtaining energy from PL.<sup>15,61,103,104</sup>

Then, according to the different technologies and possible combination of techniques described in the literature and other considerations, such as adequacy of the substrate to allow better conversion, the authors propose alternative sustainable pathways for PL valorisation (Fig. 2). They are considered as sustainable because they are intended to close the cycle; as a consequence, the output products become inputs for the next process. In this way, pollution is reduced as the wastes are reused and transformed into useful products. However, it will be necessary to evaluate the sustainability between the different alternatives in further research.

Five major steps are involved in converting PL into useful resources: pre-treatments, key conversion, products, post-treatments and applications. As pre-treatments, dewatering processes should reduce the moisture content of PL to about 10%, prior to pyrolysis/gasification processes. Thermal drying has been reported as a dewatering method.<sup>15</sup> For HTC, pre-treatment for dewatering is not required because the reaction is carried out in aqueous phase. However, for AD, due to slow digestibility of the bedding material, and the high N content and pH values, other pre-treatment technologies are required. In this case leaching and nutrient removal might be advantageous to guarantee that at the entrance to the reactor is soluble material with a low concentration of elements such as N that limit the digestion process.

The second step is key conversion through thermal and/or biochemical processes, where PL is converted into energy and bioproducts. After thermal drying, the dried PL is converted into raw syngas (CO, CH<sub>4</sub> and H<sub>2</sub>) at 500–550 °C in the absence of oxygen. After the incomplete pyrolysis of PL, the remaining solid contents are passed to an updraft gasifier where they are reacted with a gasification medium (air or oxygen). The gas produced by the combination of pyrolysis and gasification could be burned to generate electricity; also biochar is obtained. Huang et al.<sup>103</sup> obtained good results in the modelling of these combined techniques integrated with an organic Rankine cycle (to use exhaust heat of low energy and temperature, in which an organic working fluid is used instead of water or steam), among which are the technical and economic feasibility for the use of PL as feedstock, and the economic incentive due to the high profit margins when using biochar in a combined heat and power system. The carbon content

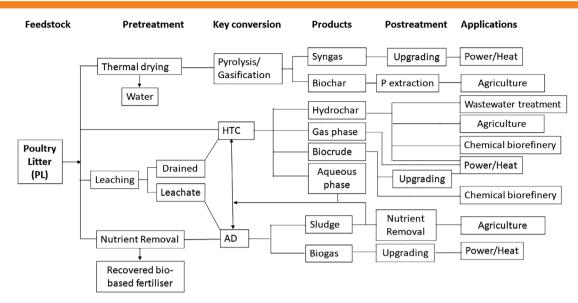


Figure 2. Pathways of PL valorisation process.

of the biochar generated was typically in the range 25–40%. Another option is using direct HTC of PL as thermal conversion without pre-treatment. HTC is operated at temperatures and pressures near and below the critical point of water, generating biocrude, aqueous-phase, gas-phase and hydrochar products.

To overcome the slow digestibility, leaching of PL can be used to separate soluble and insoluble materials before AD. After leaching pre-treatment, the bedding material is retained in the insoluble fraction (drained), with TS around 26-30%. While soluble leachate contains 0.36–0.48% of TS, which primarily has digestible manure components, being appropriate feedstock for AD. Drained material is treated through HTC, due to insoluble materials not representing problems in this thermal conversion. Another option is AD as key conversion for PL treatment as monosubstrate. After nutrient removal, nutrients such as N, K, P and S are recovered which are named in this paper as recovered biobased fertiliser, and anaerobic sludge (digestate) depleted in ammonia can be feedstock for HTC or can be recirculated inside the digester to enhance methane yield. This study was carried out by Vardon et al.<sup>104</sup> using digestate from wastewater treatment at 300 °C, 10-12 MPa and 30 min reaction time. Biocrude yield of 9.4% was obtained, the livestock composition having a strong influence on the biocrude functional group chemistry. Many applications could make use of the biocrude oil generated, such as for bunker crude, boiler or asphalt applications, similar to vacuum gas oil and vacuum residue produced from petroleum crude. At the same time, aqueous phase from HTC can be used as feedstock for AD, as long as phenol and furfural contents do not limit the digestion process. In this case methane-rich biogas is produced and fertiliser could be obtained from the liquid digestate and biochar after phase separation of HTC. A detailed overview of the parameters and conditions required to implement this pathway (HTC/AD) for lignocellulose biomass has been reported.61

The following section discusses products generated from PL biorefineries, focusing on the pathways proposed in this paper (Fig. 2). Nutrient recovery technologies are adopted as post-treatment in some cases in order to obtain subproducts with high fertiliser value.

