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Hub4Circularity

A First of a kind Hub for circularity demonstrator for Attica and peripheral regions

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Publishable summary

Sewage sludge is one of the main residual streams generated during wastewater treatment and represents both an environmental challenge and an opportunity for resource recovery. Traditionally, sludge has been managed through disposal-oriented or conventional treatment routes, such as landfilling, incineration, composting or land application. However, increasing environmental constraints, stricter regulatory requirements and the need to promote circular economy practices are driving the development of more sustainable and value-oriented management pathways.

This report is the first version of the deliverable for Task 7.5 of the THESEUS project. Task 7.5 refers to the investigation of valorisation routes for sewage sludge produced in the Attica region. The current study refers to the examination of innovative valorisation routes for sewage sludge within the scope of THESEUS, with particular focus on thermally based technologies, like pyrolysis, etc., with an objective to recover materials/energy from the sludge. This deliverable concerns the initial results of Task 7.5 performed at NTUA in cooperation with EYDAP.

To develop valorisation pathways for sewage sludge, a literature study on sewage sludge properties, management alternatives and potential valorisation routes was conducted. The sewage sludge possesses dual nature because on one hand it has valuable components, such as organic matter, nutrients, and inorganic material, while on the other hand, it may contain pollutants like pathogens and toxic organic materials. Therefore, advanced technologies must be developed in order to minimize the environmental risks while maximizing material recovery.

Different processes for sludge utilization have been considered, particularly those involving thermochemical processing. Incineration, gasification, hydrothermal processing, and pyrolysis are some of these methods. However, pyrolysis is highly attractive as it provides three distinct end products, namely biochar, bio-oil, and syngas. Depending on the characteristics of these products, several valorisation routes can be pursued (such as environmental applications, energy recovery and chemical intermediates).

In addition, the current deliverable presents the first experiments carried out in the lab of Sanitary Engineering of NTUA. The pyrogasification furnace was constructed, where dried municipal sewage sludge was treated using pyrolysis reactions. Specifically, the objective of this study was to carry out preliminary experiments to optimize the protocol, develop a method for the products' collection, as well as to make sure about the mass balances.

The parameters under which the experiments were carried out (temperature, heating rate, reaction time, condensation solvent, and chemicals treatment of the sludge) were studied to investigate their effects on the products composition. It should be mentioned that the preliminary results showed that municipal sewage sludge (dried) from Psyttalia WWTP can produce a considerable quantity of products, including biochar, liquid, and gaseous products via the process of pyrolysis. Biochar comprised the major fraction of the products. The effects of the temperature applied, and solvent used for the recovery of bio-oil were rather remarkable. In addition, ethyl lactate proved to be a very effective condensing agent for the recovery of bio-oil at intermediate temperatures.

Lastly, an initial characterization test on the biochar was carried out. The results revealed that the produced biochar was rich in mineral content as well as highly alkaline with significant ash content. With the increase

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of pyrolysis temperature, the content of volatile matters decreases, whereas the inorganic compounds' content increases. Further analysis concerning biochar's physicochemical properties revealed information about surface development. In this regard, parameters, such as pH, point of zero charge, Specific Surface Area and cation exchange capacity, were assessed in order to determine biochar's functionality. Finally, it should be noted that the content of heavy metals in the solid fraction was enriched. Thus, the environmental safety assessment will have to be addressed prior to any soil application.

In summary, the present deliverable contributes to the scientific basis for the accomplishment of Task 7.5. The preliminary experimental results of pyrolysis of dried municipal sewage sludge show its potential to be valorized to recoverable products. This represents a starting point that has to be followed up through subsequent experiments in order to confirm our initial observations and expand the characterization of the obtained products.

For the continuation of Task 7.5, optimization of the thermochemical process will be pursued in addition to the characterization of biochar, bio-oil and syngas. Product safety and potential applications should also be considered. Moreover, feedstock variations will be studied in order to identify a feasible sludge valorisation pathway.

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Abbreviations

Abbreviations	Full name
CEC	Cation Exchange Capacity
EC	Electrical Conductivity
FAAS	Flame Atomic Absorption Spectroscopy
FAMEs	Fatty Acid Methyl Esters
GC-BID	Gas chromatography-Barrier Ionization Discharge
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
HHV	Higher Heating Value
LHV	Lower Heating Value
SS	Sewage Sludge
SSA	Specific Surface Area
TA	Total alkalinity
VFAs	Volatile Fatty Acids
WWTP	Wastewater Treatment Plant

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1 Introduction

1.1 Setting the scene

The increased interest in sustainable, resource-efficient and resilient cities has driven the emphasis on materials recovery and valorisation. The role of wastewater treatment plants in the circular economy paradigm can therefore be re-evaluated from their traditional perception as pollution control units into centers of materials recovery. Particularly in highly urbanized regions like Attica, where the complex infrastructure and growing pressures on the natural environment require more advanced solutions to resource management, the need for sustainable and circular wastewater management becomes apparent.

Of all the effluents from WWTP, the sewage sludge (SS) appears to be the most difficult to manage properly. This is because of large quantities that are produced and contain organic matter, nutrients, inorganic compounds and lots of contaminants, which allow one to obtain valuable products by reusing sludge. The high variability of sludge appearance and characteristics complicates further treatment making its ecological use more challenging.

The most widespread approaches in the treatment of SS include either their dewatering or drying, followed by incineration or land spreading if the latter approach is not available. At some major WWTP like Psyttalia it is possible to treat SS thermally at industrial level; but this method could be quite expensive both in terms of investments and running due to intensive energy usage.

The agricultural reuse of SS is complicated by lack of lands to spread SS obtained from urban sludges like in Attica area. Still, the concepts of reclaimed water and decentralized WWTP imply that it is possible to handle non-standard sources of water in a closed cycle. Lots have to be done in technical, economic and logistic fields before these solutions can become operational. In comparison, the progress achieved in water reuse is significantly higher.

Thus, the application of thermochemical conversion approaches to sludge management provides an interesting option for further investigations in this sphere, which offers several advantages. First, it allows processing materials with highly heterogeneous structure and high moisture content into solid carbon-rich substances, liquids, and gases. Second, pyrolysis and other similar processes allow achieving the goal of energy recovery along with producing high-quality materials. Third, these techniques enable more precise control over contaminants and the quality of resulting materials.

Despite all these benefits, however, the application of thermochemical conversion approaches to SS streams has not been thoroughly studied. There remain questions concerning variability of sludge characteristics, requirements for process optimization, and analysis of the properties and use of materials produced during SS treatment by these techniques.

It is obvious that a detailed investigation of this topic is necessary for moving forward from the conventional approach towards a more holistic one based on circular economy principles. This deliverable is intended as a response to this problem.

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1.2 Purpose of the deliverable

This deliverable, developed under the Horizon Europe THESEUS project, presents the first version (v1) of the work carried out under Task 7.5, focusing on the exploration of novel valorisation pathways for SS generated in the Attica region. Positioned at Month 18 of the project, it reflects an intermediate stage of development, where emphasis is placed on establishing the scientific and technical foundation of the proposed approach, alongside the initial validation of the experimental system.

Building upon the current state of the art in sludge management and resource recovery, this deliverable aims to provide a structured overview of thermochemical conversion pathways, with particular focus on pyrolysis and related processes as promising alternatives for both material and energy recovery. To this end, a comprehensive literature review is presented, covering conventional sludge management practices, emerging thermochemical routes, key process parameters, and the properties and potential applications of the resulting products. Other than that, this deliverable talks about the experimental setup of the project, which includes information about the pyrolysis unit set up at the Sanitary Engineering Lab of NTUA, the type of feedstock to be used, and analysis method. The objective is to establish a clear and reproducible methodological basis for the systematic investigation of sludge valorisation under controlled conditions, bridging the gap between theoretical potential and practical implementation. This draft highlight preliminary results from the early experiments carried out using SS taken from the Attica region, focusing on the distribution of yields, basic characterisation of materials used and some observations from the experiment in general, and hence providing a first estimate of the functioning of the system.

Overall, the deliverable contributes to the progress of the alternative utilisation routes of sludge based on current scientific knowledge and practical application thereof. The deliverable paves the way for the next phases of the project where process optimisation and more extensive characterisation will take place.

1.3 Relation with other tasks/deliverables

This deliverable is developed within Task 7.5 of Work Package 7 and contributes to the broader THESEUS objective of advancing Industrial–Urban Symbiosis (I-US) through the integrated management and valorisation of water, energy, and material flows in the Attica region. While several project components focus on the optimisation of water use, reuse strategies, and demand-side management, this deliverable addresses a critical complementary aspect of the system, namely the management and valorisation of SS as a residual stream of wastewater treatment processes.

This deliverable provides technical and methodological insight into the transformation of sewage sludge to valuable materials through thermochemical processes. It addresses the challenges associated with the conversion of an intricate waste stream into resource streams and promotes the shift towards a more circular model of wastewater processing. Thus, it provides an essential link between upstream wastewater reuse and treatment operations, and the downstream valorization pathways of material and energy resources.

- **Work Package 7 (Water Symbiotic Flows)**: There is a direct relation to other activities under WP7 which involve the development of a circular approach for water management in the Attica Region. Indeed, the insights obtained in this deliverable serve as a base for the system-level considerations needed to develop integrated strategies where water and wastewater reuse, recovery, and minimization are

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considered. Through experimentation, this deliverable can offer feasible options for such systems where sludge valorization forms part of the system.

- **Work Package 2 (Development of the Theseus framework):** Furthermore, this deliverable is also associated with activities carried out under WP2 involving the definition of a multistakeholder ecosystem for industrial-urban symbiosis. This deliverable demonstrates the fundamental concept proof for valorizing sludge at laboratory scale. This contributes to the realization of the concept of Industrial-Urban Symbiosis, which is described in detail below.
- **Data and Decision Support Tools (WP3/WP5/WP6/WP7):** Finally, the information provided in this deliverable may provide inputs for decision support tools under the project, i.e., modelling activities in the context of different scenarios. Indeed, the information obtained can provide essential inputs for the analysis of resource flows within a circular system where sludge valorization is possible.

