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Biowaste samples quality assessment and slow pyrolysis trials

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ABSTRACT

H2STEEL project proposes an alternative solution for the production of green hydrogen by means of an integrated process based on anaerobic digestion and biomethane pyrolysis. This report contains the results of the study performed by REC and other WP 1 partners about the assessment of biowaste sector in Europe, the selection and characterization of samples, the pyrolysis tests, and the identification of suitable biowaste streams to be used for catalyst production for the H2STEEL process.

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Bio-waste, digestate, slow pyrolysis, biochar

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List of acronyms

EU – European Union
WWTP – Wastewater Treatment Plant
WFD – Waste Framework Directive
MBT – Mechanical Biological Treatment
MSW – Municipal Solid Waste
OFMSW – Organic Fraction Municipal Solid Waste
Bcm – billion cubic meters
TGA – Thermo-Gravimetric Analyser
MP-AES – Microwave Plasma-Atomic Emission Spectroscopy.
HHV – Higher Heating Value
LHV – Lower Heating Value
a.r. – as received
d.b. – dry basis
d.a.f. – dry ash free basis
b.d.l. – below detection limit

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EXECUTIVE SUMMARY

H2STEEL project proposes an alternative solution for the production of green hydrogen by means of an integrated process based on anaerobic digestion and biomethane pyrolysis. The novelty proposed by the process consists in a full valorisation of nutrients and carbon contained in the digested biowaste streams. At present, digestate from anaerobic digestion plants represents a by-product, with relevant concentration of carbon and macro-nutrients, but with a limited market demand. Digestate from anaerobic digestion of urban biowaste and agricultural residues is already adopted for the production of soil conditioners and return carbon and nutrients in soil. However, heavy metals and other contaminants (hydrocarbons, chlorine, pharmaceuticals, etc) can compromise the application of digestate in the soil. Due to this high contamination risks, digested sludge derived from both civil and industrial wastewater treatment plants are not considered usable for agriculture by the EU commission. This report contains the results of the selection, characterization, and pyrolysis of biowaste streams considered suitable and potentially relevant for the H2STEEL project. This study was performed within the task 1.1. and 1.2 of H2STEEL Grant Agreement. Task 1.1 aimed at identifying the most suitable biowaste streams on the basis of the annual production volumes, the chemical composition, the disposal cost and the availability. 4 biowaste streams have been selected. Data collection took place with harmonised protocols which included information about the type of feedstock, carbon and metals content, availability, cost supply and suitability to pre-treatment. Furthermore, the selection of biowastes was performed considering the chemical and physical characteristics of the materials, as carbon and inorganics content, moisture at collection, etc. Characterisation included thermogravimetric analysis for ash, moisture and volatiles content determination, MP-AES analysis for determination of inorganic elements, CHN. After the selection of 4 samples, the selected biowaste have been processed in a lab-scale pyrolysis unit for conversion into biochar. The pyrolysis was performed at mild temperature at different residence time. Heating rate was fixed at 20°C/min. These tests will make available to H2STEEL diverse biochar samples which will be characterized in laboratory. Characterisation of biochar samples includes: ash, moisture and volatiles content determination, MP-AES analysis for determination of inorganic elements, CHN. The concentration and the type of inorganics, and the volatile matter of biochar will be considered as key parameters for the selection of the raw biochar samples to be upgraded by chemical leaching process. Phosphorus, calcium and other micronutrients have been seen as crucial for the application of the leaching process, as well as metals for the biomethane cracking.

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1 INTRODUCTION

Bio-waste is waste consisting of organic matter, usually from food and green waste, with two main fractions, garden and park waste and food and kitchen waste, which comes from households, offices, restaurants, wholesalers, canteens, catering and retail premises as well as food processing plants[1]. This type of waste is considered a key stream with a high potential for contributing to a more circular economy, as useful resources can be obtained from it, e.g., soil-improving materials, fertilizers and renewable energy in the form of biogas[2]. As the quality of bio-waste and its final applications depend on its management (including collection, treatment and recovery through specialised channels), clear quality standards and quality assurance processes are necessary to facilitate integrated bio-waste management.

Despite the importance of bio-waste management, there is no unified management model for the EU27 and UK, and the existing methods vary among nations[3]. In this context, a recent revision of waste legislation as part of the EU's circular economy policy established a number of aims and rules that will drive both the prevention and sustainable management of bio-waste. The legislation also includes regulations that require bio-waste to be separated from other municipal waste, as a proper treatment of bio-waste requires ensuring that the raw material is as clean as possible since contaminants such as plastics and glass can damage the equipment[4]. From this revision, it was concluded that recycling is crucial, given that 30-40% of municipal waste is currently bio-waste and that the EU target is for 65% of municipal waste to be recycled by 2035[1,2]. In this regard, municipalities are obliged by the EU (Directive 2018/851/EU) to coordinate the separation of bio-waste from other municipal waste by 2023. In addition, the Directive prohibits the incineration of separately collected biowaste[1]. Similarly, a new legislation will mandate separate food and general waste collections in the UK, with the goal of eradicating food waste from landfills by 2030[4]. Apart from the Circular Economy vision, there are other environmental drivers for better management of bio-waste, e.g., the risk of soils losing organic matter due to land use changes, modern agricultural practices and climate change, and environmental concerns associated with waste. It is estimated that about half of European soil has a low organic matter content, diminishing its capacity to absorb water and minerals and store carbon[5]. Compost production from collected bio-waste can be a useful source of stable organic matter. Repeated application of compost contributes to soil carbon stock and increases soil organic matter. However, the presence of contaminants in compost and digestate (PFAS, heavy metals) could have harmful effects in the long term. Regarding food waste, it accounts for approximately 60% of the total waste produced.

[1] Interreg Europe. The biowaste management challenge: A Policy Brief from the Policy Learning Platform on Environment and resource efficiency; 2021.
[2] Brusselaers J, van der Linden A. Bio-waste in Europe—turning challenges into opportunities. EEA Report 2020;2020(4)
[3] European Biomass Industry Association (EUBIA). D9.2 EU Policy on biowaste management: a review; 2019.
[4] Nageler-petritz H. Food waste recycling on top of UK businesses' green agenda. WEKA Industrie Medien GmbH 2022, 27 October 2022; Available from: https://waste-management-world.com/resource-use/food-waste-recycling-in-top-of-uk-businesses-green-agenda/. [December 27, 2022]
[5] Favoino E, Giavini M, Rupp M. Bio-waste generation in the EU: Current capture levels and future potential. Bio-Based Industries Consortium (BIC): Brussels, Belgium 2020.

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Hence, a target to halve food waste by 2030 was included as part of the Sustainable Development Goals[2]. This aims to optimise the food chain and reduce the demand for food by avoiding food waste. This would considerably reduce the environmental impact associated with food production, processing and transport, considering that the impact of preventing food waste is far greater than any environmental benefits derived from recycling.

In addition to compos and digestate, Biowaste is a potential source of chemicals, products and energy and therefore, there are many different treatment options, being anaerobic digestion and composting currently the most common. Between 118 and 138 million tonnes of bio-waste are generated annually in the EU, of which around 40 percent, i.e., 47.5 million tonnes per year, is properly recycled into high-quality compost and digestate. The bulk of municipal waste produced in Europe is still disposed of either landfilling (24%) or incineration (27%), with less than half being recycled (31%), and composted (17%)[6]. Up to 50% of MSW should be diverted from landfills and used to produce biomethane, and high value products.

The present report aims to analyse the value chain of most common biowaste streams in Europe, in order to identify the most interesting materials to be used as feedstock for the H2STEEL value chain.

2 BIOWASTE CATEGORIES AND AVAILABILITY

2.1 Biowaste definition and categories

Following the approach presented in the BEE study[7], the most up-to-date overview of state-of-the-art biomass resource assessment, biowastes are defined consistently with the European guidelines presented in the Eurostat. **Errore. L'origine riferimento non è stata trovata.** summarises the biowaste definitions. The waste potential is assessed using Eurostat or national waste generation and waste treatment data as input as, since 2004, data on waste generation and treatment are collected per EU member state[8], according to fixed categories (European Waste Classification for statistical purposes). Wastes are differentiated between households (HH) and waste from business activities (NACE[9] classification).

Table 1. Waste categories selected from Eurostat and assessed in this deliverable for the estimation of the waste potential

Waste type	Definition	NACE code (HH, household code)	Explanation
Paper and cardboard wastes	This category includes non-hazardous fibre, filler and coating rejects from pulp, paper and cardboard	W072.TOTAL	
		(EP HH.W072)	Total paper
		W072.C17_C18	Paper from manufacture of paper and paper products;

[6] Eurostat. Municipal waste landfilled, incinerated, recycled and composted, EU-27,1995-2018; 2019.
[7] See BEE project website: http://www.eu-bee.com/
8 Regulation on waste statistics (EC) No. 2150/2002, amended by Commission Regulation (EU) No. 849/2010, prescribe that data on the generation and treatment of waste is collected from the Member States.
[9] Nomenclature statistique des Activites economiques dans la Communaute Europeenne or Statistical classification of economic activities in the European Community)

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	production. These wastes are largely generated by three activities: separate collection, mechanical treatment of waste and pulp, and paper and cardboard production and processing.		printing and reproduction of recorded media
Wood waste	These contain wooden packaging, sawdust, shavings, cuttings, waste bark, cork and wood from the production of pulp and paper; wood from the construction and demolition of buildings; and separately collected wood waste. They mainly originate from wood processing, the pulp and paper industry and the demolition of buildings. For some countries this category overlaps with the 'other forestry industry by-products'. Wood wastes are hazardous when containing hazardous substances like mercury or tar-based wood preservatives, which makes it only suitable for incineration and not recycling.	W075.TOTAL (EP_HH.W075)	Total wood
		W075.C16	Wood from manufacture of wood and of products of wood and cork, except furniture; manufacture of articles of straw and plaiting materials
		W075.TOT_excl_above	Wood from other economic sectors
Animal and mixed food	These wastes are animal and mixed wastes from food preparation and products, including sludges from washing and cleaning; separately collected biodegradable kitchen and canteen waste, and edible oils and fats. They originate from food preparation and production (agriculture and manufacture of food and food products) and from separate collection. Animal and mixed waste of food preparation and products are non-hazardous.	W091.TOTAL (EP_HH.W091)	Total animal and mixed food
		W091.A	AnMixfood from Agriculture, forestry and fishing
		W091.C10-C12	AnMixfood from Manufacture of food products; beverages and tobacco products
		W091.E	AnMixfood from companies in water collection, treatment and supply; sewerage; remediation activities and other waste man. Serv.
		W091.G-U_X_G4677	AnMixfood from all services (except wholesale of waste and scrap)
		W091.TOTAL - 4 above	AnMixFood other
Municipal Solid Waste (MSW)	They contain household waste, bulky waste, street-cleaning waste like packaging, kitchen waste, and household equipment except separately collected fractions. They originate mainly from households but can also be generated by all sectors in canteens and offices as consumption residues.	W101.TOTAL (EP HH.W101)	Total MSW

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Common sludges	These are non-hazardous wastewater treatment sludges from municipal sewerage water and organic sludges from food preparation and processing. They mainly originate from households and industrial branches with organic waste water (mainly pulp and paper as well as food preparation and processing). They can also occur in waste water treatment plants or in the anaerobic treatment of waste.	W11.TOTAL (EP HH.W11)	Total common sludges
		W11.C	Common sludges from all manufacture manufacturing companies
		W11.E	Common sludges from Water collection, treatment and supply; sewerage; remediation activities and other waste management services

The process to be developed in the project aims at integrating existing biowaste anaerobic digestion facilities in a new disruptive value chain based on converting biomethane and digestate into high value products: hydrogen, inorganic P-rich fertilisers, biocoal. Suitable wastes must therefore be available at competitive (even negative) costs and at a scale that fits conversion facilities, from local production up to full industrial scales. This study addresses all those biowastes which are commonly processed by anaerobic digestion to be converted into biomethane, and digestate. With the term "digestate" the study refers to the solid fraction of the digested biowaste after being processed by solid-liquid mechanical separation.

