

Article

Manufacturing of a Granular Fertilizer Based on Organic Slurry and Hardening Agent

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Abstract: The manufacturing of a granular fertilizer based on organic slurry (OS) and sorptive materials aims to enhance the circular economy. This article describes a technology that was conceived after appraising the chemistry of the anaerobic digestate and wood ash and the synergies of combining both materials. The information available in the literature about similar materials such as cattle slurry and lime was also considered to build a better understanding of the underlying science. The processes and machinery designed were optimized from the points of view of energy and material consumption, cost of storage, transportation and land application. The system was sized to process 1 tonne of OS (97% moisture) in a 10 h batch-shift, consuming 140 kg of wood pellets and 0.55 kW of electricity for the fan blowing preheated air. The results of the market research allowed us to reach the most economically viable routes for the commercialization of granular fertilizers. Based on the financial study, an initial investment of GBP 20,000 is needed to successfully implement the value proposition and business plan. The wide adoption of the composite fertilizer improves the management of the OS and reduces the contamination of air, soil, and water derived from intensive agricultural practices.

Keywords: waste valorization; fluidized bed drier; ammonia sorption; pelletization; granulation; slow release; nutrients recovery; composite fertilizer; market research; business plan



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1. Introduction

Recent developments of fertilizers and manures for application in farmlands have increased in recent times. This includes the manufacture of granular fertilizers, application of anaerobic digesters and utilization of manures. There are several factors that promote the implementation of manure treatment techniques, such as anaerobic digestion (AD), in farms [1]. These factors include pressure from policies and regulations; the ease of the export of manure off the farm; the production of bioenergy; the increase in the price of chemical fertilizers; the potential income due to the sale of processed products; and the control of diseases, pathogen and odors.

According to Hou et al. [1], on-site manure treatment is applicable to farms with more than 50 livestock units. Technologies such as AD and drying (pelletizing) are perceived by the stakeholders of the agro-industry as only applicable at an industrial scale or farm cooperatives. However, mechanical solid–liquid separation can be implemented at a lower scale. The present study aims to promote the acceptance of technologies for the valorization and downstream processing of the OS at a farm level to avoid the unnecessary cost of storage and transportation of a large volume of OS.

Currently, much more animal manure is applied to land as a soil amendment than an anaerobic digestate because of the high capital expenditure (CAPEX) and operational expenditure (OPEX) associated with the implementation of AD in the farms [1]. In 2008, the EU27 produced 259 million tonnes of municipal solid waste [2], and the organic

fraction (OFMSW) represented 87.7 million tonnes that year [3] (p. 23). In 2020, the European Commission expected a production of OFMSW of 96.4 million tonnes in the EU27 [3] (p. 24). Even if all the OFMSW were processed via composting or anaerobic digestion, the amount of these materials that is employed as soil amendment would be much lower than the animal manures. The key chemical species in the organic slurries (animal slurry, anaerobic digestate, compost, etc.) are ammoniacal nitrogen ($\text{NH}_4^+\text{-N}$), phosphorus in the form of orthophosphate, carbonate/bicarbonate and volatile fatty acids (VFA) [4,5]. The reason is the similar nature of the feedstock and the fermentation taking place in the anaerobic digester [6] and the guts of livestock [7]. The differences between the complex matrices of animal manures, anaerobic digestates and other types of soil organic amendment can be further simplified by lumped analysis of the VFA as part of the total carbon. In order to improve the marketability of the organic fertilizer, it is necessary to improve the aesthetic properties of the organic materials and the nutrient content [8–10]. Due to the presence of phosphorus and inert carbon in the wood ash, this material has been identified as the additive to the anaerobic digestate that enables the preparation of a composite fertilizer [11–14].

Figure 1 show the two main roles of the additives to the organic slurries: as nutrient supplement or as a sorbent to improve the properties as a slow-release fertilizer. The acids are widely used in the industry [15,16] to minimize the volatilization of NH_3 during storage and land application. Mild acidification helps to better preserve the slurry before land application since the lower pH reduces the microbial activity [17–19]. The use of H_2SO_4 , HNO_3 , and H_3PO_4 implies increasing the content of sulfur, nitrogen and phosphorus in the OS. The addition of mineral fertilizers to the slurry is an option [19–21], although the supplementation is usually preferred after land application [22–25]. This supplementation aims to improve the use efficiency of carbon [4] and crop nutrients such as nitrogen [26]. This practice relies on the optimum nutrient ratio for each type of soil and crop and the nutrient quotas established in the regulations to avoid pollution of the environment [27–30]. Additives such as biomass ashes or biochar, in addition to providing the slurry with trace metals, also promotes sorption processes [31] and restores the soil as a carbon sink [32,33]. Figure 1 includes acid and thermal procedures for the activation of the biomass ash, which are used to improve the management of organic soil amendments. The activation of the sorbents enables greater crop yields upon land application of the amended fertilizers, less need for covered storage facilities for organic slurries with 97% moisture [34], and also reduces the cost of transportation.

The aim of the OWAS (Organic Waste Adsorption Stabilization) project is to introduce a preliminary design of a process flow diagram prototype for the treatment of the OS and the manufacturing of a composite fertilizer. In this paper, Section 1 introduces the review, while Section 2 presents the materials and methods. Section 3 presents the results on the process design, while Section 4 presents the discussion on the findings and the development. Section 5 is the future research perspective, while Section 6 presents the concluding remarks with some recommendations for the research.