In summary, this deliverable plays a complementing role within the THESEUS project, as it provides technical information on sludge valorization. It is expected that this will enable the development of integrated and circular water, material, and energy flows within the framework of an industrial-urban symbiosis approach to the problem.

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2 Literature review on Sewage Sludge valorization

2.1 Sewage Sludge as a resource

Rapid growth in population and urbanization has resulted in a higher demand for resources such as land, water, food, and energy, alongside aggravating pollution problems linked to resource management [1]. All the above-mentioned factors put sustainable development under threat and trigger global concerns in finding more effective and environmentally friendly ways for resource utilization and management of wastes. A consequence of this condition will be a consistent increase in the quantity of municipal sewage generated, leading to the production of sewage sludge. Various authors state that Europe produces an annual amount of 10 million tons of sewage sludge. The largest producers are Germany, UK, and Spain. On the other hand, Greece produces 0.1 million tons per year [2]. This leads to the problem of SS management being crucial for today's environmental and technical situation and, thus, necessitates more sustainable and efficient approaches to sludge processing and utilization.

SS is a composite material derived from sewage water treatment systems (Figure 1). This sewage sludge consists of primary sludge, secondary or waste activated sludge, chemical sludge, and anaerobic digestion sludge. Since there is a difference in sewage and sewage water treatment processes in different treatment facilities, the characteristics of SS may vary significantly in terms of moisture content, organic material, contamination, and nutrients [3].

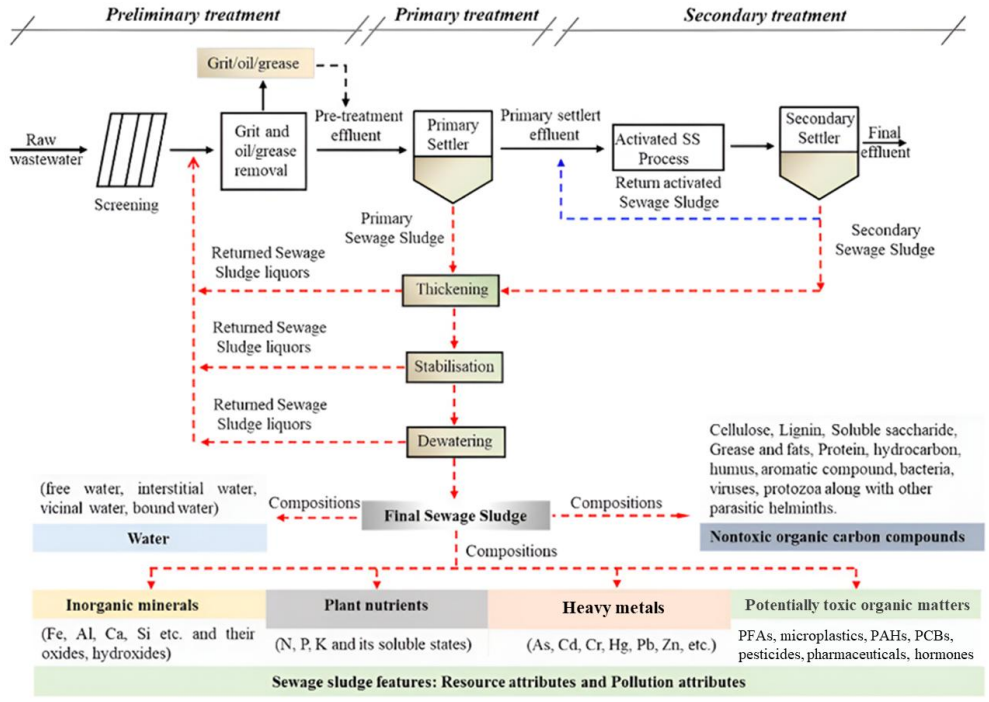


Figure 1 Typical sewage sludge production from wastewater treatment plant and its basic compositions. Adopted from M. Hu et al., (2022)

As for the typical composition, SS consists of (i) organic carbon compounds, (ii) nitrogen- and phosphorus-containing substances, (iii) organic and inorganic pollutants (the latter are potentially toxic), (iv) pathogens

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and microbiological contaminants, (v) inorganic materials, and (vi) water [4]. In terms of concentrations, these substances make up no more than 1% (potassium), 1.2-3% (phosphorus), 2.8-4.9% (nitrogen), and 20.5-40.3% (organic carbon) [5] of the sludge mass.

In terms of SS management, traditional approaches have viewed this material as a hazardous waste due to its high water content, pathogen presence, possible toxicity, and odors of organic substances. In particular, urban sludge may contain various heavy metals such as nickel, copper, zinc, cadmium, chromium, mercury, and arsenic as well as various micropollutants like polycyclic aromatic hydrocarbons and others [6]. The mentioned above factors give rise to serious environmental problems, especially those associated with pollution, greenhouse gas emissions, and soil contamination when conventional management practices such as landfilling, incineration, and land spreading are applied to manage SS [7].

It should be recognized that the significance of sewage sludge as a source has been continuously rising recently. The reason behind this is the possibility of utilizing sewage sludge as an energy source due to high organic matter content in sewage sludge [8], as well as high nitrogen and phosphorus content. A considerable part of organic matter contained in wastewater, which exceeds 60%, remains in sludge and results in its great energy recovery potential and extraction capability [4]. Moreover, inorganic compounds contained in sewage sludge (calcium, iron) have material application possibilities. Thus, sewage sludge shows the dual nature, representing both a source of pollution and a valuable resource. Therefore, nowadays, one of the main priorities associated with sludge is the transition from traditional methods of management and utilization to advanced technologies aimed to extract the maximum value from this resource.

2.2 Sewage Sludge management pathways

Management of sewage sludge (SS) represents an essential part of wastewater treatment systems, as it deals with managing the sludge containing a great number of pollutants extracted during the process of wastewater treatment. Furthermore, sludge can have valuable components that must be recycled in order to avoid contamination. This means that proper SS management requires balancing contamination avoidance and resource recycling.

The range of SS management techniques adopted in various European states proves their different choices concerning the use of possible approaches to sludge management. Figure 2 shows that there are distinctions in choosing particular SS management techniques in European countries [9]. The agricultural application of SS is one of the most popular techniques used in Western and Northern European countries because of its capacity to recycle nutrients [3]. The growing problem of contaminants has limited the use of this method significantly. In contrast, thermal SS management is practiced more widely in those countries which have advanced waste management systems. Landfilling is not practiced broadly, while composting has limited applications as well. This means that particular European countries employ a variety of SS management techniques [9].

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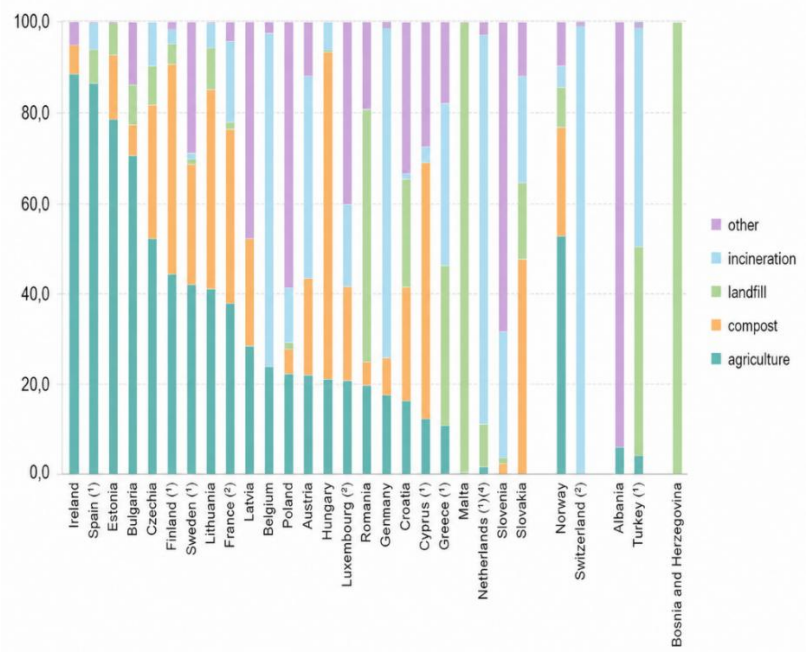


Figure 2 Disposal of sewage sludge from municipal wastewater treatment by disposal method, 2020 (% of total). Adopted from A. Eleftheriadou et al., (2023)

To systematically evaluate these management pathways, the methods identified in the literature [3] can be categorized into conventional, alternative, and innovative approaches, as presented in Table 1. This classification reflects both the technological maturity of each method and its alignment with sustainable resource recovery principles.

Table 1 Conventional, alternative, and innovative methods of sewage sludge treatment

Conventional/High TRL 8-9 methods	Alternative methods (TRL 5-8)	Innovative methods (TRL 3-6)
Direct application to soil	Pyrolysis	Bio-electrochemical system
Mono-incineration/co-incineration	Gasification	Supercritical water oxidation
Anaerobic digestion	Hydrothermal liquefaction	Biodiesel production
Landfilling		Thermophilic aerobic membrane treatments
Composting	Reclamation purposes	Upflow anaerobic sludge osmotic membrane bioreactor
Drying		

Traditional approaches in treating sludge include direct land application [11], incineration (mono-or co-) [12], anaerobic digestion [13], landfilling, composting, and drying [14]. The described approaches are broadly applied and form a basis for modern practices of sludge treatment. Of all listed alternatives, anaerobic digestion and composting are often considered superior because of the possibility to recover energy and

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nutrients. Direct land application and landfilling techniques are often criticized nowadays and recognized as less preferable approaches due to contamination issues, emission generation, and soil-groundwater pollution.

Alternative technologies comprise such methods as pyrolysis, gasification, hydrothermal liquefaction, and reclamation activities and can be viewed as transitional stage to innovative approaches [4]. The listed methods allow improving resource recovery and process control by converting waste into energy and materials that can be used as valuable products in different sectors of economy. Thermal conversion techniques such as pyrolysis and gasification are usually considered promising because of their ability to produce such products as biochar, bio-oil, and syngas [15].