With these premises, the materials object of this study can be divided in two main categories: *sludge* and *digestate*, where "*sludge*" is defined as the residual product obtained after anaerobic digestion and solid-liquid separation of primary, secondary and tertiary sludge in industrial or civil wastewater treatment plants, and "*digestate*" refers to the solid residue obtained after solid-liquid separation of digested substrate resulting from the anaerobic digestion of urban biowaste, and agricultural residues.

As a summary, three biowaste streams categories are object of this report: wastewater treatment sludge, urban biowaste, agricultural waste. In the first part, the present study analyses the annual production capacity, the existing value chain, disposal, and valorisation solutions currently available in Europe of each of the identified categories. In the second part, the study focuses on the characterization and quality assessment of different biowaste samples, obtained by different actors. In the third part, the results of the slow pyrolysis trials performed in laboratory are reported, together with the characterization of the obtained biochars, and an assessment of the performed tests. As a conclusion, suitable samples of biowaste streams are selected for being used in H2STEEL integrated process and, thus, tested in the Proof of Concept unit under development in WP3.

2.2. Civil and industrial sludge

Sludge represents the main residual product originated by wastewater treatment. The aim of wastewater treatment plants (WWTPs) is to remove pollutants from the wastewaters of domestic, urban and industrial origin, including rain- and run-off waters. The contaminants contained in wastewaters are multiple: organic substance, which decomposes and is the cause of molest odours; nutrients, which represent a source of phosphorus and nitrogen for aquatic flora that can be over-nourished with environmental impacts; hazardous substances for human health and

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environment, which ranges from pathogen microorganisms to toxic substances (mutagens, carcinogenic and teratogens) to organic pollutants. The first criticality of sludge treatment concerns thus the elevated content of the detrimental substances that are removed from water. Since the seventies and eighties of the last century, the development of environmental awareness and the acknowledgment of long-term effects of wastewater constituents on human health and receiving water bodies have led to the definition of increasingly restrictive discharge limits by authorities over the years. Consequently, more and more effective water treatment processes have been performed, resulting in higher removal efficiencies of water pollutants and in the production of higher sludge volumes.

Sludge can be defined as a suspension of water and dry matter, which includes organic and inorganic solids. The organic content is attributed to the biological treatment of wastewaters, which involves microorganisms for the conversion of organic compounds. Biodegradable organic compounds in wastewater are partly oxidized to carbon dioxide, while the rest becomes part of the microbial cellular material. Organic matter of sludge includes then active biomass (continuously removed by sludge extraction from settlers), endogenous decay residuals (which represent dead biomass), and persistent constituents which have not been totally degraded. Depending on the content of the treated wastewater, different quantities of nutrients (nitrogen (N), phosphorus (P), potash (K)), hazardous components (as pathogenic microorganisms) and heavy metals can be found.

The relevance of sludge as source of carbon and raw materials depends on the composition of its dry matter. Dry matter expresses the solids content of sludge and varies depending on the section of the wastewater treatment plant which produced it. However, dry matter ranges from around 0.5-1.5% for secondary (or biological or active) sludge, to up to 6% for primary sludge, which originates from primary settling. Primary, secondary and tertiary sludge are usually mixed and dewatered by centrifugation. After centrifugation, the dry matter content in the solid fraction raises to around 25-30%. Despite the increase of dry matter, it is evident that the prevalent fraction of sludge is water, and this is a second critical issue of sludge treatment.

Despite the average volume of sludge produced by a WWTP represents just 0.3-2% of processed water, the costs attributed to sludge management range from 20% to 50% of the overall expenses of a treatment plant. For this reason, sludge management (treatment, recovery and disposal) is a critical issue from a technical and economical point of view, but it is the inevitable consequence of a correct and high removal efficiency wastewater treatment.

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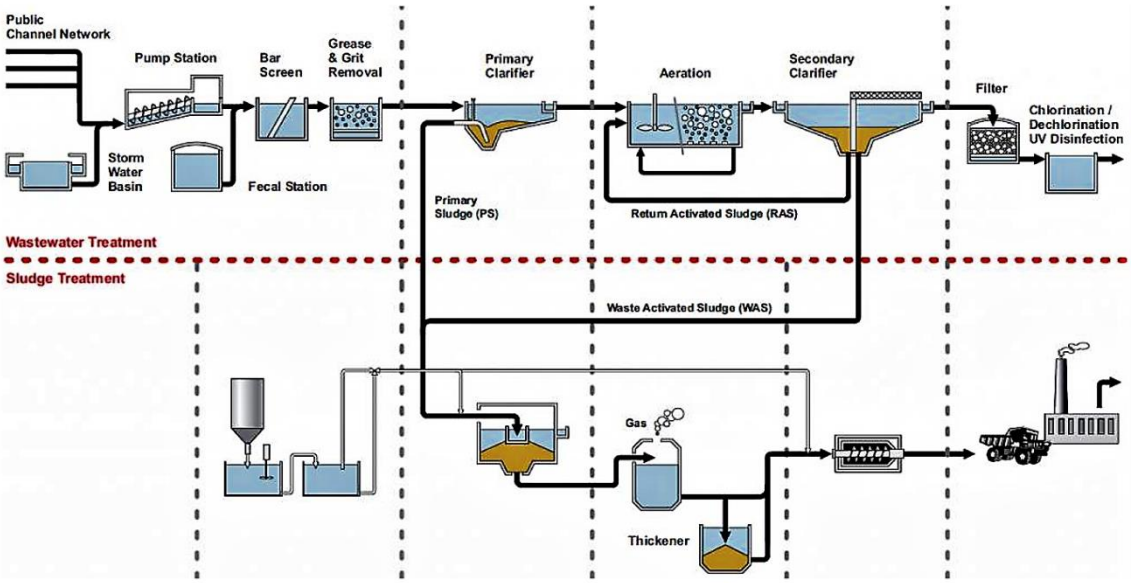

Figure 1 - Conventional activated sludge WWTP.

For these reasons, sludge is classified as waste and has its own EWC code (European Waste Catalogue) in the European List of Waste, instituted by commission decision 2000/532/CE and regularly revisited. Sludge identification chapter code, which identifies the source generating the waste, is 19, which includes "wastes from waste management facilities, off-site waste water treatment plants and the preparation of water intended for human consumption and water for industrial use". Likewise other waste, they are distinguished into dangerous and non-dangerous. Differently from other wastes of the plant (materials from water screening, sands, oil and fats), sludge has its own treatment line in the plant, as mentioned before.

2.2.1. Sludge annual production in Europe

According to Eurostat and other sources, the production of sludge in the European Union (EU) amounts to around 9-13.3 millions of dry tons per year[10]. Considering that the source reporting around 9-9.5 million tons of dry substance per year refers to civil sludge only, it is reasonable to estimate that industrial sludge production amount to about 3-4 million tons of dry matter per year. The enactment of the Urban Wastewater Treatment Directive (91/27/EEC and successive amendments and implementations), which legislates the treatments to be performed on municipal and industrial wastewater, determined the installation of a wide number of wastewater treatment plants. An increase of annual sludge production of around 50% has been observed from 1992 to 2005 [7], as a consequence of the improved wastewater treatment systems. In fact, members states were obliged to connect all the agglomerations of more than 2000 person equivalent to systems for the collection and treatment of municipal wastewater, so that, currently, the number

[10] https://www.ncbi.nlm.nih.gov/pmc/articles/PMC8036911/

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of operating plants in the EU amounts to over 50 000, which produce more than 10 millions of tons of dry matter every year[11].

According to Eurostat, Germany, Spain, France, and Italy contribute to around 60% of the total sewage sludge production in the EU, while Luxembourg, Cyprus and Malta produce the least quantities. Their low production can be attributed to small population. The data of sludge production and disposal in the EU reported and discussed in this and in the following paragraph, reported by Eurostat, are referred to sewage sludge, which is originated from urban wastewater treatment. Indeed, Eurostat distinguish sludge origin between urban WWTPs and "other" WWTPs. This choice is due to the wide availability of data concerning sewage sludge in the EU against industrial sludge production and disposal information. Sewage sludge of urban origin data enables to make a comparison among the member states situation and give an overall perspective of the European context.

2.2.2 Sludge disposal systems

Sludge disposal route must be selected according to the priority criteria on waste management defined in the Waste Framework Directive (WFD - 2008/98/EC), which establishes the hierarchy for waste management from the most preferable option (prevention) to the least favoured (landfill disposal). Landfilling disposal is discouraged by the Landfill Directive too (1999/31/EC), as it obliges the member states to respect restrictions and quantitative targets for the biodegradable waste sent to landfill, including sludge. Sludge use on land is legislated by the Sewage Sludge Directive (1986/278/EEC), regulating sludge use on soil as a fertilizer to prevent damages to human health and environment (soil, vegetation, animals) and water impairing (surface and ground) and to encourage its safe use in agriculture. In particular, it specifies the concentration limits of heavy metals (Cd, Cu, Ni, Pb, Zn, Hg, Cr) which must not be overcome in sludge and soil and the maximum annual quantities of heavy metals that may be added to the soil. It can be observed that 16 out of 27 countries have set stricter limits for heavy metals concentrations in sludge and 10 out of 27 countries for heavy metals concentrations in soil[12]. In addition, most EU countries prohibit the disposal of untreated sludge in soil, despite not being always foreseen by the Sewage Sludge Directive. Treated sludge is the sludge which has undergone an appropriate process to reduce its fermentability and the health hazards resulting from its use. In 2019, the Fertilizing Products Regulation (Regulation (EU) 2019/1009), amending Sewage Sludge Directive, was published. It covers 7 categories of fertilising products, among which fertilisers (inorganic, organo-mineral and organic), soil improvers and growing media, defining their safety, quality and labelling requirements. It defines the "rules to apply to design, manufacture and placing on the market of EU fertilising products"[13]. It includes the definition of the feedstocks that can be used for the production of fertilizing products to be CE-marked, of the maximum levels of contaminants and pathogens and of the minimum content of nutrients. In the new EU regulation, sewage sludge use as feedstock for CE fertilizers production is avoided, being struvite, phosphate salts and ashes

[11] AST s.r.l., "SLUDGEtreat project - Preliminary market analysis - review," vol. 7. pp. 1–1, 2014, doi: 10.1109/wscar.2014.6916768

[12] A. Kelessidis and A. S. Stasinakis, "Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries," *Waste Manag.*, vol. 32, no. 6, pp. 1186–1195, 2012, doi: 10.1016/j.wasman.2012.01.012.

[13] European Union, "Safe and effective fertilisers on the EU market (from 2022)." https://eur-lex.europa.eu/legal-content/EN/LSU/?uri=CELEX:32019R1009.

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after incineration the only fertilizing products allowed to be obtained from sewage sludge. In general, the EU regulates the disposal of sludge on landfills and the toxic emissions generated by sludge incineration. The following chart reports the disposal methods for sewage sludge distinguished by EU member, referring to the most recent available data and expressed as percentage of the total disposed sludge[14].