#### **BIOREFINERY PRODUCTS** Energy and bioproducts

Primary products such as syngas, biogas and bio-oil can subsequently be burnt (in furnaces, steam turbines, gas turbines or gas engines) to produce energy in the form of heat and/or electricity. Products generated from different pathways for the PL valorisation process as well as subproducts and possible applications after pre-treatment are shown in Fig. 2.

The remaining ashes after direct combustion of PL are rich in P and K.<sup>10</sup> However, such ash may contain heavy metals, which are hazardous for human health if used as substitute of synthetic fertiliser. Pandey et al.<sup>56</sup> recommended that fly ashes from PL gasification need post-treatment if utilised as a fertiliser due to the presence of higher concentrations of Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb and Se in the fly ashes, being classified as a hazardous material. Hence, the extraction of P from ashes has been carried out by companies like Finnish company Outotec, which adds alkaline additives and heats the ashes to high temperatures (1000 °C) in order to gasify the heavy metal compounds. Phosphorus is recovered as calcium hydrogen phosphate (CaHPO<sub>4</sub>) and commercialised as chemical mineral fertiliser. However, for combustion processes involving high energy consumption, in addition a thorough flue gas cleaning system is needed and post-processing to remove heavy metals for P recovery; hence extraction of P from combustion ashes is not a sustainable practice.<sup>54</sup>

Biocrude, gas phase, aqueous phase and hydrochar are generated during hydrothermal conversion. The gas phase mainly consists of CO<sub>2</sub>. Biocrude oil can be upgraded for commercial utilisation (Fig. 2). Complicated reaction mechanism is not required for the upgrading of biocrude from HTL because it has less moisture and oxygen content and hence the fine hydrotreatment will enhance the quality.<sup>61</sup> According to Vardon *et al.*,<sup>104</sup> some functional groups such as short aliphatics, long-branched aliphatics, alcohols, ethers, carbohydrates, aromatics, olefins, esters, carboxylic acid ketones and aldehydes were detected in biocrude oil from HTL of anaerobic sludge. These compounds can be extensively used in biorefinery industry for manufacturing chemicals.

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There are many differences between hydrochar and biochar. Hydrochar has less ash content as compared to biochar produced via slow pyrolysis; also it has many oxygen-containing functional groups that are retained over its surface, and this means it has a wide number of applications.<sup>64</sup> Hydrochar can be employed as solid fertiliser,<sup>15</sup> also as contaminant soil remediation and wastewater treatment because of its high adsorption ability, focusing on heavy metal ion adsorption. Other applications are found like carbon sequestration, bioenergy production and as raw material for extraction of chemical compounds.<sup>64</sup>

Digestate is a residual nutrient-rich sludge from AD. Digestate can be used as a biofertiliser for arable land, enabling recirculation of plant nutrients, and thus reducing the need for fossil fueldependent inorganic fertilisers.<sup>105</sup> Despite its high potential, in some countries like those of the European Union, digestate is still categorised as animal manure in fertiliser legislation.<sup>54</sup> Inadequate digestate use could represent a problem in crops especially in high-nutrient regions. Strict N and P fertilisation levels in the framework of environmental legislations, as well as large volumes and high transportation and storage costs hinder the use of digestate is required in order to concentrate and recover the nutrients of high quality, thereby overcoming the barriers related to the direct application to soil and crops.

#### Technologies for nutrient recovery from digestate

Nutrient recovery from digested as marketable products has become an important task for AD plants to meet both market demands and regulatory drivers, while producing an internal revenue source. Frequently, to recover nutrients from digestate, mechanical separation into a liquid fraction and solid fraction is needed, aiming at dewatering. The solid fraction is rich in recalcitrant organic matter, Ca, Mg and P, while organics and mineral salts are present in the liquid fraction (rich in N).<sup>107</sup> The potential to recover soluble nutrients from the liquid fraction by use of extraction techniques is better than that from the solid fraction.<sup>108</sup> Stripping–scrubbing, membrane filtration, NH<sub>3</sub> and P adsorption, struvite precipitation and biological nutrient removal are well-known nutrient recovery technologies.