Bio-electrochemical technology [16], supercritical water oxidation process [17], production of biodiesel [18], thermophilic aerobic membrane process [19], and up-flow anaerobic sludge osmotic membrane bioreactor [20] represent examples of innovative techniques for the treatment of sludge. Nevertheless, these techniques lack technical development, hindering their wide application despite their enormous potential.

Present trends in sludge treatment include a slow transition from waste elimination practices to those focused on sustainable resource and energy use. Conventional sludge treatment and management techniques work effectively; however, they pose significant dangers due to contamination and other environmental issues. At the same time, innovative techniques become popular because of their enormous potential for overcoming current problems.

2.3 Thermochemical conversion of Sewage Sludge

Of all the high-technology techniques referred to above, thermochemical conversion methods appear to be among the highly efficient approaches to the management and processing of sewage sludge [15]. Thermochemical conversion methods, as a general category of high-technology techniques, imply the application of heat to process organic substances into different products according to the presence or lack thereof of oxygen in the process. More specifically, thermochemical conversion refers to an approach to sewage sludge treatment through certain methods, such as incineration, gasification, and pyrolysis, distinguished by their own sets of parameters, including temperature and amounts of oxygen used. In addition to this variety of techniques, another reason for choosing thermodynamic methods is the fact that this approach enables one to solve most of the problems associated with sewage sludge treatment, namely the reduction of sludge volume and removal of toxic substances. Thermochemical conversions are also considered an efficient technique for overcoming environmental problems of sludge management, including pathogens and micro-pollution [22].

Based on the above, thermochemical conversion processes become relevant for the THESEUS project since their implementation can make it possible to develop innovative ways of managing sewage sludge. In this regard, the below paragraphs will review the most notable thermochemical conversion processes used to process sewage sludge.

2.3.1 Overview of thermochemical processes

Thermochemical conversion technologies represent several methods, using heat for transformation of biomass and waste products into other types of energy sources and additional products. Thermochemical

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processes of sewage sludge utilization are of special importance, as they help decrease volume, stabilize hazardous components and generate additional energy sources and valuable substances. Incineration, pyrolysis, gasification and hydrothermal processes represent thermochemical treatment of sewage sludge, all of which have their own conditions and transformation features [15].

One of the simplest methods of distinguishing between the processes under consideration is to differentiate them according to two key parameters – the level of oxygen and temperature (Figure 3) at which transformation takes place. In fact, such parameters determine the basic reactions and, consequently, the composition and quantity of products. According to these parameters, thermochemical conversion represents an endless line from oxygen-deficient to oxygen-abundant processes and low-temperature to high-temperature conditions [23].

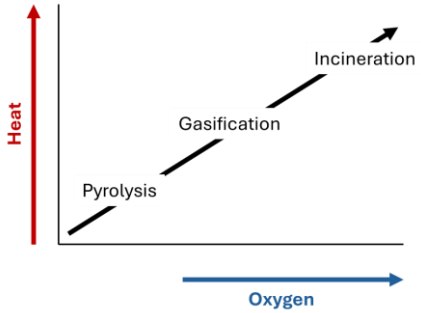


Figure 3 Thermochemical Processes as a Function of Oxygen and Temperature

Firstly, incineration involves burning the solid waste using a large quantity of oxygen at temperatures above 850 °C. As a result, heat, flue gases, and ash will be produced during the process. Incineration serves to reduce the bulk of solid waste, pathogen elimination, and destruction of pollutants. Nevertheless, the primary goal of incineration is energy recovery, meaning that solid waste cannot be further used as a resource. Incineration often requires additional steps related to emissions management and waste treatment [15].

As the oxygen level reduces, a process known as pyrolysis occurs. Here, solid waste decomposes under the absence of oxygen at around 400–700 °C. Without oxygen, organic matter decomposes producing solid, liquid, and gaseous products in a combination which changes with temperature, rate of heating, and retention time. This technology benefits from producing various fractions simultaneously; however, the quality of produced fractions depends on the quality of solid waste, especially when high levels of moisture or ash are involved [15].

Gasification falls in between pyrolysis and incineration. It involves relatively higher temperatures of around 700–1000 °C as well as oxidants such as air, oxygen, or steam. Partial oxidation is used primarily to generate combustible gas as a product. The process of gasification consists of several stages, namely drying, devolatilization, oxidation, and reduction. In essence, gasification can be regarded as pyrolysis followed by further transformation of secondary pyrolysis products into gas. Although this process has great potential in terms of energy recovery, problems associated with tar production, catalyst fouling, and input feedstock variability remain critical challenges [15].

Hydrothermal processing distinguishes itself by operation in aqueous environment and elevated pressure besides other conditions. Hydrothermal carbonization, hydrothermal liquefaction, and hydrothermal gasification can be distinguished according to process conditions. One of the advantages of hydrothermal

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treatment consists in a direct conversion of wet SS, whereas disadvantages include high pressure requirements, the need to separate phases, and corrosion resistance demands [15].

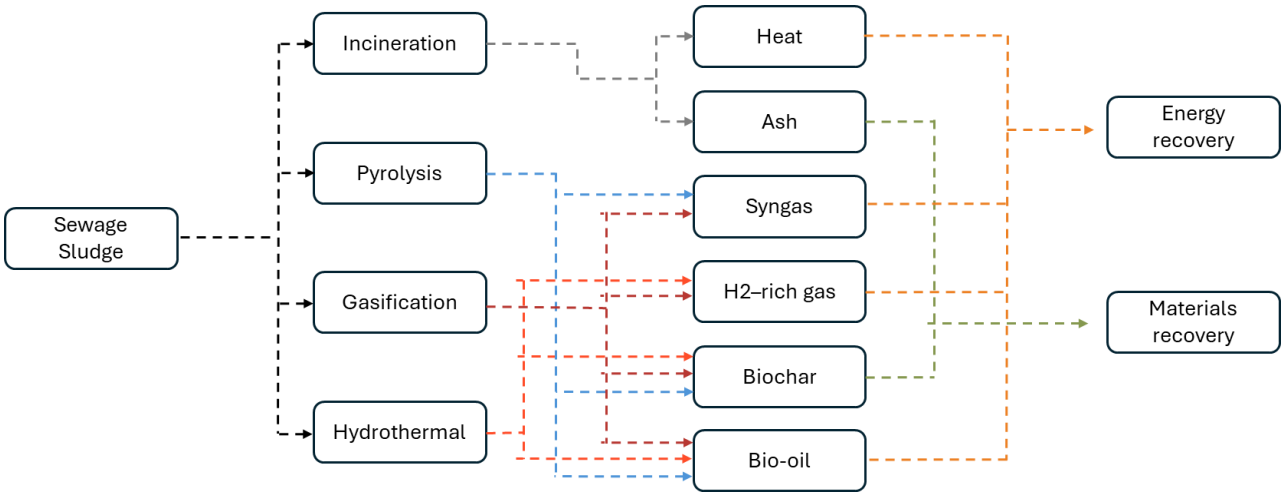


Figure 4 Thermochemical Conversion Routes of Sewage Sludge and Product Utilization

Thus, it should be pointed out that in practice no thermochemical processes produce a sole product. Instead, every process produces a combination of solid, liquid, and gaseous products, with one of them dominating under corresponding conditions. The selection of a certain technique should be made with regard to desired product mix and applications (Figure 4).

Taking into account various operating conditions and conversion mechanisms associated with thermochemical conversion of SS, as well as different distributions of products, a comparative analysis of these techniques will be provided below.

2.3.2 Comparison of pathways

To better understand thermochemical conversion of biomass, it is necessary to examine its main types considering specific thermodynamic aspects including reactions occurring and heat exchange. A schematic representation of the key features of thermochemical conversion methods could be created based on biomass combustion under various conditions of the presence of oxygen.

Incineration is complete oxidation. Complete oxidation results in biomass being completely turned into CO_2 and H_2O when oxygen is sufficiently available, and a large amount of heat is released due to the chemical process. The reason why additional energy is released during incineration consists in the stability of the CO_2 and H_2O molecules, which results in lower energy of the system. Incineration is the most common exothermal process, and thus it is also regarded as the upper limit concerning heat release within thermochemical reactions. In addition, biomass is totally degraded without any energy carrier in such reactions, and all its chemical energy is converted into heat. Pyrolysis is a reaction that contrasts complete oxidation as it takes place in the absence of oxygen and is characterized by bond breakage rather than formation. During thermal decomposition, bonds between atoms of carbon are broken, and it requires heat input. At the same time, no stable compounds, such as CO_2 and H_2O, are formed in a reaction; hence, a low amount of heat is released. As a rule, pyrolysis is endothermic, and despite the need for heat input, it provides solid and liquid high-energy products in a reaction. In addition, products do not contain oxygen and moisture, so they contain

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more energy than initial biomass. Thus, it is possible to define pyrolysis as a method of fuel conversion. [27]. Finally, gasification combines incineration and pyrolysis since it is performed with limited oxygen or in presence of steam and allows partial oxidation of biomass. Such a condition makes it possible to release some heat due to partial oxidation to support the process; moreover, gases containing most of the energy of biomass are produced in such processes. Therefore, gasification could be called an autothermal process where heat is mostly used as an energy carrier [25].

To Firstly, thermodynamics views the three paths as three stages in a continuous process during which the amount of available oxygen alters. Furthermore, the particularities of biomass (in our case, the biomass we are going to consider is our sewage sludge) are of significance for the process as well. This concerns especially humidity, ash content, and pretreatment (for example, through stabilization and/or drying).