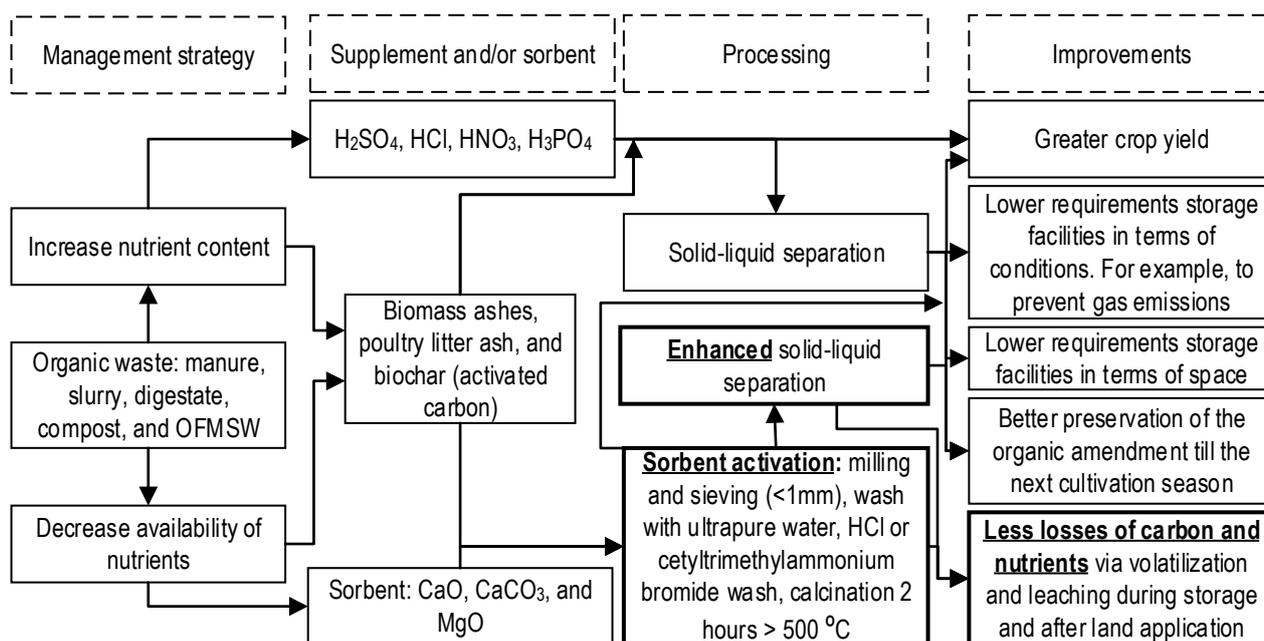


Figure 1. Management strategies for organic wastes and the intended economic and environmental improvements.

2. Materials and Methods: Level of Stability of the OS

The levels of stability are key concepts in processing organic slurries, and these are defined in Figure 2. These levels were based on the intended properties for the advanced fertilizers to be produced by treating the OS with the addition of an HA. Other types of stabilities, such as thermal stability, could also be interesting for processing the OS for bioenergy purposes and the preparation of a fertilizer. For example, for the production of biofuel via hydrothermal liquefaction [35–37], the impact of the composition of the digestate in its thermal stability would need to be assessed [38], since the pyrolytic behavior of this raw material affects the processing and the properties of the end products. Pyrolyzed biomass with a carbon content higher than 50% is recognized as biochar; otherwise, it is called pyrochar [39]. The differentiation of the adsorbent materials could also be made from the point of view of the manufacturing process. For example, the hydrochar produced via hydrothermal carbonization (HTC) presents lower porosity and surface-specific area than the biochar (usually $>400 \text{ m}^2$ per gram of biochar). Furthermore, biochar presents greater content of condensed polyaromatic structures, which makes this material a good adsorbent for various contaminants. Nevertheless, due to the presence of oxygen-rich functional groups on the surface of hydrochar, its adsorption capacity is also high [39]. The thermal stability was considered to be less relevant for the production of the stabilized organic amendment because it is more difficult to relate to the desired properties of the soil organic amendment than the other levels of stability defined in Figure 2. The levels of stability displayed in Figure 2 helped to elucidate the processing steps and the way of combining the HA and the OS to create a novel fertilizer. In fact, they were conceived after reviewing the technologies most widely employed for the production of a digestate based granular fertilizer [31].

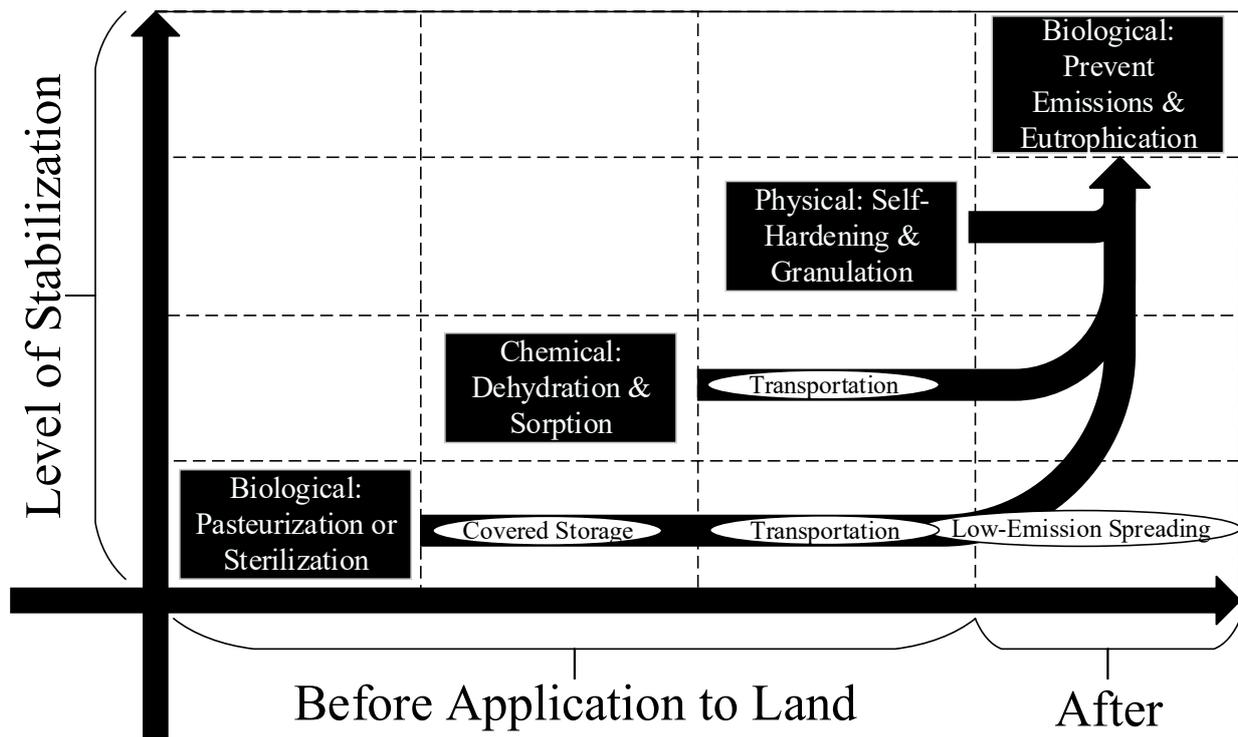


Figure 2. Different levels of stabilization of OS with 97% moisture [12]. Reproduced with the permission of the first author—A.M.A. and Elsevier Publishers, copyright granted on 13 February 2022. Source: Journal of Environmental Chemical Engineering (Elsevier).

2.1. Biological Stabilization before Land Application

The first level of biological stabilization (as seen in Figure 2) is cited in the industry regulations and publicly available specifications, such as the PAS 110 [40], which establishes the specifications of the anaerobic digestate in the UK. The level of biological stability is measured with a biochemical methane potential test [41]. The carbon use efficiency (CUE) could be a better measurement of the biological stability [42]. The CUE is a parameter used in soil science that measures which fraction of carbon is employed for microbial growth (i.e., g biomass—C synthesized/g substrate—C consumed) and which is not lost as part of the microbial respiration (i.e., carbon mineralization). In some of the UK and European regulations, the terms stability and maturity are used indistinctly [43–45]. The biological stability is related to the reactions affecting the fate of carbon, which is the most abundant element in organic materials, and the maturity focuses on all the other elements. Some of them are nutrients necessary for plant growth (e.g., N, P, K, etc.), while others are phytotoxic compounds (e.g., Cd, Hg, Pb, etc.) which limit seed germination and root development. It is important to mention that the excess of any type of nutrient has a detrimental effect on the soil biota and the environment. In this communication of the OWAS project, the term nutrient is used to refer to those essential elements that are required for the plants to grow. Therefore, it includes primary (nitrogen, phosphorus and potassium) and secondary (calcium, magnesium, sodium, and sulfur) macronutrients [46]. Furthermore, carbon is also a nutrient for the microbes in the soil. Since the biological stability defined in the regulations is only related to the utilization of the nutrients after land application, the term biological stability before land application was applied to refer to an organic amendment that has been pasteurized (i.e., pathogen-free) or sterilized (i.e., does not contain any microbes alive).