#### Ammonia (NH<sub>3</sub>) stripping–scrubbing

NH<sub>3</sub> stripping-scrubbing is the most frequently applied option for NH<sub>3</sub> removal, which involves the physical mass transfer of NH<sub>3</sub> from the liquid to the gas phase. The temperatures of typical processes range from 50 to 85 °C. The gas is then transferred to an air scrubber, where mass transfer and absorption of NH<sub>3</sub> from the gas to a liquid phase, using sulfuric acid  $(H_2SO_4)$  or nitric acid  $(HNO_3)$ as scrubbing agents, takes place in order to form and recover a concentrated solution of ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) or ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) as an end product.<sup>109</sup> Both N-rich salts are considered valuable fertilisers for agriculture (typical N recovery of 80–90%).<sup>54</sup> Sigurnjak et al.<sup>102</sup> obtained good results using  $(NH_4)_2SO_4$  and  $(NH_4NO_3)$  with a similar effect on crop yield and risk for nitrate leaching as compared to conventional synthetic N fertiliser. The same authors observed great variability in N concentration present in the salts, which is considered the biggest challenge for their recognition as N fertilisers.

#### Membrane filtration

This nutrient recovery technology shares certain similarities with the stripping process, where  $NH_3$  is recovered in an acidic

Use of membrane extraction, such as reverse osmosis, electrodialysis and transmembrane chemosorption, has potential for NH<sub>3</sub> recovery from effluents.<sup>28,111</sup> However, clogging and fouling of the membrane are technical problems resulting in significant chemical and energy requirements. More studies are needed to improve the performance of membrane filtration in terms of chemical and energy requirements, as well as operational costs.<sup>54</sup>

Tampio *et al.*<sup>107</sup> achieved a concentrate with 17.9 kg N (tFM)<sup>-1</sup>, 0.3 kg P (tFM)<sup>-1</sup> and 9.0 kg K (tFM)<sup>-1</sup> in the treatment of liquid digestate of food waste by combining both reverse osmosis and evaporation. The condensate was obtained at 80 °C with addition of H<sub>2</sub>SO<sub>4</sub> to regulate pH to avoid loss of NH<sub>4</sub><sup>+</sup> during evaporation, and then was treated with reverse osmosis. This combination of techniques was considered an efficient system in concentrating N from the feedstock into fertiliser products due to the low mass of the product (16%) and low energy consumption of the treatment (80% energy saving during transportation in contrast to untreated digestate liquid).

#### NH4<sup>+</sup> and P adsorption

Adsorption of nutrients like ammonium  $(NH_4^+)$  and P can be achieved using a packed column with the following materials: zeolites, clays and resins. At the end of the process a concentrated solution of  $NH_4^+$  and/or P can be recovered. The advantage of this nutrient recovery technology is that adsorption media can be regenerated using nitric acid  $(HNO_3)$  washing, sodium chloride (NaCl) washing or biologically, depending on the adsorption material and the desired P end product.<sup>54</sup>

Natural zeolites have been used successfully in the treatment of wastewater, for example as adsorption agents for final NH<sub>4</sub>-N removal.<sup>112,113</sup> Zeolites can be used as an intermediate step in the digestate treatment train.

Mineral-based materials such as red mud, metal oxide/hydroxide and zirconium sorbents for P sorption and recovery have been used. P may be removed from solution via selective sorption to a solid phase. The end use depends on the purity desired; P could be used in direct form as a fertiliser or soil conditioner, or may subsequently be stripped from the solid sorbent and chemically precipitated as a high-purity fertiliser. Cost–benefit analyses for nutrient recovery from digestate using zeolites or other kinds of sorbents are needed to improve this nutrient recovery technology.<sup>54</sup>