There are advantages and drawbacks in the three paths in terms of technological readiness, ecological impact, and product usability. As for the most developed of the three processes, namely, incineration, it provides a guaranteed energy conversion of waste with a relatively good energy efficiency, is consistent with infrastructure and has no problem with scale-up; however, it produces harmful emissions (CO2, NOx, SOx, and particles); thus, additional gas treatment technologies should be applied, and waste ash disposal issues appear. High humidity of sludge also requires additional pretreatment (e.g., drying). The next path, gasification, is more universal. It allows producing the rich in energy gas, which can be burned to generate electricity or serve as raw material for chemical synthesis. This technology requires large investments, a complicated technical structure that may cause troubles like tar accumulation or even poisoning of the catalysts. Pyrolysis has its advantage because the output products here may include not only gas but also liquids and solids. Its other pros include lesser emissions, ability to retain inorganic contamination (such as heavy metal contamination) in solid residue, although it has some difficulties with controlling the parameters of the process, and pretreatment requirements for the feedstock. Pyrolysis results in numerous usable products. In general, thermochemical conversion aims at optimizing several parameters depending on each path; these are energy yield (incineration), gas production (gasification), and versatility of the resulting products (pyrolysis) [15].

Nevertheless, for sewage sludge, applicability and operational performance of thermochemical conversion pathways are considerably dependent on the feedstock properties. Sludges' characteristics lead to varying characteristics of the processes, such as the type of products obtained, operational requirements, and process efficiency. The following table illustrates the dependency of thermochemical conversion pathway suitability on the sewage sludge characteristics.

Table 2 Indicative suitability and operational constraints of thermochemical conversion pathways for different sewage sludge types

Sludge Type	Pyrolysis	Gasification	Incineration	Hydrothermal Liquefaction
High-moisture raw sludge (≈ 95–99% water)	Requires energy-intensive drying; moisture reduces bio-oil and char yields; poor mobility and low calorific value hinder stable operation	High moisture: low calorific value and high energy demand for drying; poor gasification efficiency	Incineration possible but requires large energy input for drying; high flue-gas emissions (NOx, SOx, particulates)	Best suited for wet sludge; water acts as medium/reactant; avoids drying; but needs high-pressure reactors, expensive and complex

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Dewatered sludge (20–30% solids)	Still moisture-sensitive; drying needed for optimal product distribution	Drying still required; moisture limits syngas quality; tar formation problematic	Can be fed after drying; ash and emissions issues persist	Works without more dewatering; product distribution affected by feed properties
Dried sludge (>85–90% solids)	Most suitable feed; but high ash and low energy density can limit product quality	Suitable feed; but high ash increases slagging, catalyst deactivation, tar handling	Operationally easy; but pollutant emissions (NOx, SOx, dioxins) remain major drawbacks	Moisture too low; HTL not advantageous; water must be added
Anaerobically digested (AD) sludge	Lower volatile solids: lower energy yields; AD digestate still wet: requires drying	Lower organic content reduces syngas quality; still high moisture	Reduced calorific value increases auxiliary fuel use	AD + HTL synergistic; but HTL product water may require AD polishing
Chemically conditioned sludges	Conditioning agents alter pyrolysis behaviour; can increase tar, change kinetics	High metals (Fe, Mn) can be catalytic but also cause ash issues	Toxic compounds increase air-pollution control needs	HTL may accumulate PFAS and metals in solids

2.4 Pyrolysis of Sewage Sludge

Pyrolysis appears to be a highly attractive option in converting sewage sludge among all previously discussed thermochemical methods [28]. In view of the above considerations, the present section concentrates on pyrolysis due to its increasing scientific significance and environmental superiority over other thermochemical options as well as its ability to yield energy and product outputs simultaneously. As opposed to combustion, which results in the formation of CO2 out of almost all carbon contained in the sludge [24], pyrolysis preserves much carbon in solid and liquid phases that can serve as an energy, material or chemical source. The target should be not the production of energy alone, but the utilization of all inputs collectively for the purpose of energy, material, and chemical production.

2.4.1 Fundamentals and process configuration of pyrolysis

Pyrolysis represents a thermochemical conversion process involving the thermal degradation of organic matter at relatively high temperatures typically ranging between 400-900 °C in an oxygen-deficient environment [29]. In this way, the complex organic matrix of sewage sludge experiences the thermal degradation process resulting in the formation of various chemical species distributed in different phases including gaseous, liquid, and solid forms. Among these, hydrocarbons, phenols, aldehydes, ketones, and other oxygenates can be mentioned as some possible end-products that could serve as alternative sources of fuel compared to traditional fossil fuels [30]. The unique characteristic of this process is the lack of a definite product distribution that depends on several factors. The characteristics of the input material and the process parameters play an important role in this context as, for example, higher moisture content in the input material increases energy demand and adversely affects energy consumption and distribution during thermal processing. In addition, it should be noted that the yield ratio of the major product types – solid biochar, liquid bio-oil, and gaseous products (syngas) – is dependent on such parameters as temperature, heating rate, and residence time [31].

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In terms of its design, the pyrolysis facility includes a set of sequentially connected units that enable control over the feeding, conversion, and product separation steps. As can be seen from the schematic diagram of a conventional pyrolysis plant presented in Figure 5 below, this process follows a certain pattern starting from feeding biomass through product extraction and collection [32].

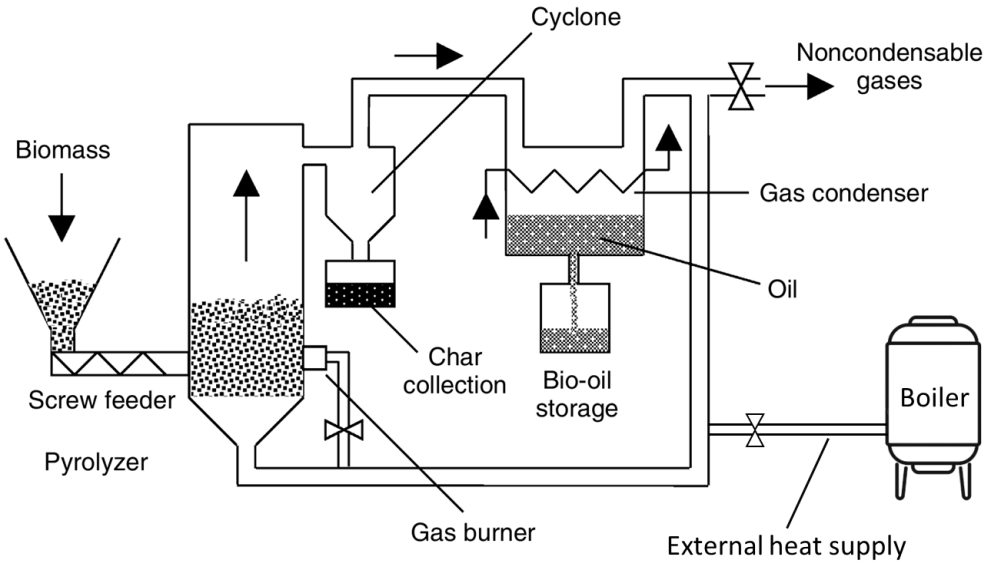


Figure 5 Simplified layout of a pyrolysis plant. Adopted from P. Basu et al., (2024)

1. Initially, the feedstock is introduced into the system through a controlled feeding mechanism, often a screw feeder, which ensures a stable supply of material while simultaneously preventing the ingress of air into the reactor. This aspect is critical, as the presence of oxygen would shift the process toward combustion rather than pyrolysis.
2. The core of the system is the pyrolysis reactor, where the thermal decomposition of SS takes place. In many configurations, particularly in fast pyrolysis systems, heat transfer is facilitated using inert bed materials, such as sand, often operating under fluidized conditions. This enables rapid and uniform heating of the feedstock, which is essential for controlling reaction pathways and product distribution. The process is inherently endothermic, requiring a continuous supply of heat. As illustrated in Figure 5, the required thermal energy is supplied externally to maintain the operating temperature of the reactor, commonly through burners, boilers, electrical heating systems, or by combustion of a fraction of the produced gases or char within the system.
3. Following thermal conversion, the resulting mixture of vapours and solid particles is directed to a separation unit, typically a cyclone, where the solid biochar is removed from the gas stream through centrifugal forces. This step is necessary both for product recovery and for protecting downstream equipment.
4. The remaining vapours are then cooled in a condenser, where condensable compounds are collected as bio-oil, while the non-condensable fraction exits as syngas. Rapid cooling at this stage is essential to prevent secondary reactions that could degrade the quality of the liquid products and to stabilize the composition of the vapour phase.

As it becomes evident, pyrolysis is not a monolithic technology but rather a set of techniques conducted under specific conditions to produce a particular product composition. In this regard, the main factor

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governing the process comes down to temperature and residence time, thereby allowing for multiple ways to conduct pyrolysis. According to Table 3, which provides an overview of the most commonly used types of pyrolysis techniques and their conditions, the identical basic technology can be made versatile by means of adjusting some parameters [33].

Table 3 Pyrolysis methods and indicative operating conditions and product distribution. Adopted from S. O. Masebinu et al., (2019)

Process	Temperature (°C)	Residence time	Bio-oil (liquid)	Biochar (solid)	Syngas (gas)
Fast pyrolysis	300–1000	< 2 s	75% (≈25% water)	12%	13%
Intermediate pyrolysis	≈500	10–20 s	50% (≈50% water)	25%	25%
Slow pyrolysis	100–1000	5–30 min	30% (≈70% water)	35%	35%
Gasification	>800	10–20 s	~5% tar (≈55% water)	10%	85%
Hydrothermal carbonization	180–300	1–16 h	5–20%	50–80%	2–5%
Torrefaction	≈290	10–60 min	0%	80%	20%

Fast pyrolysis implies high heating rates and short residence times within the range of a few seconds. The goal is to enhance the formation of liquids as much as possible. Intermediate pyrolysis involves relatively equal conditions resulting in the more homogeneous product composition including solid, liquid, and gaseous products [35]. Finally, slow pyrolysis refers to long residence times during which biochars are predominantly produced due to secondary reactions [28].

The further increasing of temperature coupled with reduced oxidation leads to the transition to gasification technology where the main task is to obtain combustible gas. Hydrothermal carbonization, in turn, requires lower temperature in combination with water and produces a carbonized solid especially convenient for wet feedstock like SS. Finally, torrefaction may be regarded as a thermal pre-processing technique whose primary purpose lies in improving biomass fuel qualities [36].