2.2. Chemical Stabilization

The chemical stabilization of the organic waste with 97% moisture [34] implies that the nutrients cannot be easily lost. In this way, this level of stabilization is, at least, required to

improve the properties of the OS as a slow-release fertilizer. The controlled availability of the nutrients is beneficial to: (a) reduce the greenhouse gas (GHG) emission and eutrophication of surface and underground water; (b) fertilize more effectively the crops by supplying only the amount needed for the plants to grow; and (c) enhance the dewatering process. The mechanism of the chemical stabilization could involve several processes [31,47]. It is noteworthy to mention the sorbent properties of calcium [48,49], which is one of the most abundant components in the wood ash, with an average content of around 18% of this element [50]. This technology can also be used for processing completely liquid wastes, such as urine [51–54]. $\text{NH}_4^+\text{-N}$ rather than organic nitrogen denotes a high level of maturity [31] but a low level of chemical stability unless the $\text{NH}_4^+\text{-N}$ is precipitated, for example in the form of struvite ($\text{NH}_4^+\text{Mg}^{2+}\text{PO}_4^{3-}\cdot 6\text{H}_2\text{O}$). The wood ashes have already been used as a source of magnesium [55] for the precipitation of struvite. A key element contained in the ashes that might also contribute to the adsorption is the unburnt carbon [56], which is similar to the activated carbon [57]. Nevertheless, Miranda et al. [58] found that the chemical stability of the cattle slurry is better with sulfuric acid than when using biochar as stabilizing agent.

The dewatering could harm the chemical stability of manures. Kavanagh et al. [59] explained that the moisture content plays an important role in preventing gaseous emissions during the handling of manure. Dinuccio et al. [60–62] clarified that the greater gas release from the dewatered manure is due to the greater surface area of the solid compared to the liquid organic waste [31]. The aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3$) and the iron chlorides (FeCl_2 and FeCl_3) are regarded to be among the best chemical stabilizers [17,59,63]. The $\text{Al}_2(\text{SO}_4)_3$ is able to reduce the gaseous emissions (NH_3 , CO_2 , CH_4 and N_2O) even after the solid–liquid separation of the raw and co-digested pig slurries [17]. According to Regueiro et al. [17], the $\text{Al}_2(\text{SO}_4)_3$ increases the total solids (TS) in the liquid fraction, but has the opposite effect in the solid fraction. It should be noted that the nutrients are more stable in the liquid fraction than in the solid fraction, due to the high moisture content and lower surface area. The $\text{Al}_2(\text{SO}_4)_3$ does not decrease the efficacy of the solid–liquid separation because the particles in the liquid fraction would be formed by coagulating the dissolved matter with the action of the sulphate, which remained in the acidic liquid fraction [17]. In fact, Regueiro et al. [17] explained the increase in the TS in the liquid fraction via formation of low molecular weight carbohydrates, due the acid hydrolysis of cellulose and hemicellulose. Thereby, the acid pH provided by the aluminum sulphate enhances the retention of nutrients in the liquid fraction, minimizing the gaseous emissions from the solid fraction. Regueiro et al. [17] found that the gaseous emissions were also minimized in the liquid fraction, due to its lower pH compared to the liquid fraction obtained from the solid–liquid separation without acidification. Moreover, the liquid fraction obtained after the solid–liquid separation has lower nutrient content than the whole slurry; hence, it is less susceptible to originate pollution of the surrounding environment. In the study of Regueiro et al. [17], the content of nitrogen, expressed in grams of nitrogen per gram of TS, decreased due to the increase in the TS that resulted from the addition of $\text{Al}_2(\text{SO}_4)_3$.

Ideally, the liquid fraction obtained after the mechanical solid–liquid separation would be discharged to the local rivers. The concentration of nutrients in the liquid fraction should be below the threshold values of the specifications of wastewater treatment plants in order to meet The Nitrates EU Directive [28,64] and the Nitrate Vulnerable Zones [65,66]. The current techniques for chemical stabilization alone do not sort out the problem of the costly transportation of the organic amendment for long distances (Figure 2). Nevertheless, the chemical stabilization of the OS might reduce the need for covered stores and the use of low-emission spreading techniques (i.e., trailing hose, trailing shoe, and soil injection), which are specified in the Clean Air Strategy of the UK [67]. These measures represent a large capital investment for farmers and the UK government is offering subsidies as part of the Slurry Investment Scheme of the Agricultural Transition Plan [68–70]. The chemical stabilization could become a CATNAP (Cheapest Available Technology Narrowly Avoiding Prosecutions) abatement technique to mitigate the pollution related to the management

of organic soil amendments [12]. The acidification treatment as a means of achieving the chemical stabilization of organic manures is already considered among the best available techniques in the UK [71] and European regulations [72]. However, a detailed assessment of the cost of mitigation needs to be carried out and the type of organic manure and the targeted pollutant needs to be taken into account [73,74].

2.3. Physical Stabilization

Dewatering has benefits such as decreasing the cost of storage and distribution (Figure 2) and better dosing of the organic soil amendment. For the blend of anaerobic digestate and ash to undergo the self-hardening phenomenon, a moisture content of approximately 20% is required [75], which acts as a binder. If the ashes are not used straight after their formation, thermal activation is recommended at least [76] to decompose the hydroxides and the carbonates. Mudryk et al. [77] focused on the process of self-hardening and subsequent granulation, and they treat this step separately from the dewatering. Nevertheless, Pesonen et al. [78] reported a large amount of ammonia volatilized while following this procedure for the production of a granular fertilizer. The optimization of the granulation step is intimately connected with the dewatering stage; hence, both need to be optimized as part of the same process. Figure 3 offers a comparison of the granules produced by Pesonen et al. [78] and a granular fertilizer generated as a proof of concept of the OWAS project before building the prototype. Pesonen et al. [78] and Steenari and Lindqvist [79] concluded that the best physical properties (i.e., mechanical durability and strength to compression) of the granules would be obtained with the lowest share of OS possible in the blend with the HA. However, some authors [10,80] also emphasize the importance of organic matter in granulation.