(1): Data for 2016 instead of 2018
(2): Data for 2017 instead of 2018
(3): Data estimated
(4): Data provisional
(5): Data for 2010 instead of 2018
(6): Data for 2009 instead of 2018
The black dashed line separates EU-15 members by EU-13 members

Figure 2 - Disposal of sewage sludge from urban wastewater treatment by method of disposal (% total)[5]

The chart shows that the preferred disposal methods are agricultural use, compost production, landfill disposal and incineration. "Other" refers to other practices, including "pyrolysis, temporary storage (e.g. Greece, Italy), long storage (e.g. Poland, Estonia, Lithuania), reuse in green areas and forestry (e.g. Ireland, Latvia, Slovakia), landfill cover (e.g. Sweden, Flanders), exportation of sludge amounts to other countries (e.g. granulated sludge from Netherlands to Germany for incineration, sludge for composting or incineration from Luxembourg to Germany)". For Italy and Denmark, the data about composting were not available, hence they have been counted as 0%; for Finland, the "other" percentage was not available and was considered 0% too. We can observe that the use of sludge as fertiliser for agricultural use represent the first destiny of sludge in three member states (Spain 80%, Ireland 79% and Denmark 64%). Sludge composting is the first disposal mode in five member states (Finland 92%, Estonia 84%, Hungary 72%, Cyprus 58 %, Luxembourg 53 % Slovakia 46 %). Incinerating is becoming the selected disposal route against

[14] Eurostat, "Water statistics". Available: https://ec.europa.eu/eurostat/statistics-explained/index.php/Water_statistics#Wastewater_treatment_and_disposal

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landfilling (as this has been limited by the EU landfilling Directive) in six member states (Netherlands 87%, Belgium 82%, Germany 65%, Austria 54%, Greece 32%, Switzerland 100%), while landfilling remains the favoured disposal method in 3 countries (Malta 100%, Bosnia and Herzegovina 100%, Italy 51% and Romania 52%)[5]. A major issue of sewage sludge disposal is represented by the use as soil conditioner. In many EU countries, one of the most adopted sludge disposal practices has been the use in agriculture. However, due to the high concentration of heavy metals and other contaminants (pharmaceuticals, hydrocarbons) this practice is being abandoned and forbidden in many countries. The EU Fertilisers Regulation (EU) 2019/1009, entered in force in 2019, does not admit the use of sewage sludge for the production of any CE marketable fertilisers.

2.2.3 Economics of sludge disposal routes

Sewage sludge and industrial sludge disposal is currently representing around 50%[15] of wastewater plant management costs and is a problem of growing concern in the EU due to the high amount of sludge produced. When disposal in agricultura is forbidden, landfilling and incineration, are the most common disposal solutions for sewage sludge and industrial sludge. These are expensive disposal practices with costs from 120 to 250 €/t of sludge[16]. Sludge reuse in agriculture has been for many years the most common disposal route adopted in the EU[17], but in the last years, it is becoming forbidden in an increasing number of European regions, due to the dangerous biological and chemical pollution of this waste category (heavy metals, organic pollutants, pathogens and other toxic compounds). The potential hazardousness of sludge prompted the European Parliament to issue the Regulation (EU) 2019/1009 on fertilising products, which excludes sludge from being used as feedstock for CE fertilizers production, contributing to the abandonment of sludge use in agriculture with the entry into force of the Regulation in 2022. The technical drawbacks of sludge incineration are sludge relatively low calorific value (around 9-14 MJ/kg for primary digested sludge[18]) which makes incineration energetically less convenient; sludge moisture, which requires a preliminary drying; sludge high ashes content, which remain as a residue to be disposed. In addition, there is scarce social acceptance of incinerators installation from population, due to impacting emissions (particles, acid gases, greenhouse gases, heavy metals, volatile organic compounds).

2.3 Digestate from urban biowaste and agricultural residues

2.3.1 Urban biowaste

The Waste Framework Directive (WFD) defines urban biowaste as biodegradable garden and park waste; food and kitchen waste from households, restaurants, caterers and retail premises. Addressing municipal biowaste is crucial for moving towards the new targets defined in the 2018

[15] Project partners data
[16] Project partners data
[17] M. Pellegrini, C. Saccani, A. Bianchini, and L. Bonfiglioli, “Sewage sludge management in Europe: a critical analysis of data quality,” Int. J. Environ. Waste Manag., vol. 18, no. 3, p. 226, 2016, doi: 10.1504/ijewm.2016.10001645.
[18] Metcalf & Eddy, Wastewater Engineering: Treatment and reuse

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WFD. The directive introduces new targets regarding recycling and preparation for reuse: by weight, at least 55 % by 2025, 60 % by 2030 and 65 % by 2035[19].

Across the European Union, somewhere between 118 and 138 million tons of biowaste arise annually, of which currently only about 40% (equivalent to 47,5 million tons per annum) is effectively recycled into high-quality compost and digestate.

Figure 3 below shows the number of biowaste treatment plants in EU member states in 2020, divided in: composting, anaerobic digestion, anaerobic digestion+composting.

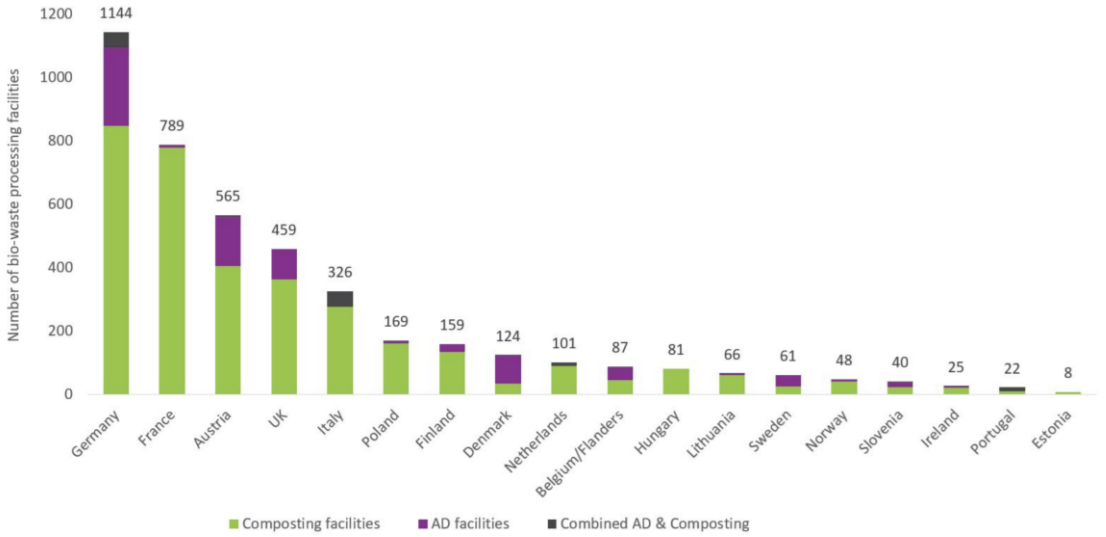

Figure 3. Number of urban biowaste treatment facilities in EU by country (Source. European Compost Network)

The majority of municipal waste generated in Europe is still disposed of through landfilling (24%) or incineration (27%), with less than half recycled (31%) and composted (17 %). Moreover, anaerobic digestion of biowaste is still covering a small fraction of biowaste treatment plants. According to the European Compost Network, of the 47.5 million tons of urban biowaste collected annually, 11.7 tons of compost are produced, and only about 4.8 million tons of digested are produced in Europe, for a total of 15.8 Million tons of compost and digestate[20]. Numbers are confirmed by Ramboll, 2019[21], that estimate a production of about 17.3 million tonnes per year (with a possible range of 13-18 million tonnes), of which around 14 million tons derived from green waste and separately collected biowaste. In the report, it is also mentioned that compost is produced from mechanical biological treatment (MBT) of mixed municipal solid waste (MSW) in some smaller countries, but a current EU-wide figure could not be derived. About digestate, Ramboll study estimated that, in 2019, 46 million tonnes of digestate was produced from the MBT of organic fraction of mixed MSW, at least 7 million tonnes from source separated biowaste.

[19] Bio-waste in Europe — turning challenges into opportunities, EEA Report No 04/2020, ISSN 1977-8449
[20] ECN Status report 2019
[21] Digestate and compost as fertilisers: Risk assessment and risk management options, Final Report, Ramboll, Wood Environment & Infrastructure Solutions UK Limited 2019

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The data reported in the two studies do not specify the reference moisture content of the material. In order to estimate the quantity on dry basis, average reference moisture is considered of 50% for fresh MSW, and of 60% for produced compost, and stabilized digestate. As a result, it can be estimated that about 23.7 million tons of dry biowaste is collected annually, and that about 8-8.5 million dry tons of compost are produced, and around 2.5-3.5 million dry tons of digestate every year.

These data are estimated to increase in the next years, thanks to the revised Waste Framework Directive which requires a separate biowaste collection or recycling at the source by 31 December 2023 (Directive 2018/851/EU). This means that all municipalities must plan and implement separate biowaste collection schemes. This is usually obtained by organising door-to-door collection, or with smart, monitored biowaste collection points where citizens can drop off their biowaste. Moreover, given the strategic importance of biomethane for Europe, Gas for Climate have recently estimated that up to 38 bcm of biomethane could be produced in 2030, of which about 7% derived from urban biowaste (green waste, separated organic fraction of municipal solid waste), for a total of 2.66 bcm[22]. A significant number compared to the current (2020) EU biomethane production estimated by EBA of about 2.3 bcm. On the basis of this last mention, the below table reports the estimated quantity of urban biowaste digestate produced today, and a forecast within 2025 and 2030, thanks to the increase of anaerobic digestion plants and of the entry in force of the updated Waste Framework Directive.

2.2.2 Digestate from anaerobic digestion of agro-residues

For digestate, RAMBOLL analysis[23] suggests that around 180 million tonnes of digestate are produced in the EU28 per year. With 120 million tonnes, the majority of digestate produced in the EU is agricultural digestate (typically a mixture of manure and plants, particularly energy crops). About 46 million tonnes are produced from the organic fraction of mixed MSW (from MBT), at least 7 million tonnes from source separated biowaste and smaller quantities (around 1.7 million tonnes each) from sewage sludge and agro/food industry by-products. The vast majority of digestate is used directly as a fertiliser.

[22]Biomethane production potentials in the EU, a Gas for Climate Report, July 2022. https://www.europeanbiogas.eu/wp-content/uploads/2022/07/GfC_national-biomethane-potentials_070722.pdf

[23] Digestate and compost as fertilisers: Risk assessment and risk management options, Final Report, 2019. Wood Environment & Infrastructure Solutions UK Limited. https://ec.europa.eu/environment/chemicals/reach/pdf/40039%20Digestate%20and%20Compost%20RMOA%20-%20Final%20report%20i2_20190208.pdf

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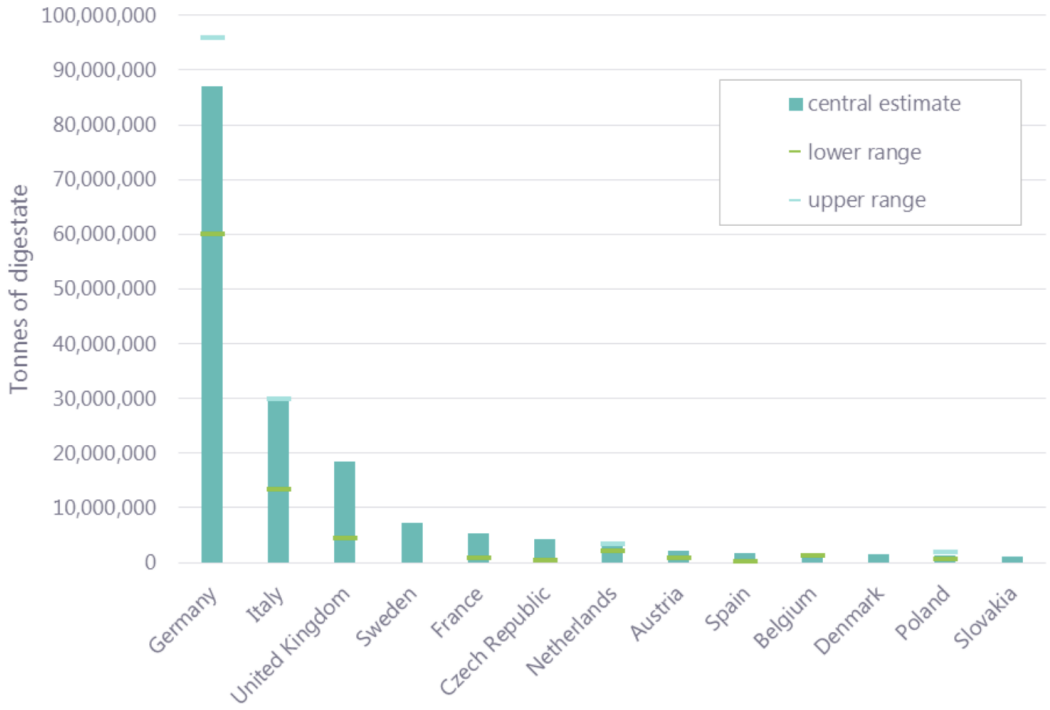

Figure 4. Estimated quantity of digestate per country, in tons (only >1 million tons shown)[14].