These differences highlight the high flexibility of pyrolysis technology, in which modification of the parameters makes the conversion go in the required direction. Therefore, pyrolysis is characterized by high versatility as compared to other thermochemical techniques. Process optimization is the key to achieving the highest efficiency, which is covered in the next chapter.

2.4.2 Thermochemical mechanisms of pyrolysis

Having presented an introduction into pyrolysis as well as a description of its products and the types of biomass which are suitable for use in the pyrolysis, we should consider further details regarding the processes in terms of chemical conversions occurring in the process. It should be noted that while pyrolysis is normally

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viewed as producing three types of material – solid, liquid and gas – the exact share of these depends on several competing chemical reactions taking place under specific conditions. The knowledge about such processes is vital both from a theoretical and engineering standpoint.

The Figure below presents three processes which occur during pyrolysis: formation of char, depolymerization and fragmentation [38]. All of them take place simultaneously and affect each other depending on the conditions of the process.

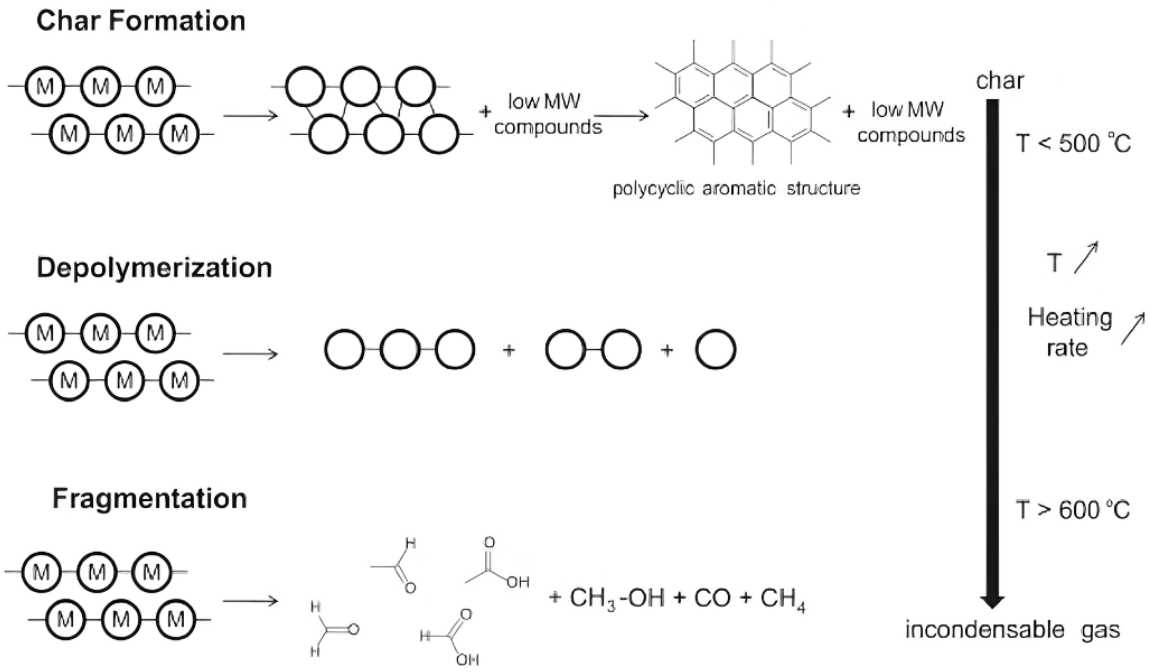


Figure 6 Schematic representation of pyrolysis mechanisms. Adopted from A. K. Vuppaladadiyam et al. (2023)

Firstly, char formation involves the process that will result in a solid fuel formation. At a molecular level, it refers to a reorganization of molecules within itself and one another forming a stable carbon-based solid. First, large macromolecules in biomass disintegrate into smaller pieces due to thermal effect. Instead of completely evaporating, they will begin to undergo reorganization. Some molecules will lose their particular groups, such as H_2O, thus creating aromatic rings. Afterward, the molecules will start to react by linking themselves and will create large polycyclic structures. Due to this, carbon structures will take place, creating a dense matrix resembling graphite. Meanwhile, hydrogen and oxygen are emitted, taking such forms as H_2O, CO, CO_2, and CH_4 and vaporizing. With time, the solid fuel will gain more carbon and become highly thermally stable [38].

Depolymerization involves the breaking of monomers' bonds to release bio-oil. At the depolymerization stage, the links between monomers in polymer chains are broken down. Cellulose and hemi-cellulose have long chains consisting of repetitive structures. Depolymerization leads to the destruction of bonds between monomers, reducing the polymerization degree resulting in oligomers and individual monomers. They will reach a state in which the molecules can become gaseous and evaporate. However, most of those will be heavy hydrocarbons. Cooling of those will lead to condensation, and, as a result, bio-oil will emerge. Thus, depolymerization transforms polymer chains into light and condensable vapors, thus turning it into bio-oil at low temperatures [38].

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Fragmentation is another chemical reaction that is responsible for biomass conversion. In contrast to depolymerization, fragmentation leads to more widespread destruction of bonds, both intramolecular and intermolecular. Thus, the products are very small; they are represented by non-condensable gases (CO, CO_2, CH_4, H_2) and oxygenated products (aldehydes, ketones, and carboxylic acids). Therefore, the reactions will lead to the formation of non-condensable gas and volatile light substances contributing to bio-oil and char formation [41].

The resulting substances may not necessarily be final ones at that point, as the volatile compounds formed by depolymerization and fragmentation tend to undergo secondary reactions within the reactor vessel itself [42]. There are mainly two routes: cracking reactions, through which heavy molecules get cracked down to give off gases; and recondensation reactions, wherein volatile molecules get combined to yield larger ones [43,44].

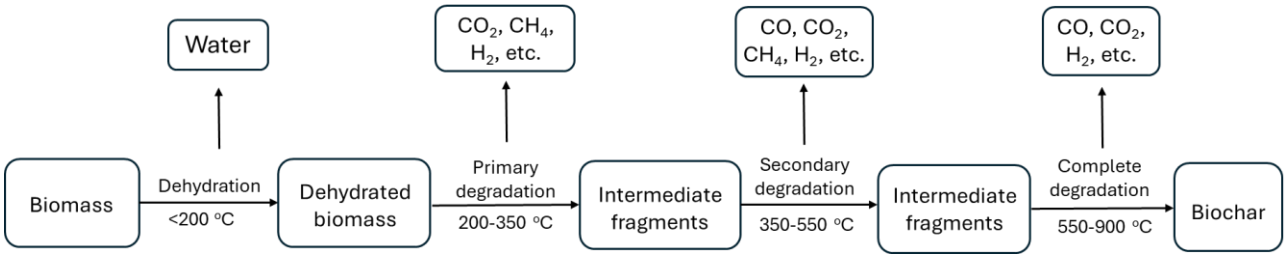


Figure 7 Process flow of thermochemical conversion during pyrolysi. Adopted from J. Shao et al., (2008)

In conclusion, it can be noted that pyrolysis refers to a chemical reaction which has several simultaneous reactions going on within the reactor. These reactions include char production, depolymerization, and cleavage. It is the condition of the process that determines which of these reactions is dominant, and in turn, influences the yield of solid, liquid, or gaseous products.

2.4.3 Process parameters affecting pyrolysis

Having analysed the fundamentals of the pyrolysis mechanism, one should note that apart from the technology of pyrolysis and products obtained from this technological process, the results are greatly dependent on the mode of its operation. As was noted above, pyrolysis is highly sensitive to operating modes, and thus, any slight alteration in it may lead to changes in yield, output amount, and products properties. To operate the reactor efficiently, optimize the process and increase productivity, it is important to find out which factors affect pyrolysis.

As seen from Figure 8, there are mainly three groups of factors influencing pyrolysis: the properties of the feedstock, the operating conditions, and the reaction environment and parameters of the process itself. Interplay of all the listed factors defines both the yield of biochar, bio-oil, and syngas and the characteristics of the obtained products.

First, the properties of feedstock play an important role in the process of pyrolysis. Such factors as particle size, moisture content, and biochemical composition (cellulose, hemicellulose, lignin, and sewage sludge) influence heat and mass transfers in the feedstock, as well as volatilization rate. Fine particles ensure better heat transfer, while increased moisture content reduces the efficiency due to the need for additional energy required to evaporate water. At the same time, biochemical properties of biomass are essential in terms of thermal decomposition.

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Operating conditions can be regarded as control factors of the process. Temperature, heating rate, and residence time are the most important of them, where temperature plays the central role [34]. Indeed, increasing the temperature reduces the yield of biochar because of devolatilization but increases the output of bio-oil and gases [48]. However, properties of biochar become better with temperature because the produced material contains more carbon and becomes more alkaline [49]. Concerning bio-oil, yield grows till certain level and then drops because of the cracking of condensable vapors into non-condensable gases [15]. At the same time, the content of gases also increases with temperature due to enhanced concentration of CO and H_2 accompanied by decreased CO_2 content in gas phase [49], meaning higher calorific value of the latter.

In addition to temperature, heating rate and residence time of biomass and vapors determine the outcome of pyrolysis. High heating rate results in quick devolatilization and less secondary reactions, promoting formation of liquids, typical of fast pyrolysis [34]. Slow heating with long residence time favors secondary reactions (cracking, recondensation) thus causing decrease in the yield of liquid products and increase in the yield of biochar and gases [50]. Residence time of vapors plays an especially crucial role because extended time of their stay under elevated temperature promotes their further decomposition with the result being shift to gas products [48]. These factors also affect the environmental impact of the process in terms of emission of NH_3, HCN, and SO_x depending on their combinations [51].