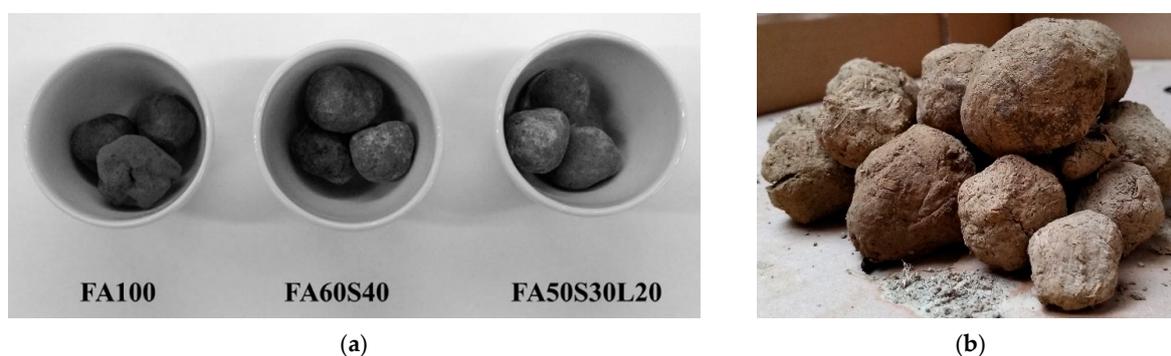


Figure 3. (a) Granular fertilizer (10 mm diameter) prepared by Pesonen et al. [78] with 100% fly ash, 60% fly ash and 40% sludge, and 50% fly ash, 30% sludge and 20% lime ($\text{Ca}(\text{OH})_2$). Reprinted with permission of the Journal of Environmental Chemical Engineering (Elsevier). (b) Granular fertilizer (greatest diameter around 30 mm; 3% moisture) prepared during the OWAS project, involving only the step of physical stabilization of anaerobic digestate (80%) with wood ash (20%).

2.4. Biological Stabilization after Land Application

Similar to both the chemical and physical stabilizations, the biological stabilization can be used alone (i.e., without achieving other levels of stabilization) to improve the management of the organic waste as soil amendment after land application (e.g., use of nitrification inhibitors). However, it is necessary to take a holistic approach in order to avoid pollution swapping [81,82]. An appropriate carbon to nutrient ratio in the organic fertilizer ensures that soil microbes and plants use more efficiently these elements [83,84]. This means that the blending ratio of the HA with the OS should not be designed only by thinking about the optimization of sorption, dewatering, and self-hardening. The optimization of the biological stability would require tests in the field after its application on the soil (or land) [23–25]. In the marketplace can be found cocktails of microorganisms that aim to achieve simultaneously chemical and biological stabilizations of the organic waste [63,85], although these products do not aid the dewatering.

All the above technologies are used to improve the management of the nutrients of the organic soil amendments, and they are grouped as STRUBIAS (STRUvite, Biochar and ASH) [39]. Aragón-Briceño et al. [86] proposed improvements for the HTC manufacturing process: (a) extraction of the nutrients that remain in the aqueous phase and (b) further densification of the hydrochar, which might be attained by enhancing the solid–liquid separation and subsequent granulation [10,80]. Although this depends on the type of feedstock, including raw and digested OFMSW, the best conditions to perform the HTC are around 200 °C for 1 h in an airtight autoclave-type reactor [87]. The operation needs to be optimized to achieve the best properties of the final product. According to Pawlak-Kruczek [88], the HTC changes the anaerobic digestate into more hydrophobic products; hence, this technology can be employed for the preparation of a slow-release fertilizer that avoids unnecessary leaching. Additionally, this type of thermal treatment improves the biological stability, prevents the putrefaction of organic matter and restores the soil as a carbon purifier (or carbon sink) [32,33].

3. Results: Process Design

Figure 4 illustrates a process that could be implemented in an energy recovery device for a small wood pellet boiler (i.e., pilot scale prototype). It is similar to the Solvay process [89] in the sense that infusive acidification with CO₂ is used to control the availability of volatile nutrients such as ammonia [90,91]. In the process displayed in Figure 4, the flue gases used as the source of CO₂ for acidification carry the wood ashes and transport the heat from the drying end. The idea of using the combustion of biomass to produce the heat for drying both the digestate and ashes to allow the self-hardening and subsequent granulation was firstly proposed by Jewiarz et al. [92]. However, the drying, the addition of the ashes, and the granulation of the blend takes place in different steps in Jewiarz's process. In the system shown in Figure 4, the drying, sorption, and even some of the granulation are intended to take place simultaneously to maximize the synergies among them. In addition, it is also intended to minimize the use of energy and resources. A different configuration to enhance the sorption and the separation of solids from the gaseous stream is included in the supplementary material (Figure S1). In this way, the main difference between Figure 4 and Figure S1 is the order of the heat recovery using, i.e., a condenser and the cyclone. A higher degree of hydration of the solid particles in the condenser might help to retain more NH₃ and other volatile components of the slurry [59–62]. According to any of the process flow prototypes (Figures 4 and S1), the ashes would not require an additional step of activation as sorbent via calcination at 500 °C [76,93], since they are used straight after the formation in the combustion chamber.

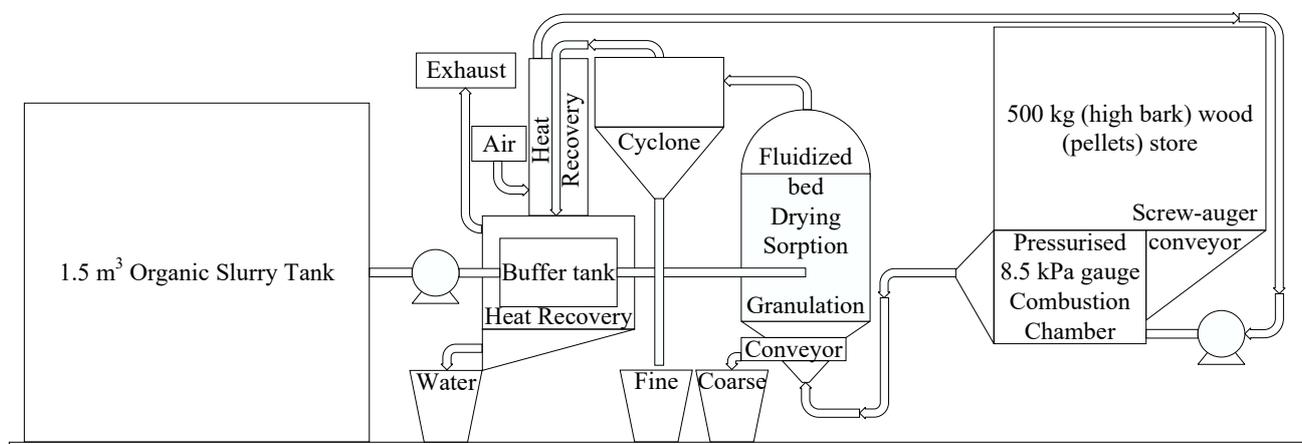


Figure 4. Modified wood pellet boiler for processing 1 tonne of fresh OS (95% moisture) in a 10 h batch operation, consuming 180 kg of wood pellets [94]. The granular organic amendment (51 kg) contains 0.03% of wood ash, in addition to the dried manure (99.97%). Inspired in the media slurry drier of Nara Machinery Ltd. (Tokyo, Japan) [95].