2.2.3 Uses of agricultural and urban biowaste digestate

Since agricultural digestate is usually liquid (70-90% water content), it is mostly applied by the same equipment used for raw slurry spreading. Trailing hoses, trailing shoes or direct injection into the topsoil should be preferred for digestate spreading, since they minimise digestate's exposure to air, preventing nitrogen losses by ammonia volatilisation. Digestate is usually spred as received from the biogas plant, since it contains all input nutrients, micro nutrients, organic matter and water. In other cases, digestate is further treated including: "separation into liquid and solid fractions (well established); drying (also established); ammonia striping (also used) micro filtration (tested and promising); precipitation (tested in waste water treatment sector and promising in agriculture)". The application doses of digestate depend on mineral concentration of the mixture and plant demand. In EU countries, application doses of digestate vary between 10 and 40 m^3 per hectare for a year, but, in case of Nitrate Vulnerable Zone, limits are set (usually 170 kg), depending by country based on what is considered 'manure' too.

2.3.4 Economics of biowaste digestate valorisation routes

Urban biowaste treatment, if separately collected, is less expensive than sewage or industrial sludge, with a cost of 80-100 €/t[24], as it contains less water, it produces more biomethane, and it consists in organic fraction MSW (OFMSW), with less contaminants, usable with other wastes to produce compost. However, compost demand is low and a large fraction of collected urban biowaste is not fulfilling compost quality requirements. Therefore, in case that the total, or parto f

[24] Internal data

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the composted digestate overcomes the limits for incineration, it must be disposed in landfill, or incinerated. A composting plant, on the other hand, requires a lower CAPEX of about 350-400 €/t[25] and the produced compost has a market value of 5-12 €/t, with not compostable matter to be disposed as process residue[26]. Economics are different in the case of agricultural digestate, which is usually produced and reused locally by anaerobic digestion facilities of animal and arable farms. The critical aspect of agricultural digestate is related in the case of lack of land available for safely reusing all the digestate available (nitrate directive limitates the use of digestate in soil depending on the season, and farming practices), which could bring to additional digestate drying and disposal costs.

2.4 Potential availability, present use, market price, and disposal cost

The following table summarizes the current potential availability, the forecast for 2030, the current use, the market value and the disposal costs of digestates originated from different biowastes (urban separated biowaste, agricultural, mixed MSW) and sludge (civil and industrial).

Table 2. Overview of digestate and sludge potential availability, current use, market price and disposal cost.

Material	Urban separated biowaste digestate	Agricultural digestate	Civil and industrial sludge	Digestate from mixed MSW
Current availability (million dry tons)	2.5 - 3	18	13	9.2
Potential production in 2030 (million dry tons)	9 - 15	22	15	3 - 4
Present use	Agriculture	Agriculture	Landfilling/ incineration	Landfilling/ incineration
Market value (€/ton)	5-12	10-20	-	-
Disposal cost (€/ton)	-	-	100-200	100-200

3 SELECTION AND CHARACTERIZATION OF BIOWASTE SAMPLES

3.1 Materials and methods

3.1.1 Materials

Based on the biowaste streams identified above, 8 samples have been collected and characterized. Samples' names and codes are listed below:

1. Industrial sludge from food industry (ISL1)

[25] Internal data
[26] https://www.interregeurope.eu/sites/default/files/2022-04/Biowaste%20challenge.pdf

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2. Industrial sludge from pharmaceutical industry (ISL2)
3. Mixed urban biowaste digestate (BWD 1)
4. Urban biowaste digestate (BWD 2)
5. Ash-rich civil sewage sludge from WWTP in Tuscany (CSL 1)
6. Conventional civil sewage sludge from WWTP in Piedmont (CSL 2)
7. Agricultural Digestate (AGD1)
8. Agricultural Digestate (AGD2)

3.1.2 Methodology

To characterize the samples from a chemical and physical point of view, the following analysis have been conducted on a laboratory scale, based on standard analysis methods:

Proximate analysis, which consisted in the definition of moisture, ashes and volatiles content (expressed as %). It was performed via Thermogravimetric Analyser (TGA).

Ultimate analysis, which consisted in the definition of carbon (C), hydrogen (H), nitrogen (N) contents (expressed as %), via CHN-S analyser.

Macro and micro elements analysis, which consisted in the definition of metals and other non-metal elements (e.g. P) which are part of the inorganic component of the analysed sample, via Microwave Plasma-Atomic Emission Spectroscopy (MP-AES).

Heating Value analysis, which consisted in the definition of the higher heating value (HHV), via bomb calorimeter.

The table below sums up all analysis carried out, the corresponding assessed parameters, the used instruments used (and devices models) and the reference standard.

Table 3. Analysis, parameters, instruments and standards of biowaste samples characterization.

ANALYSIS	PARAMETER	INSTRUMENT (MODEL)	STANDARD
Proximate Analysis	Moisture	TGA (LECO TGA701)	UNI EN ISO 18134-2: 2017
	Ash	TGA (LECO TGA701)	UNI EN ISO 18122: 2016
	Volatiles	TGA (LECO TGA701)	UNI EN ISO 18123: 2016
Ultimate analysis	C	CHN Analyser (LECOTruSpec CHN)	UNI EN ISO 16948: 2015
	H	CHN Analyser (LECOTruSpec CHN)	UNI EN ISO 16948: 2015
	N	CHN Analyser (LECOTruSpec CHN)	UNI EN ISO 16948: 2015
Macro and micro elements analysis	Metals and other elements	MP-OES (Agilent MP-AES 4200)	UNI EN ISO 16967: 2015 UNI EN ISO 16968: 2015
Heating value analysis	HHV	Bomb calorimeter (LECO AC500)	UNI EN ISO 18125: 2018

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3.1.3 Instruments

Instruments used for the analysis are described below.

3.1.3.1 Proximate analysis - TGA



Figure 5. TGA (LECO TGA701).

Proximate analysis allows to assess the percentage composition of the material in terms of moisture, ashes and volatile compounds. These components have been defined by means of a thermogravimetric analyser (TGA), a device equipped with a thermo-balance that heats and weights the sample and measures its weight loss against temperature. The process is held in controlled temperature, temperature ramp rate and atmosphere. The furnace consists of 19 crucibles (plus one reference blank). One of the parameters evaluated by TGA is moisture content, which is the material water. Moisture is calculated on a wet basis (w.b.) after heating at 105°C by air fluxing until constant weight of the material is reached:

$$Moisture\ (\%\ \frac{m}{m}\ w.b.) = \frac{initial\ mass - dry\ mass}{initial\ mass} \cdot 100$$

Ashes represent the inert component of biomass, being the residual matter of complete combustion of organic compounds. Ashes percentage determination procedure requires a temperature of 550 °C (or 710 °C) of the sample and oxygen atmosphere (after moisture removal). Ash content is calculated on a dry basis (d.b.) as the percentual residual weight after complete combustion:

$$Ash\ (\%\ \frac{m}{m}\ d.b.) = \frac{ash\ mass}{dry\ mass} \cdot 100$$

Volatiles are defined on a dry basis as the percentual weight loss after heating of the dry sample in absence of air (by nitrogen fluxing) to 600 °C:

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$$Volatiles\ (\%\ \frac{m}{m}\ d.b.) = \frac{initial\ dry\ mass - dry\ mass\ at\ 600°C}{dry\ mass} \cdot 100$$

Volatiles are more reactive compounds to temperature, which react then at lower temperatures. For each parameter (moisture, ashes, volatiles), three samples have been analysed, so that the assumed value of the parameter is the mean of the analysed samples.

3.1.3.2 Fixed Carbon – calculation

Fixed carbon represents the recalcitrant fraction of total carbon, that is the non-volatile carbon. Fixed carbon percentage is determined indirectly subtracting ashes and volatiles percentage from total mass, being then defined on a dry basis:

$$Fixed\ carbon\ \left(\%\ \frac{m}{m}\ d.b.\right) = 100 - (ashes + volatiles)$$

3.1.3.3 Ultimate analysis (C, H, N) – CHN analyser



Figure 6. CHN-S analyser (LECOTruSpec CHN).

Ultimate analysis aims to identify the elemental composition of the material in terms of carbon, hydrogen and nitrogen. To define C, H and N percentage composition, a CHN-S analyser has been used. The samples are combusted at high temperature, so that carbon is converted into CO_2, hydrogen into H_2O, and nitrogen into N_2. Three samples of DSL have been analysed, and the mean of the results was assumed as the parameter value. The results are expressed as percentage.

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3.1.3.4 Macro and micro element composition – MP-AES



Figure 7. MP-AES (Agilent MP-AES 4200).

The mineral fraction of the analysed biowaste contains many elements, most of which are metals. The macro and micro elements composition has been defined by Microwave Plasma-Atomic Emission Spectroscopy (MP-AES), an analytical technique that gives, as a result, the concentration of some metals (and three non-metals, i.e. boron (B), phosphorus (P) and silicon (Si)) which can be found in a liquid sample. For this reason, solid samples have been previously mineralized using a solution of H_2O_2 and HNO_3 to remove organic compound and to dissolve inorganics. Inside this device, the liquid sample enters a nebuliser where it is converted into aerosol. The aerosol is then transferred to nitrogen plasma: here ions and atoms undergo an excitation process and release then a radiation, which is characteristic of every element. The radiation is detected and converted into an electric signal, which is used to trace the analyte that released the radiation. This radiation is used, after the construction of a calibration curve, to define the analyte concentration. The analysis gives the concentration value in ppm (mg/kg) as a result.

3.1.3.5 HHV – bomb calorimeter



Figure 8. Bomb calorimeter (LECO AC500).

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To measure HHV, a bomb calorimeter has been used. By this device, a sample of the material is burnt in a pure oxygen atmosphere, and the heat released by the combustion reaction is taken up by a steel barrel. Here, the sample is put in contact with a nickel wire that ignites the combustion when electric current passes through the resistance. The combustion of the sample generates heat that is taken up by the distilled water, of known volume, where the barrel is submerged. Known the water temperature variation, the calorimeter thermal capacity, the distilled water mass and the water specific heat it is possible to determine the heat released by the unit mass of the sample. For biowaste and biochars characterization, we use LHV, expressed in MJ/kg on a dry basis, calculated by HHV, moisture content and hydrogen content.

3.2. Characterization of biowaste samples

Samples have been collected by their producers and characterized according to the methodology described above. In the below paragraph, each sample is described and analysed.

3.2.1 Industrial sludge (ISL1, ISL2)

The industrial sludge samples characterized in this study have been collected by two industrial actors:

- a pharmaceutical industry
- a food industry

Both sludges have been produced by the wastewater treatment plant of the industrial facility, mechanically separated from the liquid fraction and then dried, before being disposed. Samples are named as follows:

1. Industrial sludge from pharmaceutical industry (ISL1)
2. Industrial sludge from food industry (ISL2)

In **Table 4** the proximate and ultimate analysis of the materials are reported.

Table 4. Proximate and ultimate analysis of the industrial sludge (ISL1, ISL2).

Parameter	Unit	ISL 1	ISL 2
Moisture	% a.r.	8.2	33.8
Dry matter	% a.r.	91.8	66.2
Ashes 550°C	% d.b.	20.7	26.0
Ashes 710°C	% d.b.	63.1	26.0
Volatiles	% d.b.	63.1	66.7
Fixed C	% d.b.	16.2	7.3
C	% d.b.	43.0	39.5
H	% d.b.	5.2	5.7
N	% d.b.	7.5	7.0
S	% d.b.	0.9	2.3
Cl	% d.b.	0.40	0.11
LHV	MJ/kg d.b.	16.6	16.9

Table 5 shows the macro and micro elements concentration in the industrial sludge on dry basis.