Finally, reaction environment and process-related factors (gas flow rate, pressure, and catalysts) matter significantly [34]. Increased flow rate of gases removes volatile products from reaction zone thus inhibiting secondary reactions. Catalysts provide another opportunity to control the process of pyrolysis through affecting the yield and composition of products. They can be introduced either prior to the process (pre-catalysis), during the process (catalyst addition), or post-process (vapor upgrading). Catalytic substances include metal oxides (CaO, MgO), metal salts ($ZnCl_2$, KCl), zeolites (HZSM-5), which facilitate cracking, deoxygenation, and aromatization reactions, lowering the need in activation energy and improving selectivity [52].

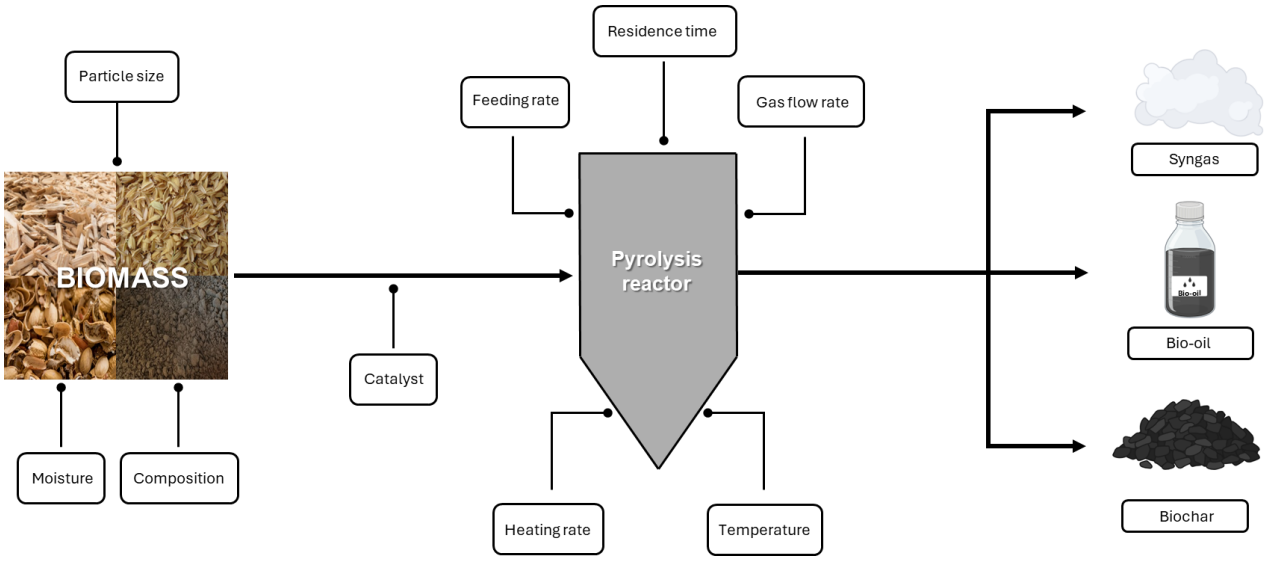


Figure 8 Key factors influencing the pyrolysis process and product distribution

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2.5 Properties and applications of pyrolysis products

Considering the discussion about the mechanism of pyrolysis, as well as related thermochemical processes, one could draw a conclusion that the conversion of biomass produces not one, but three products, namely biochar, bio-oil, and syngas. Though they have the same origin in terms of the thermochemical process, yet they differ radically in physicochemical characteristics, which, in turn, determines the possible ways to utilize them.

These products' physicochemical characteristics are not defined unilaterally by the nature of the biomass used, but highly depend on other factors – mainly on the parameters of the process itself – as has been mentioned above. As a result, we can state that the pyrolysis can be viewed as a highly malleable technology, wherein the product properties will change depending on process parameters. This means that by manipulating these parameters, it is possible to adjust the properties of products according to certain criteria.

In general, the applications of all the three products can include various activities: the energy generation, treatment of wastes, environmental protection, as well as the production of various compounds for multiple uses. Specifically, Figure 9 illustrates the distribution of these applications for the three product streams considered. Nevertheless, these applications are not coincidental and they are directly related to the intrinsic characteristics of each product: carbon content and porosity for biochar, oxygen content and chemical composition of bio-oil, and composition and caloric content of syngas.

Therefore, one should consider all these aspects when designing a proper system for converting biomass through pyrolysis. The next sections are dedicated to the consideration of each particular stream in more detail: the emphasis will be made first on product properties and the formation process, and only then – on possible applications and their limitations.

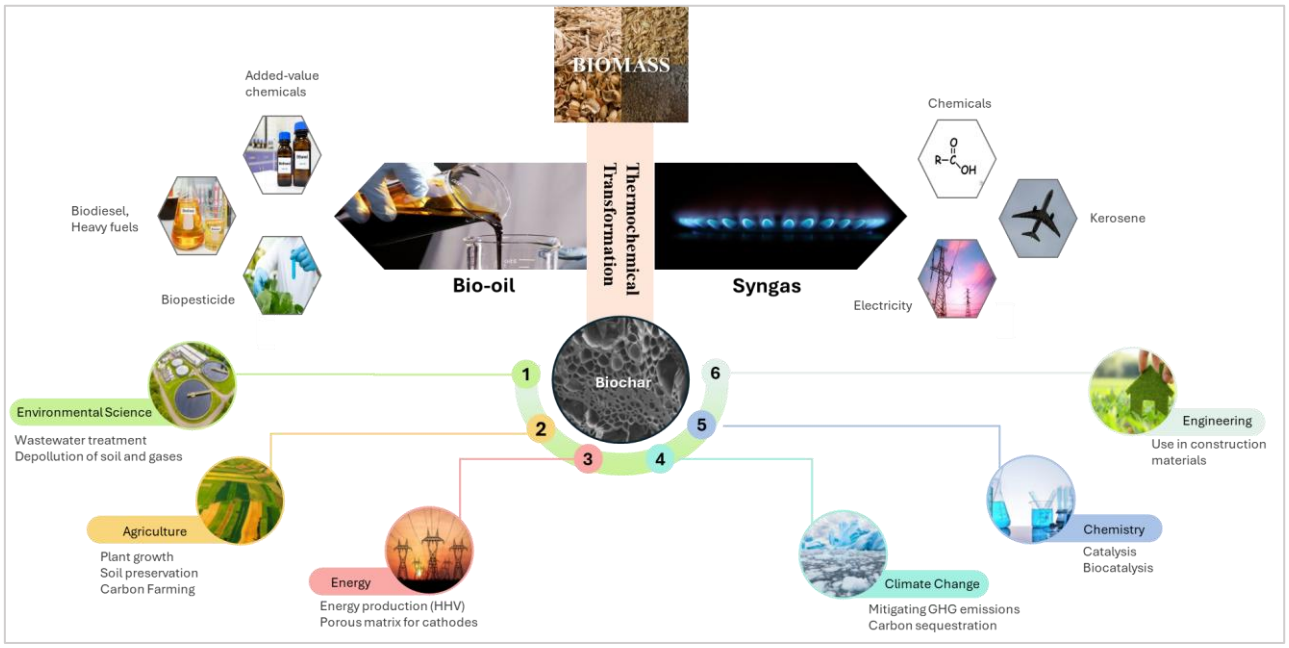


Figure 9 Main Pyrolysis Products and Their Valorization Pathways

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2.5.1 Biochar from Sewage Sludge

One of the products obtained during pyrolysis is biochar, i.e., the solid residue of pyrolysis that contains a large amount of carbon and mineral substances contained in the original raw material. In the case of sewage sludge, the product will be characterized by high heterogeneity and will have properties both of organic and inorganic materials [24].

As was mentioned earlier, possible applications of the material depend entirely on its intrinsic properties. Thus, before discussing possible applications of SS-derived biochar in detail, it is important to outline the main physicochemical properties of the material to identify possible ways of utilizing it. Subsequently, several possible applications of the material will be considered with a view to demonstrating that the connection between physicochemical properties and the utilization options is quite robust.

This is a material that has a relatively high concentration of carbon. In other words, it is quite stable and cannot degrade via any biological process. Organic molecules with volatile components and oxygen are eliminated during pyrolysis, making it possible to achieve a dense aromatic carbon structure. Moreover, sewage sludge biochar features an elevated ash content, since pyrolysis results in accumulation of minerals within biochar. The reason for that is a correlation between pyrolysis temperature and volatility rates of organic components. Thus, as the temperature increases, volatile components leave the material faster, whereas silicon, aluminum, calcium, and iron oxides remain in it [51].

The presence of inorganic and organic contaminants is worth mentioning as a property of interest of sewage sludge-derived biochar. Contaminants may include heavy metals, PAHs, dioxins (PCDDs/PCDFs), PCBs, VOCs, pharmaceuticals, hormones, pesticides, and herbicides. Most of the pollutants listed are highly persistent, bioaccumulative, and toxic. Therefore, it is necessary to identify and quantify all pollutants contained in the biochar in question, to ensure its safety when used further [53].

It is also worth considering that the sewage sludge-derived biochar under analysis might feature high pH values. Elevated pyrolysis temperature leads to the accumulation of alkali and alkaline earth metals (such as potassium, sodium, magnesium, and calcium) in biochar, mostly in the form of oxides and/or salts. Simultaneously, decomposition of organic acids causes the formation of alkaline materials, resulting in a pH and EC increase [33].

In addition, another critical surface parameter is the Point of Zero Charge (PH_{PZC}). PH_{PZC} increases with temperature since there is a tendency towards decrease in acidic functional groups as the temperature rises. In other words, due to the increasing dominance of basic minerals, pH_{PZC} values will be higher at higher temperatures. Since surface charge depends on whether pH values exceed PH_{PZC}, it is essential to know the latter in order to predict electrostatic interactions [54].

One more parameter of interest is Cation Exchange Capacity (CEC), which is indicative of ability to retain or release cations. CEC is influenced by surface groups and minerals; therefore, temperature changes can affect CEC in different manners. While lower temperatures result in higher carbon-based surface groups, thus causing higher CEC values, higher temperatures lead to higher mineral concentrations in biochar [55].