#### Struvite precipitation

Struvite is a mineral that contains Mg,  $NH_4^+$  and P in equal molar concentrations (Mg $NH_4PO_4 \cdot 6H_2O$ ). Struvite precipitation has been amply investigated as a post-treatment process in wastewater treatment for phosphate ( $PO_4^{3-}$ ) recovery. Also, it can be used for nutrient removal in liquid digestate, after solid–liquid separation. Struvite precipitation could be an alternative for the sustainable and economical recovery of P from P-rich organic residues, mostly involving the addition of magnesium and sodium hydroxide to a solution containing soluble  $PO_4^{3-}$  and  $NH_4^+$ . The formation of struvite is conditioned by several physicochemical parameters such as pH, temperature, chemical composition of wastewater and a combination of factors such as the presence of crystal seeds, thermodynamics and mass transfer between solid and liquid phases.<sup>114</sup> For struvite precipitation, technologies like stirred tank and fluidised bed reactors are the most widely used.<sup>115</sup> These techniques not only alleviate the scale problem in wastewater treatment plants, but also provide a pelletisable fertiliser product, showing both environmental and economic benefits.<sup>115</sup> Münch and Barr<sup>116</sup> reported that a treatment plant can recover 1 kg of struvite from 100 m<sup>3</sup> of wastewater.

High-purity struvite crystals may be obtained under appropriate conditions. The pH range in which struvite may precipitate is between 8.3 and 10.<sup>117</sup> Some authors have indicated that calcium can interfere with struvite precipitation by formation of amorphous calcium phosphates.<sup>118</sup> Crutchik and Garrido<sup>119</sup> reported that with a fixed NH<sub>4</sub><sup>+</sup>/PO<sub>4</sub><sup>3–</sup> molar ratio of 4.7 pure struvite can precipitate; however, with a ratio of 1.0, precipitates of amorphous magnesium and calcium phosphates are obtained.

Struvite precipitation can be used to improve AD during processing of PL, by adding inside the digester mixed magnesium phosphate compounds. Romero-Güiza *et al.*<sup>120</sup> reported an NH<sub>3</sub> reduction up to 80% and a 40% increase in CH<sub>4</sub> production during the AD of pig manure. However, long-term digester operation is required to assess the feasibility of such digestion and to ensure that the chemicals do not induce problems for the anaerobic microorganisms.

#### Biological nutrient removal

The use of microalgal growth as a wastewater treatment method is considered a promising solution in the environmental field, to overcome the high costs of microalga cultivation and, at the same time, to remove excessive nutrient in effluent. Unlike the methods discussed above, which are based on physicochemical considerations, microalgal growth is examined for biological nutrient recovery. This method has advantages in terms of high photosynthetic efficiency in CO<sub>2</sub> fixation, growth rates and biomass production.<sup>121</sup> The biomass obtained by alga/macrophyte cultivation could have various applications, such as feedstock for the chemical and biofuel industry, animal feed and fertiliser.<sup>43</sup>

The ability of microalgae to assimilate excess nutrients from nutrient-rich effluent has been thoroughly studied. The digestate from AD is particularly promising for its high content of mineralised nutrients.<sup>5</sup> Franchino *et al.*<sup>122</sup> obtained a high removal efficiency (>90%) for NH<sub>3</sub>, total N and PO<sub>4</sub><sup>3–</sup> using the green alga *Chlorella vulgaris* as treatment in diluted digestate from pig slurry and corn, and significant reduction of toxicity (73.6–81.7%) for the organisms that showed the highest sensitivity to digestate without treatment.

The use of microalgal growth using various types of digestate, namely dairy manure,<sup>123</sup> cattle slurry, raw cheese whey<sup>124</sup> and from municipal wastewater treatment plant,<sup>125</sup> showed a good potential for nutrient removal. However, design of the alga cultivation system at pilot and full scale needs more attention due to problems such as inhibitions, inconsistent slurry components and unstable biomass production.<sup>106</sup>

In general, although the high N contents in PL make difficult its digestion by AD, this can be considered an opportunity to generate through nutrient recovery technology a recovered biobased fertiliser (Fig. 2). These technologies can be used both as pretreatment to improve AD and as post-treatment of the digestate to market as valuable fertiliser. Due to the simplicity and cost-effectiveness of these technologies they can be coupled in the biorefinery pathway, which allows closing of cycles and therefore maximising the PL valorisation process.