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Table 5. Macro and micro elemental analsyis of the industrial sludge (ISL 1, ISL 2).

Parameter	Unit	ISL 1	ISL 2
Al	mg/kg d.b.	7575	4730
Ba	mg/kg d.b.	122	44
Ca	mg/kg d.b.	30240	42802
Cd	mg/kg d.b.	b.d.l.	b.d.l.
Co	mg/kg d.b.	2	b.d.l.
Cr	mg/kg d.b.	22	46
Cu	mg/kg d.b.	11	67
Fe	mg/kg d.b.	504	51777
K	mg/kg d.b.	3630	2034
Li	mg/kg d.b.	7	1
Mg	mg/kg d.b.	2571	2324
Mn	mg/kg d.b.	238	455
Mo	mg/kg d.b.	b.d.l.	b.d.l.
Na	mg/kg d.b.	8600	1638
Ni	mg/kg d.b.	9	b.d.l.
P	mg/kg d.b.	11838	20043
Pb	mg/kg d.b.	b.d.l.	16
Si	mg/kg d.b.	795	1576
Ti	mg/kg d.b.	5863	26
V	mg/kg d.b.	b.d.l.	2
Zn	mg/kg d.b.	93	416

3.2.2 Digestate of Urban Biowaste

Digested urban biowaste has been collected by two anaerobic digestion plants located in Emilia Romagna, and Lombardy. The digested biowaste has been previously separated from the liquid fraction by centrifugation, then sent to RE-CORD laboratory. Samples are named as follows:

1. Mixed urban biowaste digestate, from Emilia Romagna (DBW 1)
2. Urban biowaste digestate, from Lombardy (DBW 2)

In **Table 6** the proximate and ultimate analysis of the materials are reported.

Table 6. Proximate and ultimate analysis of the digested urban biowaste (BWD 1, BWD 2).

Parameter	Unit	DBW 1	DBW 2
Moisture	% a.r.	80.2	74.8
Dry matter	% a.r.	19.8	25.2
Ashes 550°C	% d.b.	39.1	25.6
Ashes 710°C	% d.b.	36.7	21.4
Volatiles	% d.b.	52.6	63.6
Fixed C	% d.b.	8.3	10.8

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C	% d.b.	32.4	38.2
H	% d.b.	4.0	4.6
N	% d.b.	2.9	1.3
S	% d.b.	0.5	0.4
Cl	% d.b.	0.70	0.67
LHV	MJ/kg d.b.	11.6	14.3

Table 7 shows the macro and micro elements concentration in the urban biowaste digestate on dry basis.

Table 7. Macro and micro elemental analysis of digested urban biowaste (DBW 1, DBW 2).

Parameter	Unit	DBW 1	DBW 2
Al	mg/kg d.b.	12115	4778
B	mg/kg d.b.	325	174
Ba	mg/kg d.b.	b.d.l.	2
Ca	mg/kg d.b.	62790	50555
Cd	mg/kg d.b.	b.d.l.	b.d.l.
Co	mg/kg d.b.	b.d.l.	b.d.l.
Cr	mg/kg d.b.	98	b.d.l.
Cu	mg/kg d.b.	114	19
Fe	mg/kg d.b.	42853	4757
K	mg/kg d.b.	15289	2027
Li	mg/kg d.b.	16	5
Mg	mg/kg d.b.	5598	7858
Mn	mg/kg d.b.	738	501
Mo	mg/kg d.b.	bdl	b.d.l.
Na	mg/kg d.b.	5920	14101
Ni	mg/kg d.b.	35	b.d.l.
P	mg/kg d.b.	16913	8755
Pb	mg/kg d.b.	59	b.d.l.
Ti	mg/kg d.b.	177	104
V	mg/kg d.b.	14	b.d.l.
Zn	mg/kg d.b.	293	179

3.3.3 Civil Sludge

Civil sludge has been collected by two different wastewater treatment plants, both equipped with anaerobic digestion. The first sludge comes from a plant in Tuscany, and it is characterized by a high ash content, the second sludge comes from a plant in Piedmont.

The sludge from Tuscany has been collected by RE-CORD after centrifugation, and then dried at RE-CORD laboratory. The sludge from Piedmont has been received dried. Samples are named as follows:

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1. Ash-rich civil sewage sludge from WWTP in Tuscany (CSL 1)
2. Conventional civil sewage sludge from WWTP in Piedmont (CSL 2)

In **Table 8** the proximate and ultimate analysis of the materials are reported.

Table 8. Proximate and ultimate analysis of the civil sewage sludge (CSL 1, CSL 2).

Parameter	Unit	CSL 1	CSL 2
Moisture	% a.r.	73.9	9.9
Dry matter	% a.r.	26.1	90.1
Ashes 550°C	% d.b.	49.3	33.6
Ashes 710°C	% d.b.	48.5	33.1
Volatiles	% d.b.	46.0	58.9
Fixed C	% d.b.	4.7	7.5
C	% d.b.	23.6	35.7
H	% d.b.	4.0	4.9
N	% d.b.	3.8	5.8
S	% d.b.	0.8	1.5
Cl	% d.b.	0.05	0.04
LHV	MJ/kg d.b.	9.5	14.8

Table 9 shows the macro and micro element concentration in the civil sludge on dry basis.

Table 9. Macro and micro elemental analysis of civil sewage sludge (CSL1, CSL 2).

Parameter	Unit	CSL 1	CSL 2
Al	mg/kg d.b.	40574	23944
B	mg/kg d.b.	6	b.d.l
Ba	mg/kg d.b.	784	280
Ca	mg/kg d.b.	23550	28746
Cd	mg/kg d.b.	0	b.d.l
Co	mg/kg d.b.	0	b.d.l
Cr	mg/kg d.b.	77	152
Cu	mg/kg d.b.	702	292
Fe	mg/kg d.b.	15763	49537
K	mg/kg d.b.	6055	3161
Li	mg/kg d.b.	20	6
Mg	mg/kg d.b.	5792	6539
Mn	mg/kg d.b.	358	285
Mo	mg/kg d.b.	0	b.d.l
Na	mg/kg d.b.	842	1194
Ni	mg/kg d.b.	96	b.d.l
P	mg/kg d.b.	37498	28176
Pb	mg/kg d.b.	61	b.d.l
Ti	mg/kg d.b.	277	244
V	mg/kg d.b.	34	12

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Zn	mg/kg d.b.	453	830

3.3.4 Agricultural digestate

Agricultural digestate has been collected by two different anaerobic digestion facilities, both in Lombardy, operating with mixed corn silage and manure. Both digestate samples have been collected at the plant after centrifugation, and dried at RE-CORD laboratory. Samples are named AGD1 and AG2.

In **Table 10** the proximate and ultimate analysis of the agricultural digestates is reported.

Table 10. Proximate and ultimate analysis of agricultural digestate (AGD 1, AGD 2).

Parameter	Unit	AGD 1	AGD 2
Moisture	% a.r.	73.3	84.2
Dry matter	% a.r.	26.7	15.8
Ashes 550°C	% d.b.	15.0	10.0
Ashes 710°C	% d.b.	14.4	9.9
Volatiles	% d.b.	68.4	68.5
Fixed C	% d.b.	16.6	21.4
C	% d.b.	44.4	45.7
H	% d.b.	5.3	5.4
N	% d.b.	1.4	2.2
S	% d.b.	0.50	0.17
Cl	% d.b.	0.64	0.35
LHV	MJ/kg d.b.	16.4	17.3

Table 11 shows the macro end micro element concentration in the agricultural digestate on dry basis.

Table 11. Macro and micro elemental analysis of agricultural digestate (AGD 1, AGD 2).

Parameter	Unit	AGD 1	AGD 2
Al	mg/kg d.b.	713	119
B	mg/kg d.b.	b.d.l	b.d.l.
Ba	mg/kg d.b.	13	6
Ca	mg/kg d.b.	21330	4808
Cd	mg/kg d.b.	b.d.l	b.d.l.
Co	mg/kg d.b.	b.d.l	b.d.l.
Cr	mg/kg d.b.	9	4
Cu	mg/kg d.b.	38	4
Fe	mg/kg d.b.	2498	1068
K	mg/kg d.b.	21803	23473
Li	mg/kg d.b.	1	b.d.l.
Mg	mg/kg d.b.	4246	2930
Mn	mg/kg d.b.	189	97

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Mo	mg/kg d.b.	b.d.l	b.d.l.
Na	mg/kg d.b.	6318	329
Ni	mg/kg d.b.	b.d.l	b.d.l.
P	mg/kg d.b.	8725	7188
Pb	mg/kg d.b.	b.d.l	b.d.l.
Ti	mg/kg d.b.	18	3
V	mg/kg d.b.	3	b.d.l.
Zn	mg/kg d.b.	189	67

3.3 Selection of biowaste samples for pyrolysis

The selection of biowaste streams to be used for pyrolysis tests was performed with the principle that, given the early stage of the proposed technology, all the identified four materials could be of interest for the H2STEEL value chain. Therefore, one sample for each biowaste category has been selected according to the evaluation explained below.

3.3.1 Industrial Sludge

Among industrial Sludge from pharmaceutical plant (ISL 1) and industrial Sludge from food industry (ISL 2), **ISL 2 has been selected as more suitable for the H2STEEL project scope**. The main reason stays in the fact that ISL 1, despite of an interesting composition, is derived from a process which can't be properly defined as "biological". In fact, the organic matter contained in the wastewater treated in the WWTP is derived from a pharmaceutical production process, thus not necessarily of biological origin. On the contrary, ISL 2 is part of the bioeconomy value chain and, even if of industrial origin, it can be identified as a biowaste material.

3.3.2 Digested Urban Biowaste

As reported in paragraph 3.2, two samples of digested organic fraction of municipal solid waste have been collected. The samples presented different composition with reference to: ash content, iron and aluminium content. In particular, DBW 1 presented a higher ash concentration (around 39% d.b.) of which ashes resulted to contain high amount of aluminium, and iron. These characteristics have been found to be typical of digested sewage sludge, where iron chloride, and aluminium chloride are used as flocculating agents. DBW 2 resulted in ash amount of about 26% d.b., thus with higher carbon content, and reduced concentration of iron, and aluminium, more appropriate for a material which should derive from household food waste. Therefore, **DBW 2 was adopted for further pyrolysis tests.**

3.3.3 Civil sewage sludge

About civil sewage sludge, two types were characterized, deriving from two different plants in Italy. The CSL 1, produced in Tuscany, has shown an ash content of almost 50%, while the second, CSL 2, resulted in about 33% of ash content, with consequent higher carbon content. Aluminium,

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Iron and phosphorus content were comparable. The amount of ashes of the first sludge (CSL 1) was considered higher than the average, according to data reported in literature[27], which usually report an ash content of 30-40% d.b., and a carbon content of around 30-40% d.b., values similar to CSL 2. For this reason, it was decided to **use CSL 2 as sample for further pyrolysis tests.**

3.3.4 Agricultural digestate

Two types of agricultural digestate have been characterized in laboratory: AGD 1 and AGD 2. Main differences identified are the ash content (15% d.b. in AGD 1, 10% d.b. in AGD 2) and the fixed carbon content, higher in AGD 2 (21.4% d.b.), lower in AGD 1 (16.6% d.b.). Among other waste streams, agricultural digestate represents a material of higher quality, already commercialized as soil conditioner in the market. At the same time, it could be promising as carbon source for producing the H2STEEL catalysts. Therefore, it was decided to include AGD as the "best quality" biowaste stream. Following this approach, **the AGD 2 digestate has been selected due to its higher fixed carbon content.**

4 SLOW PYROLYSIS OF BIOWASTE SAMPLES

4.1 Instruments and methodology

The laboratory scale pyrolysis tests have been performed via TGA, Leco 701. All 19 TGA crucibles have been filled up with 3-5 g of biowaste sample, then operating parameters have been set and pyrolysis started. At the end of the test, crucibles have been taken out from TGA and char has been weighted and collected.