Biochar is characterized by its porous structure and specific surface area (SSA), both of which increase gradually during pyrolysis due to the decomposition of organic compounds. As a result, volatile compounds leave void spaces in the material, which become pores. In the temperature range between 300 and 500°C, it

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is mainly micro- and mesoporosity that develops, together with the growth in SSA. However, there exists a temperature threshold beyond which structural reorganization and shrinking take place, which is accompanied by decreased SSA. Therefore, the maximum value of SSA can be achieved within an optimal temperature range [56].

Surface chemistry of biochar depends mainly on the type of functional groups contained in it, which can be detected via FTIR method. Examples of such groups include hydroxyl groups (–OH), carboxyl groups (–COOH), carbonyl groups (C=O), among others, containing oxygen and nitrogen atoms. As the temperature grows, the intensity of the groups diminishes as a result of aromatization and condensation of carbon skeletons. The resulting structure is less reactive than it is before pyrolysis since it is characterized by fewer oxygen-containing groups [53].

Another property of the material is calorific value (or heating value), which depends directly on its high carbon content and indirectly on low moisture and oxygen contents. In the case of biochar from sewage sludge, the heating value is estimated to be within 5 and 21 $MJ \cdot kg^{-1}$, depending on initial conditions. However, calorific value of the material also depends on how the feedstock is treated. The example is that digestion and drying of SS prior to pyrolysis decrease the organic matter in the material, and, consequently, the heating value drops down to 8.5–17 $MJ \cdot kg^{-1}$. Untreated SS, by contrast, could yield higher values, up to 23 $MJ \cdot kg^{-1}$ [57].

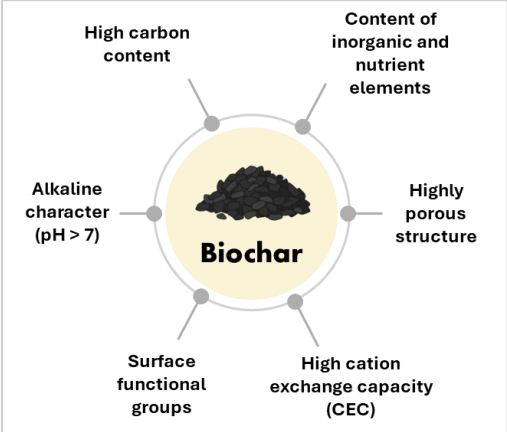


Figure 10 Physicochemical Properties of Biochar

As a continuation from the discussion of physicochemical properties of the material, we should focus on its applications. In fact, sewage sludge-derived biochar can be used across multiple fields including environmental protection, agriculture, energetics, chemical industry, and engineering, among others (Figure9).

Speaking about the most popular field of application of biochar, it would be appropriate to refer to environmental technologies. Biochar proves itself useful as an adsorbent that allows purifying water from different impurities, substituting or supplementing activated carbon in this process. Several mechanisms of adsorption can operate: the porous structure promotes physical adsorption through van der Waals forces, while oxygen-containing groups (for example, -COOH, -OH, and $-NH_2$) allow for chemical adsorption. In addition, the presence of minerals makes biochar able to perform ion exchange and precipitation of metal ions, which is also facilitated by surface charge. In other words, thanks to these mechanisms, it is possible to adsorb a wide variety of pollutants, for example, heavy metals (Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}), nutrients (NH_4^+ and

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PO_4^{3+}), dyes, pesticides, pharmaceuticals, etc. (Figure 11). Noteworthy is that biochar can not only adsorb contaminants but also recover resources (in particular, P), thus supporting principles of the circular economy [58].

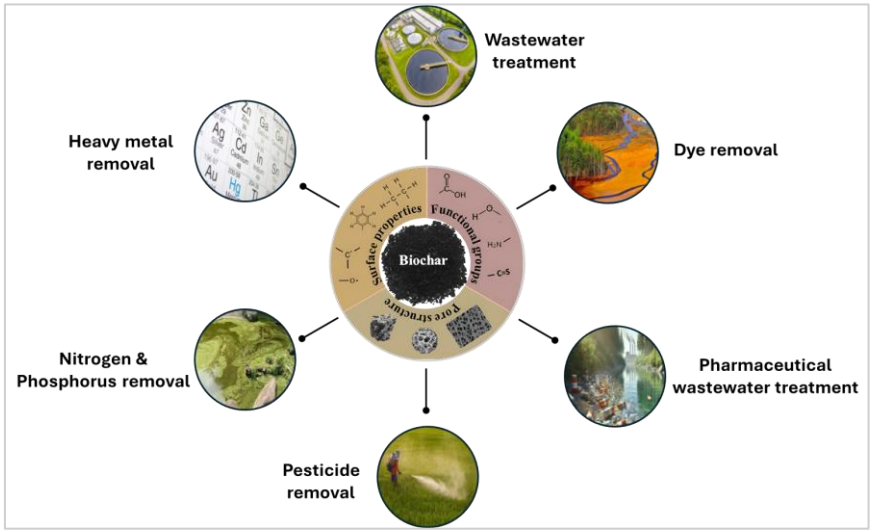


Figure 11 Biochar Applications in Environmental Technology

In agriculture, the main function of biochar is to act as a soil additive that improves soil structure, water retention capability, and nutrient supply. High cation exchange capacity makes the material suitable for retaining nutrients and supplying them gradually, while its porous structure facilitates the development of microbes and roots in the soil. Further, carbon in the material proves to be inert and stable for an extended period of time; hence, the material serves to be a good carbon sequester and carbon farmer [59].

Biochar as an alternative fuel based on its high energy density due to high levels of carbon and low moisture is also an active area of research. First of all, biochar cannot be regarded as the main energy source in comparison with other bioenergy sources such as bio-oil and syngas; however, it can serve as one under certain conditions, when biochar is formed after carbonization during pyrolysis. In addition, more and more attention is given to the use of biochar to improve the anaerobic digestion process, due to its high electric conductivity, which favors DIET and leads to enhanced electron exchange between bacteria and higher methane production [33].

Mitigation of climate change can be linked with carbon sequestration due to its carbon sink property and with emissions reductions in energetic and environmental applications based on biochar use. It is one of the reasons why pyrolysis technologies become not only a technology of energy utilization but carbon cycle management technique as well. Chemical applications include usage of biochar as catalysts or supports for catalysts during reaction process because the surface chemistry of this product can be tuned. In addition, biochar can be involved in gas-phase reactions and affect syngas quality [59].

The engineering uses of biochar include their usage as additives to composite materials, such as concrete. It has been established that the addition of biochar to composites enables both strengthening of these materials and sequestration of carbon within building materials [59].

It is therefore clear that pyrolysis not only encompasses energy generation but also opens up possibilities for manufacturing materials with various applications.

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2.5.2 Bio-oil from Sewage Sludge

One of the byproducts obtained through the pyrolysis process is the so-called bio-oil. The latter corresponds to the liquid portion condensed from volatiles formed during the thermal degradation process. As far as SS is concerned, bio-oil is defined as a complicated blend of organic compounds, containing carboxylic acids, alcohols, esters, aldehydes, ketones, phenols, aromatics, and various other oxygen-containing substances. It should be emphasized that in most cases, bio-oil contains up to several hundred components. The chemical diversity makes it possible to exploit the product in the chemical sector [61].

The typical appearance of bio-oil is dark brown-to-black coloration and a distinct pungent odour, being mainly due to the presence of small molecules, such as acids and aldehydes. The density of the substance is higher compared with that of traditional fuels (1.2 kg/L), while the viscosity shows pronounced variability within quite a wide range (from lower to extremely high values) [62].

As a result of the higher oxygen content, bio-oil exhibits several disadvantages, such as decreased heating value (~40-50% of conventional fuels), high acidity, poor stability, and increased reactivity. Moreover, the immiscibility with hydrocarbons and the miscibility with polar solvents indicate that it is a rather polar compound [62].

Furthermore, the material demonstrates numerous instabilities. In particular, bio-oil undergoes aging, polymerization, and condensation relatively easily, leading to an increase in the viscosity of the liquid and its separation into fractions, especially when the temperature rises. Moreover, chemical composition along with the level of ash, metal ions, and moisture content may adversely impact the properties of bio-oil. Thus, it should be noted that the quality of the end product depends not only on feedstocks but also on the process parameters [62].

These properties have a negative influence on the usability of the material. Nevertheless, bio-oil is regarded as a promising intermediate product rather than as fuel. Among its advantages include storage capabilities and transportation ease when compared with solid and gas fuels, as well as high calorific value compared to syngas.

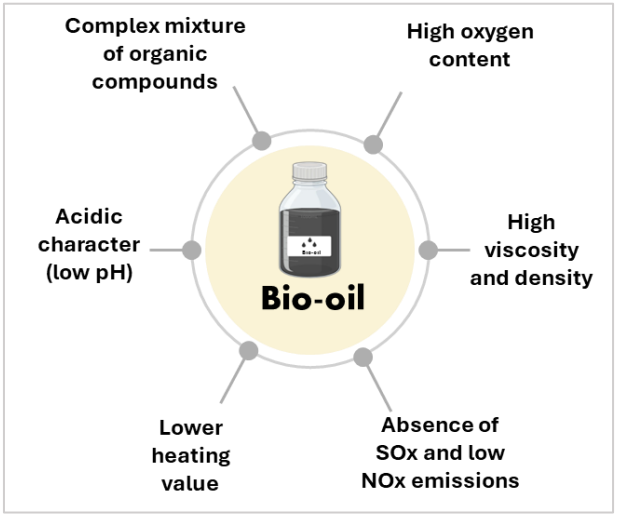


Figure 12 Physicochemical Properties of Bio-oil

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Thus, the above-mentioned physicochemical properties allow suggesting the ways of further utilization of bio-oil that are considered more thoroughly in the next chapter.

As was shown earlier (see Figure 9), the possible applications of bio-oil cover not only the energy sphere but also the chemical one. Thus, the substance might be applied both as fuel and chemical intermediate.