This prototype (Figure 4) would be able to process 1 tonne of OS (95% moisture and 25 °C) and 180 kg of wood pellets in 10 h of operation. An intimate contact between the flue gases and the slurry is required to ensure all the heat released during the combustion of wood is efficiently used for the evaporation of the moisture of the digestate. The incineration chamber is pressurized at 8.0 kPa (gauge) by the fan that is able to provide 35 m³/h of preheated air at 70 °C (Figure S2). The validation of these numbers, which were obtained with empirical equations [96] and data from an equipment manufacturer [97], was performed via comparison with the design of the media slurry drier of Nara Machinery Ltd. [95]. Features such as the loss of nitrogen during the drying need to be assessed experimentally [98]. Other key parameters would be the durability and compressive strength of the granules for the commercialization of the novel fertilizer [77,78,99]. An advanced injection system of the wood pellet in the chamber is required to avoid the combustion gases to access the wood pellets store [100]. Although it is not represented in Figure 4, an airlock is required between the screw auger and the combustion chamber [101]. Considering the volume increase due to the high temperature of combustion, the flue gas flowrate (~286 m³/h) would be sufficient to allow the pneumatic transport of the ashes. A parameter that needs to be measured as part of the scaling up is the share of wood ashes that remain in the chamber and need to be incorporated manually to the fluidized bed reactor or employing any other procedure different from the pneumatic transport. In case the ash produced during the combustion of wood pellets is not enough to attain the stabilization of the OS, outsourced ash (i.e., generated at a different location, such as in the combined heat and power plant of a sawmill) or other activated sorptive material could be used to build up the fluidized bed. It should be noted that the concept of a mobile granulation unit for anaerobic digestate and wood ash has already been proposed by Wróbel et al. [75]. With the fluidized bed drier described in Figure 4, approximately 51 kg of granular fertilizer (3% moisture; [78]) will be obtained with the processing of the 1 tonne of organic fresh (95% moisture) slurry. For this calculation, a low amount of ash in the wood pellets (3% ash; [94]) was considered because they are produced by a stakeholder that could have interest in the prototype [102].

The conditions in which the drying takes place in the fluidized bed reactor aim to promote adsorption. The CaO formed in the combustion chamber might require conditions of hydration [49] that cannot be attained in the fluidized bed to promote adsorption and self-hardening due to the formation of Ca(OH)₂ [78]. This is an analogy to the functioning of commercial products, such as polyacrylamide, which require a certain level of hydration to be activated [61]. Since the granulation process does not affect the performance of the blend in terms of supplying nutrients to the plant [103], the finer fraction of the organic amendment that is obtained from the cyclone needs to be incorporated into the pelletization equipment (2.2 kW; [104]) before being mixed with the soil. Otherwise, it might hamper the aggregate stability of the terrain [105]. According to Merino-Martín et al. [106], the aggregate stability of the soil is convenient for reasons such as a better drainage (i.e., water infiltration) and, therefore, the mechanical properties of the soil should not increase as much as the self-hardened blend of ash and digestate. In fact, a slaking test is used for measuring the aggregate stability of the soil while a durability test is used for measuring the physical stability of the granules of fertilizer [77].

3.1. Dimensions of the Equipment

The approximate size measurements provided in this section were verified by comparison with the mineral inorganic slurry drier of Nara Machinery Ltd. [95], but some of the parts of the system (e.g., fluidized bed reactor) described in the process flow diagram of Figure 4 require further validation. Particularly, the design of the heat exchanger and the combustion chamber would require more prototyping, since the technical challenges are expected (i.e., fouling with the solid particles and injection system of air at high temperature, respectively).

3.1.1. Power of the Fan

The selection of the fan of 0.4 kW (Figure S2; [97]) aimed at the lowest consumption of electricity possible while meeting the minimum fluidizing velocity of 3 m/s and overcoming the drop in pressure of the fluidized bed (3528 Pa gauge; Table S1) condenser and cyclone. The calculations shown in Table S1 were performed following Chhabra and Basavaraj [96] and this design agrees with the process parameters reported by Nara Machinery Ltd. [95]. The fan provides 35 m³/h (Table S2) of air at 8.0 kPa gauge and 70 °C (Figure S2; [97]) that maintains a combustion rate of 18 kg of wood pellets per hour for a 10 h batch shift to process a tonne of OS. This is enough to maintain the combustion, which was calculated with an empirical molecular composition C₆H₉O₄ [107] + 0.653 H₂O (i.e., assuming the woody biomass with 7.5% moisture [94]). Figure S2 shows how it is possible to safely increase the volume of air (at 70 °C) for the combustion of the wood pellets, while keeping the system pressurized > 3528 Pa (gauge). Viscosity of 3·10⁻⁵ Pa·s was considered for the flue gases at 250 °C [108] at the entrance of the fluidized bed. The estimation of the temperature of the flue gases at the entrance of the fluidized bed relies on the an average temperature in the combustion chamber around 750 °C [50,109], the boiling temperature of water at approximately the atmospheric pressure and the optimum temperature for the treatment of flue gases with sorption processes (<100 °C; [110,111]). The conditions employed in similar industrial processes (650 °C; [112]) are not considered suitable at the farm level for the drier of OS with 95% moisture (Figure 4). Furthermore, this is a similar temperature as in the design of Nara Machinery Ltd. [95], although their system to dry mineral inorganic slurry does not include a combustion chamber but an electric (10 kW) air heater.

3.1.2. Dimensions of the Fluidized Bed Drier

The heart of the system shown in Figure 4 is a fluidized bed reactor [76], which operates at approximately 100 °C and slightly higher pressure than atmospheric (i.e., less than 10.4 kPa gauge; Figure S2) in which the flue gases are mixed intimately, in counter current, with the digestate. The velocity of the gases in the reactor, which has a diameter of 30 cm and 1 m of height, would be around 5 m/s to enable the evaporation of 95 kg H₂O/h. According to the calculations and the empirical values [95,96], the fluidized slurry can be only maintained with a particle size of approximately 3 mm in diameter, which is 10 time smaller than the granules initially prepared as proof of concept (Figure 3b). At the entrance of the reactor, the gases are set at 250 °C and the estimated drop in pressure due to the 0.6 m fluidized bed would be 4 kPa. After the drying, the 2237 m³/hour of gases (considering the evaporation of the moisture of the slurry) with fine particles (<3 mm) go to a cyclone. Some granulation takes place in the fluidized bed reactor in a similar way to the shear forces operate in the technology developed by Crutchik et al. [113] for the recovery of granules of struvite from wastewater [114]. Overall, the machine operates under similar principles to the carbon capture processes using calcium looping [112,115].