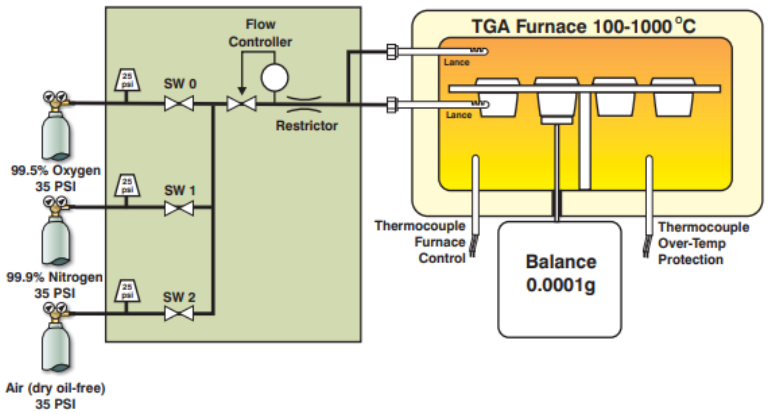

Figure 9. TGA operating scheme

[27] Rorat A, Courtois P, Vandenbulcke F, Lemiere S. Sanitary and environmental aspects of sewage sludge management. Industrial and Municipal Sludge. 2019:155–80. doi: 10.1016/B978-0-12-815907-1.00008-8. Epub 2019 Apr 19. PMCID: PMC7149543.

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Slow pyrolysis tests have been performed at different temperatures and residence times. Heating rate has been kept constant for all trials, at 20°C/min. Due to the different composition, different temperature ranges have been chosen for sludge samples, compared to solid derived digestates. Below, two charts reporting a comparison of volatiles (% on dry ash free basis, d.a.f.) and phosphorus (% d.b.) in the four biowaste samples are presented.

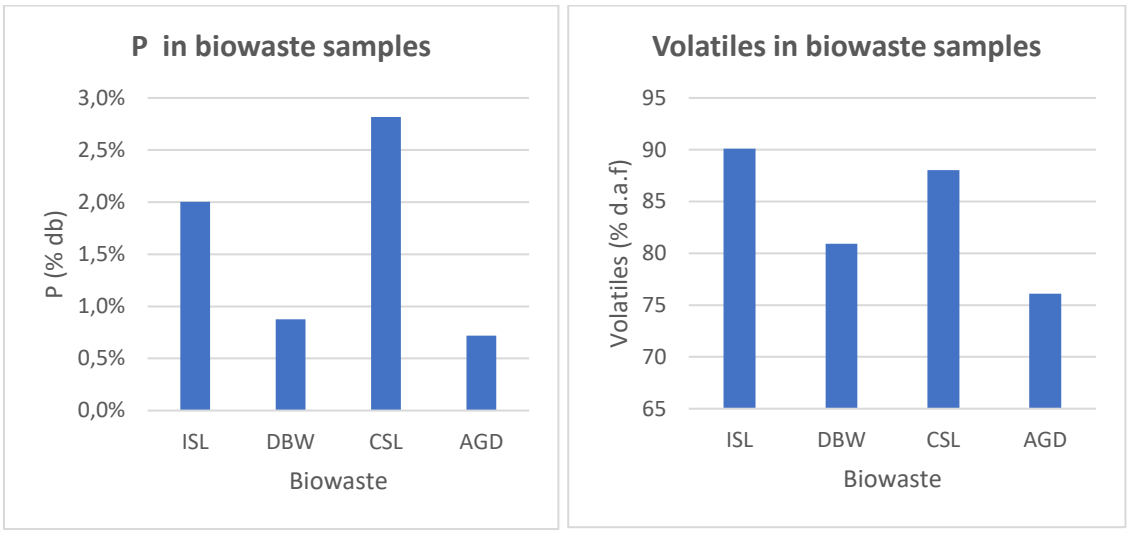

Figure 10. Volatiles and phosphorous concentration in the selected biowaste.

The range of temperatures selected for tests to be performed on digested urban biowaste and on agricultural digestate is 500-600°C. The range of temperatures selected for tests to be performed on wastewater treatment sludge is 450-550°C. This decision was taken considering the higher volatility of sludge, compared to solid derived digestate, and to the need of maximizing phosphorus recovery. In fact, it was identified by literature that phosphates solubility in biochar decreases at higher pyrolysis temperatures. In addition, a slow pyrolysis test at 700°C, was performed for all biowastes. The below table summarizes the conditions for each pyrolysis test.

Table 12. Pyrolysis tests performed by TGA on the selected biowaste.

Material	Test 1	Test 2	Test 3	Test 4	Test 5
ISL 2	450 °C, 30 min	450 °C, 60 min	550 °C, 30 min	550°C, 60 min	700 °C, 30 min
DBW 2	500 °C, 30 min	500 °C, 60 min	600 °C, 30 min	600 °C, 60 min	700 °C, 30 min
CSL 2	450 °C, 30 min	450 °C, 60 min	550 °C, 30 min	550 °C, 60 min	700 °C, 30 min
AGD 2	500 °C, 30 min	500 °C, 60 min	600 °C, 30 min	600 °C, 60 min	700 °C, 30 min

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4.2 Description of slow pyrolysis tests

Each of the 4 biowaste streams was firstly processed at four different pyrolysis conditions. After the produced biochar samples were characterized, a further pyrolysis test at high temperature was performed. The tests are all described below.

4.2.1 Pyrolysis tests on Industrial sludge

Industrial sludge digested anaerobically, received dry at RE-CORD laboratory, was pyrolyzed at 450, and 550°C, at residence time of 30, and 60 minutes, keeping heat rate at 20°C/min. **Table 13** reports the mass yield obtained during each trial.

Table 13. Pyrolysis tests performed by TGA on industrial sludge.

Conditions	Test 1	Test 2	Test 3	Test 4
Temperature (°C)	450	450	550	550
Residence time (min)	30	60	30	60
Heating rate (°C/min)	20	20	20	20
Char mass yield*	45.7%	44.6%	41.1%	40.5%

*defined as the ratio between the weight of the inlet dry feedstock and that of the collected dry char

As visible, mass yield decreases from 45.7% from test 1 to 40.5% from test 4 and it is influenced mainly by temperature, and less by the residence time.

4.2.2 Pyrolysis tests on digested urban biowaste

Urban biowaste digested anaerobically, received wet at RE-CORD laboratory and then dried, was pyrolyzed at 500, and 600°C, at residence time of 30, and 60 minutes, keeping heat rate at 20°C/min. **Table 14** reports the mass yield obtained during each trial.

Table 14. Pyrolysis tests performed by TGA on digested urban biowaste.

Conditions	Test 1	Test 2	Test 3	Test 4
Temperature (°C)	500	500	600	600
Residence time (min)	30	60	30	60
Heating rate (°C/min)	20	20	20	20
Char mass yield	43.5%	43.6%	42.2%	41.5%

As visible, mass yield decreases from 43.5% to 41.5%, from test 1 to test 4. Influenced mainly by temperature, and less by the residence time.

4.2.3 Pyrolysis tests on civil sewage sludge

Civil sewage sludge, received dry at RE-CORD laboratory, was pyrolyzed at 450, and 550°C, at residence time of 30, and 60 minutes, keeping heat rate at 20°C/min. **Table 15** reports the mass yield obtained during each trial.

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Table 15. Pyrolysis tests performed by TGA on civil sewage sludge.

Conditions	Test 1	Test 2	Test 3	Test 4
Temperature (°C)	450	450	550	550
Residence time (min)	30	60	30	60
Heating rate (°C/min)	20	20	20	20
Char mass yield	48.3%	47.3%	44.4%	44.5%

As expected, also in the case of sewage sludge pyrolysis, the mass yield decreases from 48.5% to 44.5% from test 1 to test 4. The devolatilization is influenced mainly by the process temperature. A variation of the mass yield is identified for pyrolysis at lower temperature (450°C), while almost no mass yield variation is determined at 550°C.

4.2.4 Pyrolysis tests on agricultural digestate

Agricultural digestate, received wet at RE-CORD laboratory and then dried, was pyrolyzed at 500, and 600°C, at residence time of 30, and 60 minutes, keeping heat rate at 20°C/min. Table 16**Table 14** reports the mass yield obtained during each trial.

Table 16. Pyrolysis tests performed by TGA on agricultural digestate.

Conditions	Test 1	Test 2	Test 3	Test 4
Temperature (°C)	500	500	600	600
Residence time (min)	30	60	30	60
Heating rate (°C/min)	20	20	20	20
Char mass yield	34.1%	32.3%	31.7%	30.6%

Mass yield decreases sensibly from 34.1% at 500°C, 30 min, to 30.6% at 600°C, 60 min. In this case, differently than previous tests, the devolatilization of the feedstock is influenced not only by the process temperature, but also by the retention time.

4.3 CHARACTERIZATION OF PRODUCED BIOCHAR SAMPLES

Each sample of produced biochar has been characterized. The characterization results are reported in the below paragraphs.

4.3.1 Biochar from Industrial sludge

Biochar samples produced from industrial sludge are named as follows:

- ISL_450a: biochar produced at 450°C, with RT of 30 min
- ISL_450b: biochar produced at 450°C, with RT of 60 min
- ISL_550a: biochar produced at 550°C, with RT of 30 min

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- ISL_550b: biochar produced at 550°C, with RT of 60 min

Proximate and ultimate analysis are reported in **Table 17**.

Table 17. Proximate and ultimate analysis of biochar from industrial sludge.

Parameter	Unit	ISL_450a	ISL_450b	ISL_550a	ISL_550b
Ashes 550°C	% d.b.	22.2	56.3	61.0	61.9
Ashes 710°C	% d.b.	54.8	56.1	60.7	61.5
Volatiles	% d.b.	25.9	25.0	21.3	20.7
Fixed C	% d.b.	19.3	19.0	18.0	17.7
C	% d.b.	34.2	34.1	33.3	32.4
H	% d.b.	2.1	1.9	1.1	1.1
N	% d.b.	6.3	6.3	6.0	5.7

The concentration of inorganic elements is reported in **Table 18**.

Table 18. Inorganic elements analysis of biochar from industrial sludge.

Parameter	Unit	ISL_450a	ISL_450b	ISL_550a	ISL_550b
Al	mg/kg ash	9051	9265	10037	10170
Ba	mg/kg ash	92	94	102	103
Ca	mg/kg ash	63391	64896	70302	71228
Cd	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Co	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Cr	mg/kg ash	88	90	97	99
Cu	mg/kg ash	142	146	158	160
Fe	mg/kg ash	78959	80833	87567	88720
K	mg/kg ash	3877	3969	4299	4356
Li	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Mg	mg/kg ash	4927	5044	5465	5537
Mn	mg/kg ash	862	882	955	968
Mo	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Na	mg/kg ash	3517	3601	3901	3952
Ni	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
P	mg/kg ash	61960	63431	68715	69621
Pb	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Ti	mg/kg ash	67	69	74	75
V	mg/kg ash	5	5	5	5
Zn	mg/kg ash	775	794	860	871

4.3.2 Biochar from digested urban biowaste

Biochar samples produced from digested urban biowaste are named as follows:

- DBW_500a: biochar produced at 500°C, with RT of 30 min

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- DBW _500b: biochar produced at 500°C, with RT of 60 min
- DBW _600a: biochar produced at 600°C, with RT of 30 min
- DBW _600b: biochar produced at 600°C, with RT of 60 min

Proximate and ultimate analysis are reported in **Table 19**.

Table 19. Proximate and ultimate analysis of biochar from digested urban biowaste.