#### **REFORMING POULTRY FARMS INTO BIOREFINERIES IN CUBA**

Sustainable development in Cuba, as a new concept of economic advance, is presented as a process where energy policy must be formulated in a way that achieves sustainable development from an economic, social and ecological perspective with renewable energy resources being a priority in the new Cuban economic model.<sup>9</sup> The sustainability of agricultural activities and their contribution to local development in rural communities are also at the centre of Cuban priorities, looking for revenues from the

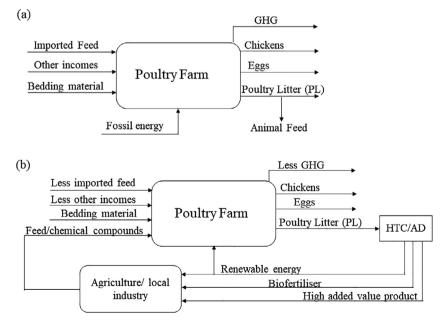


Figure 3. General scheme of poultry farm: (a) actual; (b) reformed into biorefinery.

transformation of local available resources, autonomy of enterprises and new commercial models for small-scale farmers.

The production of chicken is made, for most part, by the Livestock Business Group (GEGAN, for its acronym in Spanish), which is state property. Poultry companies are subdivided into farms, which are classified as laying, replacement and breeders.<sup>126</sup> In Cuba, around 220 poultry farms exists with 13 834 thousands of heads in total, at the end of 2018,<sup>9</sup> with a generation of 2075 tons of PL per day (considering 0.15 kg excrete-day/animal). Figure 3(a) shows a general scheme focused on the input and output products of poultry farms that are currently operating. In Cuba there are studies that recommend the use of PL as an additional feed for ruminants. These investigations are on the basis that the wastes used as bedding are enriched in terms of nutritional value due to the faeces of the chickens, food spills, feathers, insect growth and fermentation.<sup>27,127,128</sup> However, other authors have emphasised that the feeding of unsterilised poultry excreta to farm animals is potentially dangerous due to prevalence of pathogen microorganisms, antibiotic-resistant enteric key bacteria, pesticides, hormones, fungi, toxins, parasites, copper and arsenic, among others.<sup>129–131</sup> This is therefore a potential risk for transmission through the food chain and environmental risks to local farmland. On the other hand, the inadequate treatment of PL causes high emissions of GHGs such as CH<sub>4</sub>, CO<sub>2</sub> and NO<sub>x</sub>.

The use of PL as biomass for power generation has been little studied and thus poorly implemented in Cuba; there are no studies of sustainability or implementation cost of thermochemical technologies in a Cuban context. In Fig. 3(b) the general scheme of a poultry farm reformed into a biorefinery is presented. The PL could be treated through a flexible combination of HTC/DA for the generation of energy and high-added-value products. Energy production could be used to cover 100% of thermal and electrical energy demand in Cuban poultry farms, and to increase agricultural production by providing renewable energy in agricultural activities. On the other hand, digestate from AD, agueousphase effluents and hydrochar from HTC could be employed as biofertiliser to improve grain crops, replacing imported feed for chickens. In addition to hydrochar nutrient content, it can be used to purify the biogas generated during AD, due to its gas adsorption capacity. Also, hydrochar and biocrude can be inputs in the local industry for manufacturing chemicals. Overall, farmers can produce their own energy, biofertiliser and other products with high added value to become more self-sufficient by reducing external inputs. This not only helps the farmer save money, it also combats the effects of global warming by reducing GHG emissions. Employment creation, improvement of living conditions and sustainable development are also advantages of reforming poultry farms into biorefineries in rural communities.

#### CONCLUSIONS

A biorefinery of PL represents the integration of biomass conversion processes and equipment, with technologies such as combustion, thermochemical process (gasification, pyrolysis and hydrothermal combustion) and anaerobic process being used at large and small scales. There are several factors that limit the sustainable use of PL in biorefineries, such as limited digestibility of bedding, high humidity, high chemical elemental composition (mainly nitrogen, calcium, potassium) and high pH. Possible remedies such as dietary manipulation and use of PL in cocombustion or co-digestion have been successful. In this work a superstructure was proposed which contains five major sections for converting PL into useful energy and fertilisers. Three pretreatments to improve key conversion technologies were employed and two post-treatments to enhance product value as energy and fertiliser. The combination of AD and HTC pathway suggests multiple advantages because of allowing more options for the treatment of the raw material giving flexibility, being more energy-efficient and allowing better application of the products. Nutrient recovery technology could be included in biorefinery pathways of PL and improvement of AD (using PL as monosubstrate) as well digestate application as fertiliser. Reforming poultry farms into biorefineries in Cuba would allow multiple advantages such as energy and nutrient autonomy as proposed by the Cuban State.

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