3.1.3. Dimensions of the Cyclone

According to Duroudier [116], the cyclone should be designed in order to have a velocity of approximately 18 m/s. Considering flowrates leaving the fluidized bed around 2237 m³/h, the diameter of the of the cyclone (D_c; Figure 5) should be around 21 cm (Table 1).

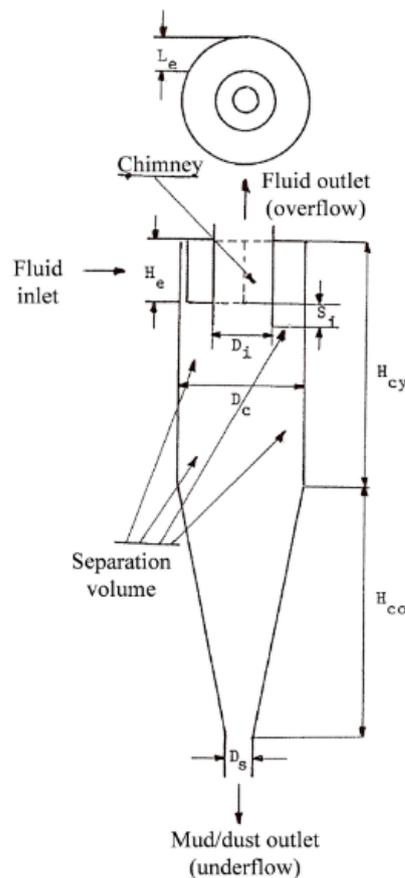


Figure 5. Proportions of a cyclone according to Duroudier [116]. Reproduced with the permission of ISTE Press Ltd. (London, UK) (Elsevier).

Table 1. Dimensions of the cyclone according to Duroudier [116].

Dimension	cm
D_c	21
L_e	5
H_e	11
D_i	11
S_i	3
H_{cy}	43
H_{co}	43
D_s	5

3.2. Economic Balance

According to the mass and energy balances, for processing 1 tonne of slurry, the incineration of the 180 kg of wood pellets it is required. Considering the electricity (GBP 0.2/kWh) to run the fan and the pump and the cost of the wood pellets, the estimated operational cost is around GBP 50/tonne fresh (95% moisture) slurry. This total operational cost includes the 180 kg of wood pellets (GBP 42; [94]). Results of the primary market research show that members of the agro-industry (i.e., potential customers) spend GBP 260,000 annually on transportation and land application of 50,000 kg of untreated slurry (data anonymized of the primary market research). This is equivalent to GBP 5.2/tonne. In governmental reports, values up to GBP 4/tonne (cost for 10-mile delivery) can be found [117,118]. Other sources reported up to GBP 10/tonne (data anonymized of the primary market research). If a 10-fold reduction in the volume is achieved with the proposed stabilization technology, the proposed treatment (Figure 4) is economically competitive with the current practices when more than 10 tonnes of slurry need to be handled (Figure 6).

Considering that a dairy livestock unit produces 20 tonnes of slurry in a single year [119], the proposed technology (Figure 4) is suitable for small-scale productions.



Figure 6. Comparison of the cost of processing of the proposed stabilization treatment (GBP 50/tonne fresh slurry) and the conventional land application without treatment (GBP 5/tonne).

It should be noted that there are other aspects that need to be taken into account and make the proposed stabilization technology (Figure 4) to be more economically viable than the traditional handling of the organic manure:

1. The longer the distance of transportation, the more economically viable the proposed process (Figure 4).
2. Currently, the digestate without treatment is sold at GBP 3/tonne [117,118]. This price is similar to that of nitrogen fertilizers, which are sold at GBP 1.09/kg NH_4^+ -N & NO_3^- -N. There is an increasing trend of farmers willing to pay more for the organic amendment [1].
3. The cost of storage ranges from open lagoons (starting from GBP 8/tonne fresh manure) to shuttered concrete stores (GBP 59/tonne fresh slurry) [120]. It is necessary to consider the subsidies available (e.g., slurry investment scheme in the UK; [68,69]).
4. The use of low-emission spreading techniques (e.g., shallow injection) to apply the slurry to land increased the cost of delivery above GBP 5/tonne [118,121], which was assumed for Figure 6. It is necessary to consider the subsidies available (e.g., slurry investment scheme in the UK; [68,69]).
5. When applying the untreated digestate, it is necessary to take into account the cost of the emissions of GHGs, which is established at a rate of GBP 27/tonne CO_2 equivalent [73,74]. Hence, the proposed fluidized drying and wood ash stabilization process (Figure 4) can be justified if it lowers emissions.

4. Discussion: Development of a Business Plan for the Commercialization of the Technology

4.1. The Opportunity

The agricultural transition plan in the UK includes a slurry investment scheme [68,69], which aims to ensure that the farmers meet the target of reducing 30% emissions of GHGs by 2030 and to achieve net-zero by 2050. These regulations aim to subsidize the acquisition of low-emission spreading equipment and the construction of covered storage facilities. Similarly to acidification alone [73], ash-based stabilization requires professional equipment and advice, whenever this technology has a readiness level of 8. Governments are promoting events and networking opportunities to invest in a farm business (i.e., farm-preneurship) [122–125], since they improve the resilience and the reliability of the food supply chain [126].

4.2. Primary Market Research

Primary market research was conducted to assess the economic viability of the commercialization of the ash-based stabilization technology. This implied the consultation of the opinion of agro-industrial stakeholders. This information was necessary to develop the initial business plan, refine value proposition, and come up with a minimum viable product. The suppliers of the anaerobic digestate to the OWAS project annually produce 17,600 m³ and 50,000 m³ of these materials, respectively [13]. This can be an estimation of the level of investment that is required for medium to larger sized stakeholders.

A survey was prepared to interview the stakeholders of the industry and understand whether the prototype system (Figure 4) was addressing their needs [127]. One of the outcomes of the primary market research was the revelation that the farmers pay approximately GBP 1/m³ of slurry for the use of biological additives (anonymized data), which aims to improve the management of the animal slurry on the farm. This cost will be on the top of the cost of transportation to the field and land application (i.e., around GBP 5/tonne). The main benefit of this product is that it improves the fluidization of the organic amendment, thus easing the pumping, storing in the pits, and charging in the trucks.