Parameter	Unit	DBW_500a	DBW_500b	DBW_600a	DBW_600b
Ashes 550°C	% d.b.	52.4	55.0	56.4	57.7
Ashes 710°C	% d.b.	43.6	45.6	47.3	48.3
Volatiles	% d.b.	21.9	23.6	20.2	19.8
Fixed C	% d.b.	25.8	21.4	23.4	22.6
C	% d.b.	41.3	41.2	41.4	39.4
H	% d.b.	1.6	1.6	1.00	0.90
N	% d.b.	1.4	1.4	1.2	1.1

The concentration of inorganic elements is reported in **Table 20**.

Table 20. Inorganic elements analysis of biochar from digested urban biowaste.

Parameter	Unit	DBW_500a	DBW_500b	DBW_600a	DBW_600b
Al	mg/kg ash	6610	6905	7165	7313
Ba	mg/kg ash	212	222	230	235
Ca	mg/kg ash	95833	100118	103876	106030
Cd	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Co	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Cr	mg/kg ash	25	26	27	27
Cu	mg/kg ash	71	74	77	79
Fe	mg/kg ash	7317	7644	7931	8096
K	mg/kg ash	32610	34068	35347	36080
Li	mg/kg ash	7	7	7	8
Mg	mg/kg ash	13391	13989	14514	14815
Mn	mg/kg ash	807	843	875	893
Mo	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Na	mg/kg ash	14766	15426	16005	16337
Ni	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
P	mg/kg ash	17858	18656	19357	19758
Pb	mg/kg ash	46	48	50	51
Ti	mg/kg ash	206	215	223	228
V	mg/kg ash	7	8	8	8
Zn	mg/kg ash	208	218	226	231

4.3.3 Biochar from civil sewage sludge

Biochar samples produced from civil sewage sludge are named as follows:

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- CSL_450a: biochar produced at 450°C, with RT of 30 min
- CSL_450b: biochar produced at 450°C, with RT of 60 min
- CSL_550a: biochar produced at 550°C, with RT of 30 min
- CSL_550b: biochar produced at 550°C, with RT of 60 min

Proximate and ultimate analysis are reported in **Table 21**.

Table 21. Proximate and ultimate analysis of biochar from civil sewage sludge.

Parameter	Unit	CSL_450a	CSL_450b	CSL_550a	CSL_550b
Ashes 550°C	% d.b.	61.9	63.1	67.1	65.2
Ashes 710°C	% d.b.	61.1	62.1	65.3	64.4
Volatiles	% d.b.	23.3	20.8	18.2	20.2
Fixed C	% d.b.	14.8	16.1	14.7	14.7
C	% d.b.	29.0	29.0	27.2	27.4
H	% d.b.	1.7	1.6	1.1	1.2
N	% d.b.	4.2	4.4	3.8	3.9

Concentration of inorganic elements is reported in **Table 22**.

Table 22. Inorganic elements analysis of biochar from civil sewage sludge.

Parameter	Unit	CSL_450a	CSL_450b	CSL_550a	CSL_550b
Al	mg/kg ash	21469	17887	23254	21887
Ba	mg/kg ash	489	430	511	485
Ca	mg/kg ash	47912	45082	57481	56000
Cd	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Co	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Cr	mg/kg ash	218	195	228	220
Cu	mg/kg ash	493	427	485	482
Fe	mg/kg ash	76749	58245	80669	77531
K	mg/kg ash	4574	3631	5177	4785
Li	mg/kg ash	ND	ND	ND	ND
Mg	mg/kg ash	14929	12675	15307	14922
Mn	mg/kg ash	403	363	407	403
Mo	mg/kg ash	b.d.l.	114	b.d.l.	b.d.l.
Na	mg/kg ash	1786	1502	1937	1798
Ni	mg/kg ash	143	121	145	141
P	mg/kg ash	48091	44647	49253	48051
Pb	mg/kg ash	114	113	121	129
Ti	mg/kg ash	439	333	452	416
V	mg/kg ash	22	17	25	23
Zn	mg/kg ash	1413	1267	1431	1408

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4.3.4 Biochar from agricultural digestate

Biochar produced from agricultural digestate are named as follows

- AGD_500a: biochar produced at 500°C, with RT of 30 min
- AGD_500b: biochar produced at 500°C, with RT of 60 min
- AGD_600a: biochar produced at 600°C, with RT of 30 min
- AGD_600b: biochar produced at 600°C, with RT of 60 min

Proximate and ultimate analysis are reported in **Table 23Table 17**.

Table 23. Proximate and ultimate analysis of biochar from agricultural digestate.

Parameter	Unit	AGD_500a	AGD_500b	AGD_600a	AGD_600b
Ashes 550°C	% d.b.	26.5	27.1	29.1	29.0
Ashes 710°C	% d.b.	24.5	25.73	27.5	27.1
Volatiles	% d.b.	15.3	14.5	11.4	11.8
Fixed C	% d.b.	58.2	58.4	59.5	59.2
C	% d.b.	57.6	58.7	60.2	59.6
H	% d.b.	2.5	2.5	1.9	1.6
N	% d.b.	2.4	2.3	2.0	2.0

Concentration of inorganic elements is reported in **Table 24**.

Table 24. Inorganic elements analysis of biochar from agricultural digestate.

Parameter	Unit	AGD_500a	AGD_500b	AGD_600a	AGD_600b
Al	mg/kg ash	699	358	404	345
Ba	mg/kg ash	22	20	20	20
Ca	mg/kg ash	16996	16719	17066	17625
Cd	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Co	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Cr	mg/kg ash	5	4	4	4
Cu	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Fe	mg/kg ash	3058	2916	2911	2973
K	mg/kg ash	40149	40680	42524	42680
Li	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Mg	mg/kg ash	18320	12556	25593	15459
Mn	mg/kg ash	272	250	272	263
Mo	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Na	mg/kg ash	771	745	768	794
Ni	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
P	mg/kg ash	27273	22436	31343	24920
Pb	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Ti	mg/kg ash	21	22	23	20
V	mg/kg ash	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Zn	mg/kg ash	213	214	199	221

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4.4. Slow pyrolysis at higher temperature

Given the expected high temperature to be achieved for methane catalytic cracking reaction, a further pyrolysis trial has been performed at 700°C, with a residence time of 30 minutes, and a heating reate of 20°C/min. The temperature of 700°C is considered the mínimum temperature at which methane catalytic cracking will be tested[28]. Higher pyrolysis temperature have not been tested for two reasons:

- the H2STEEL process include an intermediate char upgrading step by chemical leaching, for extracting nutrients like phosphorus and calcium. The solubility, and thus the extraction performance of these inorganic elements decreases with the increase of pyrolysis temperature.
- According to the intial H2STEEL concept it is considered to place the processing plants in different steps of the value chain. In particular, pyrolysis and char upgrading plants could be placed as post-treatment of any decentralized anaerobic digestion facility, while the catalytic biomethane cracking plant is estimated to be placed in a centralized hydrogen production facility.

Therefore, it is considered reasonable that the máximum temperature of slow pyrolysis process to treat digested in small-medium size plant won't overcome the 700 °C. The mass yield of the slow pyrolysis test is reported below.

Table 25. Process condition for pyrolysis test at higher temperature

Material	Unit	Test_ISL 5	Test_DBW_5	Test_CSL_5	Test_AGD_5
Feedstock	-	ISL	DBW	CSL	AGD
Temperature	°C	700	700	700	700
Residence time	Min	30	30	30	30
heating rate	°C/min	20	20	20	20
Mass yield	% db	36.7	39.9	41.9	31.5

As expected, mass yield is higher for those material having higher ash content. Agricultural digestate shows the lowest yield, of about 31.5 %db, with civil sewage sludge having the higher yield: about 41.9 %db.

4.4.1 Quality of obtained char

The biochar obtained at 700 °C shows lower volatility, higher ash content, and reduced hydrogen content. Table below shows the composition of analysed biochar produced at 700 °C

Table 26. Composition of biochar produced from 4 biowaste streams at 700 °C

	Unit	ISL_700	CSL_700	DBW_700	AGD_700
Ashes 550°C	% db	65.9	57.3	70.4	31.12

[28] Savankumar Patel, Sazal Kundu, Pobitra Halder, Mojtaba Hedayati Marzbali, Ken Chiang, Aravind Surapaneni, Kalpit Shah, Production of hydrogen by catalytic methane decomposition using biochar and activated char produced from biosolids pyrolysis, International Journal of Hydrogen Energy, Volume 45, Issue 55, 2020, Pages 29978-29992, ISSN 0360-3199, https://doi.org/10.1016/j.ijhydene.2020.08.036

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Ashes 710°C	% db	66.2	57.0	70.2	30.9
Volatiles	% db	15.9	17.5	13.3	9.48
Fixed C	% db	18.0	25.5	16.6	59.7
C	% db	32.6	36.8	26.3	54.6
H	% db	0.6	0.5	0.5	1.9
N	% db	3.8	1.0	2.6	1.0

As visible from Table 26, a stronger devolatilization results from the pyrolysis at 700°C of agricultural digestate, compared to the process applicated to higher ash material like civil and industrial sludge, or organic fraction of urban waste. This result can be due to the different organic compounds contained in the digested matter.

5 QUALITY ASSESSMENT OF OBTAINED CHAR SAMPLES

In order to select the most promising materials to be used in H2STEEL process, a comparison of biochar simples have been performed. The key elements addressed are the following

- Carbon content (% C db)
- Char stability (molar H/C ratio)
- Ash content (% ash 710°C)
- Phosphorus, Iron, Aluminum content (% ash 710°C)

5.1 Assessnebt of biochar carbon content

The carbon content (as % on dry basis) has been determined for all biochar samples. The concentration decreases slightly decrease with the increase of temperature.

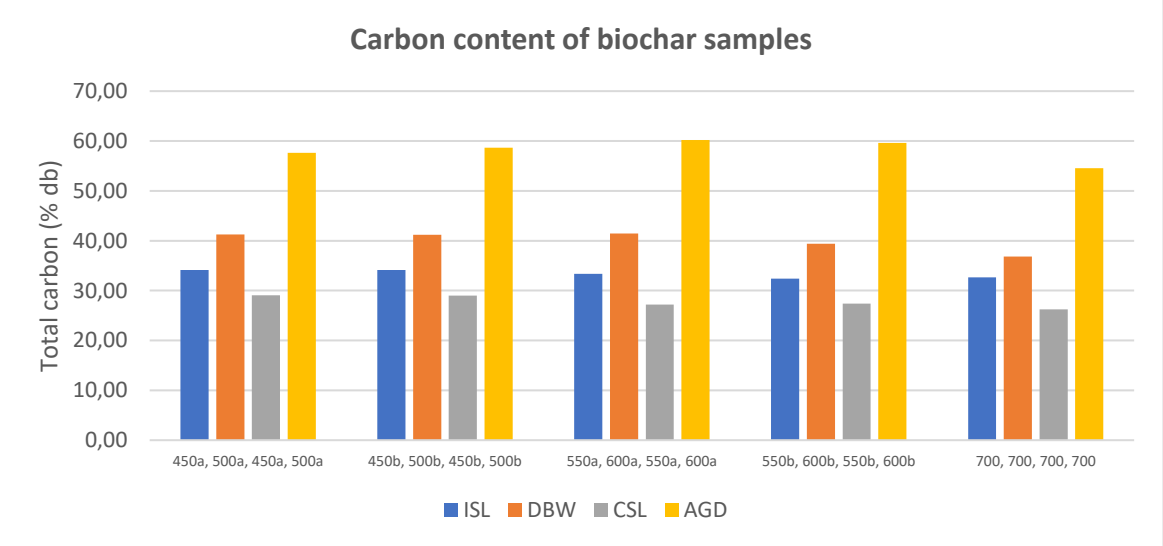

Figure 11. Carbon content of produced biochar samples

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This happens due to the high ash concentration in the processed materials. In fact, the decrease of C content at higher temperatures is more evident for industrial sludge (ISL) and civil sludge (CSL), while it remains almost constant for urban biowaste digestate (DBW) from 500 to 600 °C. In general, carbon content in the produced char simples reaches a máximum value when Agricultural digestate (ADG) is pyrolysed at 600°C. The lowest value characterizes the biochar from civil sewage sludge.

5.2 Assessment of biochar samples stability

The application of the biochar as catalysts during methane crakcing process, as well as biocoals in Steelmaking processes require that the char is stable at high temperatures. In order to determine the stability of the biochar semples, the hydrogen on carbon molar ratio (molar H/C) has been calculated. This parameter indicates the volatility of the material and, by consequence, the reactivity at high temperatures.

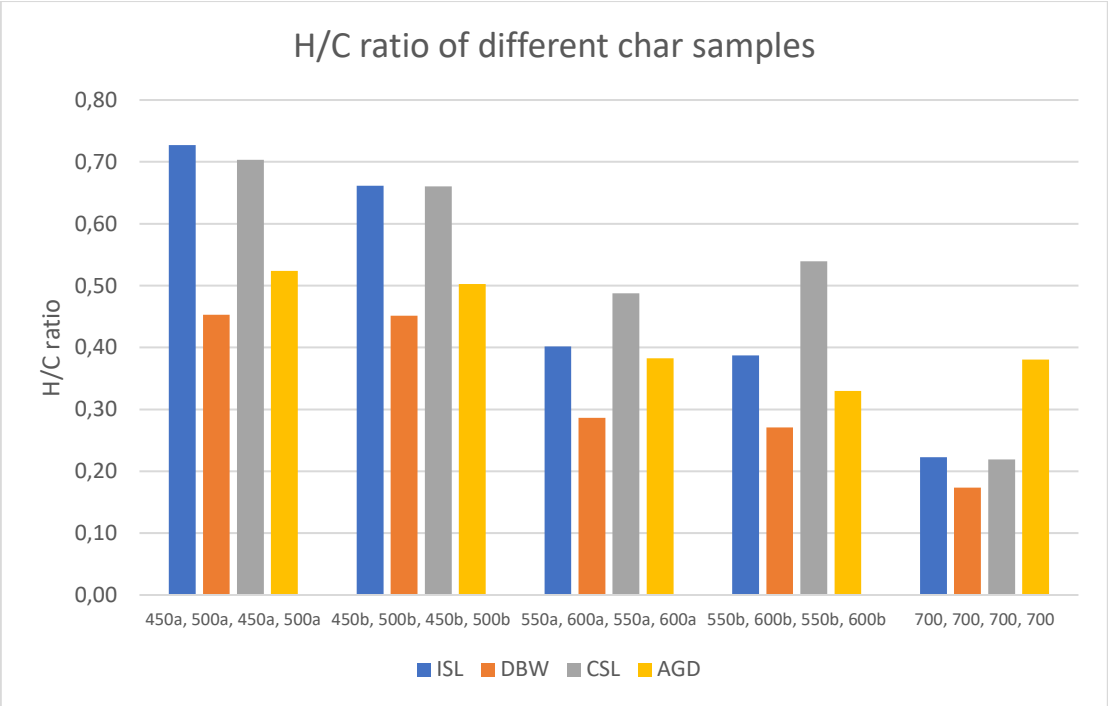

Figure 12. Molar H/C ratio of produced biochar samples

As visible in the chart, lowest H/C ratio has been achieve at 700°C for all the processed materials. Valuable results in terms of stability have been achieved for OFMSW when processed at 500°C, for 30 minutes. While the H/C of biochars produced from civil sewage sludge remained at about 0.5 even if processed at 550°C. About biochar produced from AGD, good stability is achieved at 600°C, 60 minutes residence time, even better than that resulted from the pyrolysis at 700°C. As a summary, it can be stated that, for the production of a good quality char to be used as catalyst, pyrolysis at 450°C could be a too low temperature even for civil and industrial sludge, while 550°C is recommended. For DBW and AGD, 600°C could be suitable.

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5.3 Assessment of the ash content of biochar samples

In the below figure, ash content of obtained biochar samples is compared.

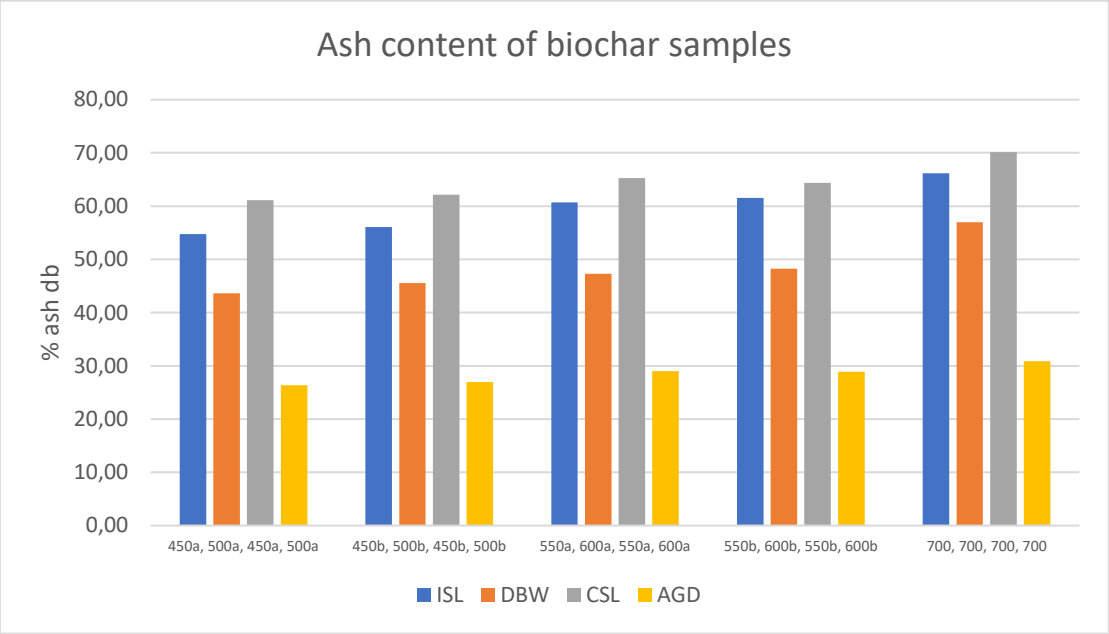

Figure 13. Ash content of produced biochar samples

The comparison of the ash content of the different biochar produced put in evidence the great difference between sludge, and digestates from urban biowaste, or agricultural residues. The ash content of the biochar produced from sludge pyrolysis, even at 450°C, overcome the 50% db, increaing to up to 70% db for the biochar obtained by civil sewage sludge pyrolysed at 700°C. Even for other materials, the ash content increases with pyrolysis temperature and residence time. The need of an upgrading step for the biochar before being used as catalyst is needed to remove the contaminants in the char, reduce ash content, and valorize nutrients like phosphorus, and other inorganics.

5.4 Comparison of phosphorus, iron and aluminum content in biochar samples

As an additional quality assessment, phosphorus, iron and aluminum concentration in the biochar ash have been compared. The importance of the three elements is related to different aspects of the H2STEEL proposed process:

Phosphorus is the highest value element in agriculture, commercialized at more than 1.5 €/kg. Moreover, phosphorus is a harmful element for the steelmaking sector, thus its extraction from char is recommended. The higher the concentration of phosphorus, the more competitive and sustainable is the biochar chemical upgrading process.

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Iron is considered a high value catalyst enhancing methane cracking process. Therefore, the presence of Iron could be beneficial when using the biochar as catalyst in methane pyrolysis reactor

Alluminum, often in the form of alluminum oxide, is also a high value element which could be extracted. At the same time, it could be harmful, or useless, during the methane catalytic process and contributes to increase the total amount of inorganic in the char.

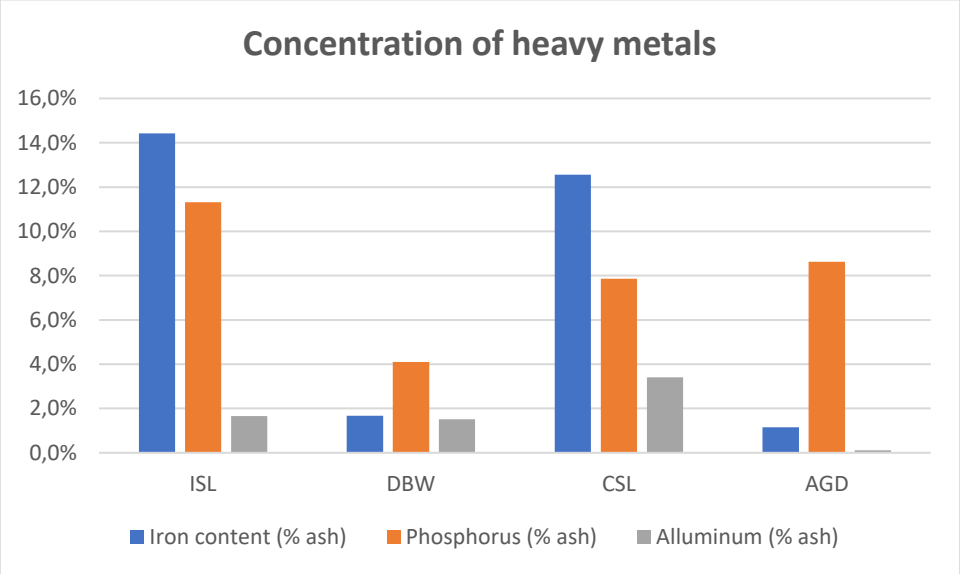

Figure 14. Concentration of iron, phosphorus and alluminum in biochar ash

In Figure 14, the concentration of P, Fe, Al, in the ash fraction of the produced biochar is reported. Given that ash is not influenced by the pyrolysis process conditions, concentration on ash, and not on each biochar sample is reported.

As shown, Industrial sludge contains the highest concentration of Iron, and Phosphorus. The high concentration of Iron is probably due to the use of Iron Chloride in the wastewater treatment process, as it is also high in civil sewage sludge. Both biochar obtained from sludge are of potential high quality given the Phosphorus and Iron content. Regarding the inorganic contained in AGD and DBW, phosphorus concentration in AGD dry ash is more than double than in urban biowaste. However, given the different ash content in biochar from BDW compared to AGD, the phosphorus concentration in BDW_600b (2.0% db) is similar to the concentration in AGS_600b (2.5% db).

6 CONCLUSION

The identification of most interesting and suitable biowaste streams to be used for biochar production in H2STEEL project has been performed by taking in account a set of economic, strategic and technical aspects. First, biowaste streams must be highly available, and preferably not used in other circular value chain. The “availability” is respected by all the 4 biowaste identified and characterized in this report. However, for both urban biowaste (BDW) and Agricultural

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Digestate (AGD), a circular valorisation solution as soil conditioner is already existing. On the contrary, civil (CSL) and industrial sludge (ISL) represent waste materials of difficult valorisation. About the chemical and physical composition of the char derived from the biowaste streams, it has been found that, despite the high ash content, the characterized industrial sludge presents interesting characteristic, with high value elements to be valorised in agriculture (P) and as catalyst in the methane pyrolysis process (Fe). Civil sludge presented a high volatility, and high concentration of ashes, estimated to contain high concentration of alumina (Al2O3) and silicates (SiO2), both useless for the process, and difficult to extract. As a summary, biochar from CSL could be of interest for phosphorus recovery and for the catalytic activity, but critical for the production of a “metallurgical grade” biocoal. Among the two other streams: BDW and AGD, the first demonstrated to be of not that high quality for the H2STEEL process, with limited P content (4% on dry ash), reduced iron content, reduced carbon and high concentration of ash. Similarly, AGD contains only reduced amount of phosphorus in the ashes, but it presents more interesting composition in terms of total carbon content, also thanks to the low ash concentration. As a summary, in the next activities the biowaste streams object of H2STEEL pyrolysis and upgrading process will be three: Industrial Sludge, Civil Sewage Sludge, Agricultural digestate.
A further selection to only two streams will be performed based on biochar upgrading trials, and on the catalyst produc

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