4.3. Competitors

There are different types of additives for organic manures in the market. Depending on the country, chemical additives (e.g., acids) could be more popular than biological ones. For example, farmers in Denmark heavily rely on the acidification of the animal slurry to minimize the emissions of NH₃ [1]. Biological additives (i.e., a cocktail of microbes) have also been evaluated in terms of minimizing gaseous emissions [85,128]. All these additives could be key for the economic viability of some of the businesses in the agro-industry. The manufacturers and the users of these type of products, which have been around for more than 40 years, claim advantages such as better performance of manure in terms of greater crop yields [129]. The Agriculture and Food Development Authority of Ireland (Teagasc) concluded that it is necessary to clearly characterize these additives, which have little empirical data to substantiate their claims [63]. These microbial cocktails do not only include biological components, but compounds such as calcium chloride (CaCl₂), which acidify the slurry and prevent the dewatering. To some extent, there are discussions about where the benefits of these biological additives are entirely derived from the decreased pH, which could be achieved using the traditional chemical amendments (i.e., acids). The utilization of CaCl₂ for this purpose [130] helps to envisage the suitability of the wood ash to achieve the chemical stabilization of the anaerobic digestate. The reason is that calcium is a major element in the wood ash and the combination of this waste stream with hydrochloric acid was found appropriate [31,131]. The Teagasc group classifies the wood ashes as a waste amendment of animal manures [63], different from the chemical amendments, which include acids and microbial cocktails. The understanding of the underlying chemistry was crucial to establish relations, make comparisons, and propose the potential applications of the wood ash-based additive that the OWAS project aimed to develop. It is important to mention that the chemical stabilization of the anaerobic digestate by means of adding wood ash implies the consumption of a greater amount of acid compared to the acidification alone. Nevertheless, the preservation of the nutrients is better when wood ash is used [11–14]. It is thereby necessary to perform a techno-economical assessment to determine whether the betterments in terms of nutrient management would be able to justify the higher cost of the chemical stabilization using the ash. When preparing this economic balance for the simplified stabilization technology, it is necessary to consider that the use of ash has the potential to allow further downstream processing of the digestate, for example, leading to the production of a granular fertilizer (i.e., physical stabilization). Furthermore, the chemical stabilization of the organic wastes via sorption implies that the amended manure will behave as a slow-release fertilizer, contrary to the chemical stabilization via solubilization, which promotes the leaching.

4.4. Barriers

The commercialization of this technology might breach environmental legislation, as it could be considered as a reckless behavior towards inappropriate disposal of waste [132], since the wood ash contains heavy metals [133]. If the blending ratio of ash and digestate is based on the maximum heavy metal content established in the quality protocols of both materials [40,134], the share of ash in the blend should be similar to the dry matter of the digestate [135]. According to the PAS 110 of the anaerobic digestate in the UK, cadmium is the heavy metal with the lower allowance and limits the preparation of a blend with a content of wood ash greater than 5% [31]. This blending ratio is also suitable for other purposes, although the valorization of wood ash is subjected to an individual end-of-waste assessment. According to the quality protocol of the anaerobic digestate [136] (p. 24), “if material is blended with waste, then the mixture becomes a waste and is regulated as such”. Despite the fact that the upgrading cannot be achieved by simple dilution of the contaminants, new regulations might ease the formalities [137,138]. For example, it might be possible to consider the same upper limits for heavy metals as they are currently stabilized for the application of the sewage sludge to land [139]. Although the content of pollutants in a waste material is an indication of its phytotoxicity, cultivation tests are required to assess the level of immobilization and bioavailability of the contaminants. Ondrasek et al. [140] found an increase in the accumulation of cadmium in radish, despite that the biomass bottom ash that they used did not increase the content of this element significantly in what they called the “chemically ameliorated” soil. The commercial processes for the valorization of the ashes opt out of isolation of a particular nutrient [99] rather than removal of heavy metals. Some of the thermochemical treatments available [141] use calcium and magnesium chlorides to promote the sorption of the particular element that is intended to be isolated. The acid treatment of the wood ash aims to produce a similar effect with the nutrients of the anaerobic digestate to achieve chemical stabilization.

4.5. Value Proposition and Customer Creation

Figures 7 and 8 represent the block flow diagrams that were proposed to be implemented at the stakeholder premises. The use of the CaO for the stabilization process of the organic manure is an important synergy since the lime is often used at a rate of 2 tonnes per hectare per year. Lime is often applied separately from 70 tonnes of manure per hectare and year. The Teagasc group has already investigated the combination of lime with animal manure but they found an increase in ammonia volatilization [81]. The acidification is required to mitigate the gaseous emissions [59,81] and is itself a management strategy for organic manures (Figure 1). As described by Pawlak-Kruczek et al. [142], the content of CH₄ in the gases released during the gasification of the torrefied sewage sludge increased with the alkaline pH provided by the CaCO₃. This study confirms the need for acidification to optimize the blending of wood ash/lime and organic manures and minimize the release of GHGs [85].

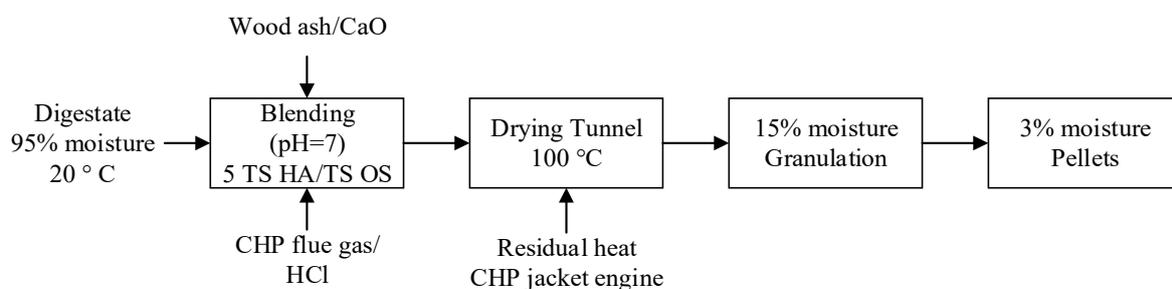


Figure 7. Proposed process A for the manufacturing of a granular fertilizer. (CHP = Combined heat and power plant) to be implemented at the headquarter of a 40,000 tonnes/year production facility of anaerobic digestate with a CHP unit for valorization of the biogas. Optimum blending ratio was defined as 5 TS HA/TS OS [31].

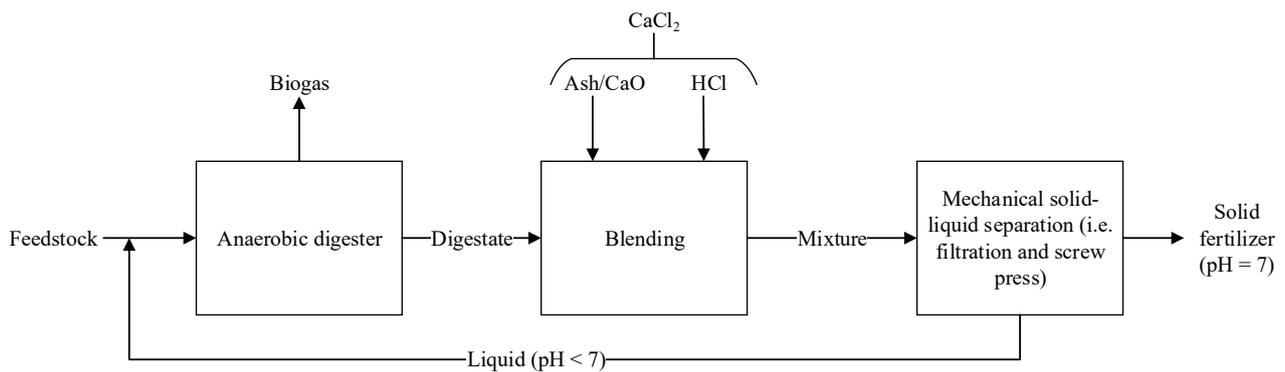


Figure 8. Proposed process B to be implemented directly at the anaerobic digestion plant of one of the stakeholders of the OWAS project.

Both processes, A (Figure 7) and B (Figure 8), were developed as part of a business plan that require lower capital investment for validation, compared to the modified wood pellet boiler for stabilization of animal manure, slurry, and digestate (Figure 4). Already-patented technology by Garrido and Crutchick [114] for simultaneous nutrient recovery and granulation due to the shear force of the circulating fluid proves the technical viability of this equipment (Figure 4) and the degree of competitiveness of the market of organic waste valorization. Using the design thinking methodology [143], a simplified prototype was built and consisted of a closed system where the moisture of the organic amendment is stripped by the CaCl_2 , which is a hygroscopic salt that can be used as desiccant [144]. In this way, the losses of nitrogen via volatilization of NH_3 will be minimized and the organic manure will preserve all its properties. Furthermore, the acid solution of CaCl_2 captures the ammonia in the headspace, as could be told by the smell of the aqueous solution. This route should be more economically favorable than using conditions to promote the NH_3 stripping off the organic amendment [145,146]. The financial study for the creation of the profitable start-up was performed according to the guidelines provided by the Galician Institute of Economic Promotion [147]. Considering the subsidies available, an initial investment around GBP 20,000 would be required for the creation of an enterprise, which will be able to commercialize the chemical technology and generate profits from the second year onwards (Figure 9).

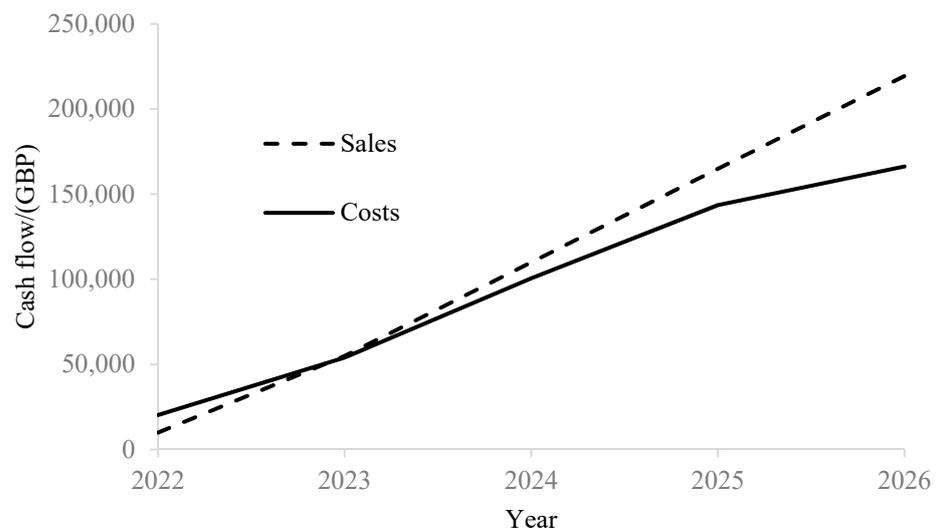


Figure 9. Representation of the profitability of the commercialization of the chemical stabilization technology (Figure 7 or Figure 8) with a business model calculated according to the guidelines of the Galician Institute of Economic Promotion [147].

5. Future Research Perspectives

There are several valorization strategies for organic manures, including thermochemical and biological degradation technologies for the recovery of biomass. The above market research in Section 4 indicates that most of these processes cannot be implemented in farms. It also showed that centralized facilities are preferred to delocalization. In favor of a wider implementation and better management of organic materials at a local level, the OWAS project proposed engagement with stakeholders of the agro-industry. This collaboration on the OWAS project is projected to enhance the use efficiency of energy and resources at their premises. The financial cost for preparing controlled-release fertilizers by simply processing the organic manures with a hardening material relies on the conditions that enable the activation of sorbent and reduces the availability of carbon and related nutrients [31]. Due to the role of the H^+ ions as cationic surfactants, the solid–liquid is enhanced under acid conditions [135]. However, the use of commercial acids to treat organic manures is not in agreement with the green chemistry principles, and the use of residual materials and waste streams is preferred [63]. In order to support the value proposition described in Figure 7, it is necessary to gather laboratory data on the optimum conditions of the use of the flue gases to promote the sorption processes [110,148]. This laboratory data about the development of affordable additives for organic manures will also offer essential data for the scaling up of the bed dried described in Figure 4.

6. Conclusions

In the current situation where agriculture is responsible for a significant share of GHG emissions, two processes of flow prototypes were proposed with different technology readiness levels. While the fluidized bed drier requires validation at a pilot scale (Figure 4), for the direct treatment of the OS with the HA, fewer technical challenges were expected (Figures 7 and 8). In combination with an appropriate business model, these technologies could be part of the solution to reduce the contamination of the atmosphere and underground water due to poor management of OS. The composite fertilizer (as shown in Figure 3b) can be commercialized due to its simple transportation and storage.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inventions7010026/s1>; Figure S1: Alternative process flow diagram of the prototype that promotes the sorption of volatile compounds under hydration conditions; Table S1: Calculation of the minimum fluidizing velocity and the drop of pressure in the fluidized bed prototype; Table S2: Calculation of the volume of air than enable the combustion of 180 kg of wood pellets and the processing of 1 tonne of OM in a 10 h batch-shift; Figure S2: Selection of the power of the fan that provides 35 m³/h of air at 8 kPa and 70 °C to the combustion chamber.

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Abbreviations

AD	anaerobic digestion
CATNAP	cheapest technology narrowly avoiding prosecution
GHG	greenhouse gas
HA	hardening agent
HTC	hydrothermal carbonization
NH ₃	ammonia
NH ₄ ⁺ -N	ammoniacal nitrogen
OS	organic slurry
OWAS	organic waste adsorption stabilization
PAS 110	publicly available specification of anaerobic digestate in the UK
TS	total solids
VFA	volatile fatty acids
CaCl ₂	calcium chloride
CO ₂	carbon dioxide
CUE	carbon use efficiency
STRUBIAS	STRUvite, Blochar and Ash
Teagasc	agriculture and food development authority of Ireland
pH	potential of hydrogen
Al ₂ (SO ₄) ₃	aluminium sulphate
FeCl ₂	iron chloride
CHP	combined heat and power plant

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