Concerning the energy sector, bio-oil might serve as a fuel in boilers, furnaces, and, in some special cases, in turbines or engines. Nevertheless, because of the aforementioned properties (oxygen content, acidity, and instability), bio-oil is hardly applicable as a direct "fuel drop-in". In contrast, the substance might undergo upgrading to become more fuel-like. Using such technologies as hydrodeoxygenation or catalytic refining, it is possible to produce biodiesel, gasoline, kerosene, methane, and LPG [60].

There is another possibility to convert the bio-oil into syngas and further use it for synthesizing liquid fuels or various chemicals through, e.g., Fischer–Tropsch process. This approach offers additional possibilities to integrate the product into the energy system [60].

Finally, the chemical diversity of the substance allows for producing various valuable chemicals, such as phenols, organic acids (levulinic acid), and related compounds. In other words, it is possible to develop the concept of biorefinery using bio-oil as an intermediate substance [60].

In summary, bio-oil is a promising product whose utilization implies the change of focus from energy recovery to chemical valorization.

2.5.3 Syngas from Sewage Sludge

Of all the products produced during pyrolysis, syngas is the name used to describe the gas product obtained due to the thermal cracking, reforming, and further secondary decomposition reactions. In SS pyrolysis, syngas consists mainly of H_2 and CO, as well as trace amounts of CO_2, CH_4, water vapor, and lighter hydrocarbons such as C_2H_4 and C_2H_6. Other gases such as tar, nitrogen compounds, etc., might also be present depending on feedstock composition and operation parameters [63].

Figure 13 shows that syngas is a gas combustible mixture having a low sulfur content compared to traditional fossil-based fuels. The main energetic component of syngas are H_2, CO, and light hydrocarbons. On the other hand, CO_2 and N_2, usually, act as diluting agents reducing syngas calorific value. Hence, syngas composition is responsible for its energetic characteristics and further utilization possibilities [62].

It is essential to note that the syngas composition depends heavily on pyrolysis process parameters such as the pyrolysis temperature, heating rates, duration, and moisture content of feedstocks. For example, at higher temperatures secondary cracking and reforming become more prevalent causing the production of H_2 and CO increasing. Vice versa, the formation of CO_2, CH_4, and heavier hydrocarbons occurs at low temperatures. Moreover, the moisture content in feedstock also influences syngas composition, enhancing the production of H_2 and CO_2 as a result of the corresponding steam reactions [64].

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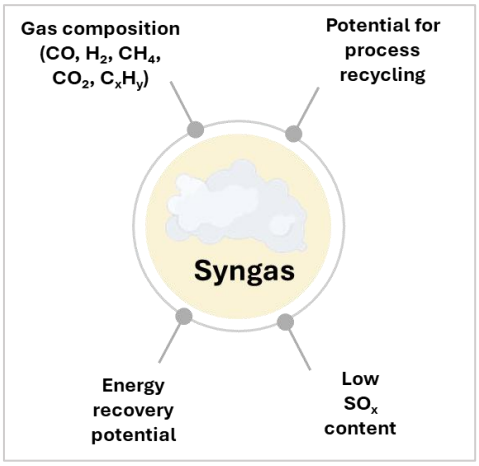


Figure 13 Physicochemical Properties of Syngas

The influence of temperature on the syngas composition is shown in Figure 14. At low temperatures, the syngas contains a lot of CO_2, CH_4, and volatiles where moisture evaporates and decomposition takes place. An increase in temperature results in higher levels of H2 and CO due to faster rates of the cracking reaction, reforming, and gasification. Once the temperature exceeds about 700-800 °C, the content of H_2 and CO increases, while the amount of CO_2 and CH_4 decreases significantly. The shift in syngas composition affects its LHV and H_2/CO ratio [64].

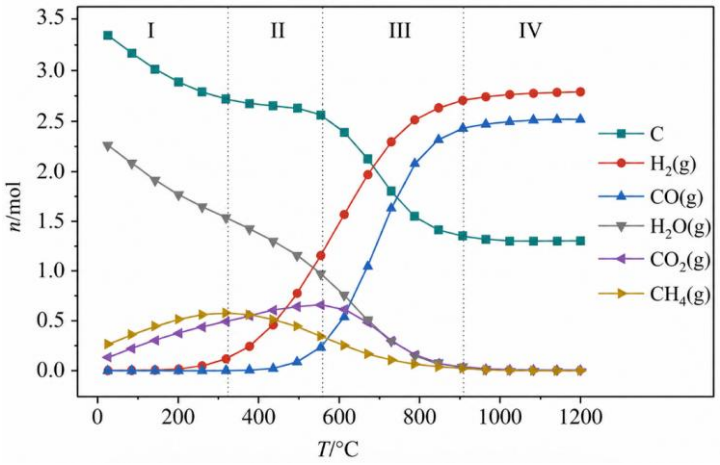


Figure 14 Effect of Temperature on Gas Product Distribution During Pyrolysis. Adopted from A. Farooqui et al., (2023)

Therefore, syngas should not be considered only as a product of the pyrolysis process but rather as an adjustable gaseous energy carrier with adjustable properties achieved due to the proper control of process parameters. Depending on its composition, syngas can be used as an energy source or as a raw material in chemical synthesis.

As already mentioned earlier, syngas can be used in various ways including the generation of heat, combustion in boilers and furnaces, production of electricity using IC engines, gas turbines, etc. In many pyrolysis systems, syngas is recycled within the process and combusted in order to supply additional energy.

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Thus, syngas combustion creates opportunities for developing energetically self-sufficient pyrolysis systems [62].

Moreover, syngas has proved to be a valuable intermediate product in the chemical synthesis processes due to its hydrogen and carbon monoxide composition. Syngas can act as a feedstock in Fischer-Tropsch synthesis, methanol production, hydrogen generation, and ammonia synthesis. Among other things, syngas' H_2/CO molar ratio plays a crucial role when deciding which application pathway is preferable [64].

Overall, one should pay attention to the second advantage of SS pyrolysis systems. Namely, pyrolysis not only allows recovering energy from waste but also produces valuable gas that can be applied both in energy and chemistry.

2.6 Economic and regulatory aspects

2.6.1 Regulatory aspects

The regulatory framework of SS management and valorization in Europe consists of a series of regulatory instruments that aim at the protection of human health and environment but also at supporting a gradual approach to recovery instead of final disposal. According to Figure 15, the main characteristic of this framework is not to consider the SS as a waste stream that needs to be disposed of, but as a material flow to be managed according to circular economy principles [65].

The principal EU legislation regulating the use of SS in agriculture is Sewage Sludge Directive 86/278/EEC. The main objective of this directive is to ensure that the use of sludge for agriculture does not lead to any harmful effects on soil, vegetation, animals, and humans. According to this directive, treated sludge is the sludge that has been subject to biological, chemical or heat treatment, long-term storage or another suitable process that significantly decreases fermentability and possible risks related to the use of the sludge. Furthermore, the sludge should always be treated before using it in agriculture [66]. It means that, in this case, the Sewage Sludge Directive 86/278/EEC provides the necessary foundation for the regulation of SS reuse, but still it does not include pyrolysis or valorization processes.

This framework is supplemented by the Waste Framework Directive 2008/98/EC. This directive introduces a hierarchical structure regarding waste. Prevention, preparing for reuse, recycling, recovery, and finally disposal represent different steps of this hierarchy that should be followed. Disposal is the last step in this hierarchy, and recovery and recycling are prioritised. In the case of SS, this hierarchy supports a shift towards nutrient and energy recovery instead of disposal [65].

Another document that reinforces this trend is the Urban Wastewater Treatment Directive 91/271/EEC, which states that sludge generated during wastewater treatment must be reused where appropriate, while disposal alternatives are required to minimise their environmental impacts. It also states that Member States must take measures to stop disposing sludge in surface water by 31 December 1998. This requirement is quite significant because it means that sludge management is connected to the overall environmental performance of a wastewater treatment plant [9].

Finally, the Landfill Directive 1999/31/EC was crucial in encouraging the reduction in the disposal of biodegradable waste streams. This document states that member states have to progressively reduce biodegradable municipal waste sent to landfills down to 35% of 1995 levels in 2016. It does not provide any

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guidelines for pyrolysis but encourages looking for alternative solutions because of the restrictions on disposal [67].

In Greece, national legislation is aligned with the framework outlined above. The management of SS is connected to the implementation of EU directives related to the sludge use in agriculture, restrictions on landfills, waste management, incineration, and environmental licensing. Recent national waste planning activities were also aimed at decreasing the landfill capacity and promoting sludge recovery. It means that, similarly to the European framework, the Greek framework identifies a number of management approaches for SS, such as agricultural reuse with restrictions, drying and using sludge as a fuel, using sludge in biogas facilities after dewatering, and using in landscaping after sanitation, stabilisation, and drying. It seems that SS management in Greece is gradually moving from the concept of disposal to recovery [9].

The situation with the regulation of SS pyrolysis products is more complicated. Unlike some other waste products, the pyrolysis products are not included into a list of substances with their own regulation regime. Depending on intended uses, compositions, and other factors, these products are subject to either product or waste regulation. For example, if SS is transformed into the substance used in soil improvement or fertilizing activities, it must be subjected to requirements concerning contaminants, heavy metals, and organic pollutants. Regulation (EU) 2019/1009 establishes requirements for fertilizing products; in its Annex II there is a description of recovered materials used for producing fertilizers. Pyrolysis and gasification materials are included in the category. Nevertheless, it is essential to note that certain parameters should be met before placing the substance on the market [65].

In this way, it means that there are no special regulations regarding SS pyrolysis products. In order to apply pyrolysis, it is necessary to follow requirements of current waste regulations. Afterward, the obtained products will depend on the intended use and composition of substances. If they are going to be used as fertilizing, then requirements for fertilizing are needed. Otherwise, these products might require a different regulatory approach, which makes it quite difficult to implement this technology.

From this point, it could be concluded that the lack of regulation is not the issue related to SS pyrolysis because current legislation establishes requirements for waste management in Europe. Nevertheless, there are no special requirements and end-of-waste criteria related to the products of this kind. It increases the uncertainty associated with this type of management that limits further adoption of the technology. Therefore, it is necessary to focus on further regulation, especially in relation to agricultural applications.

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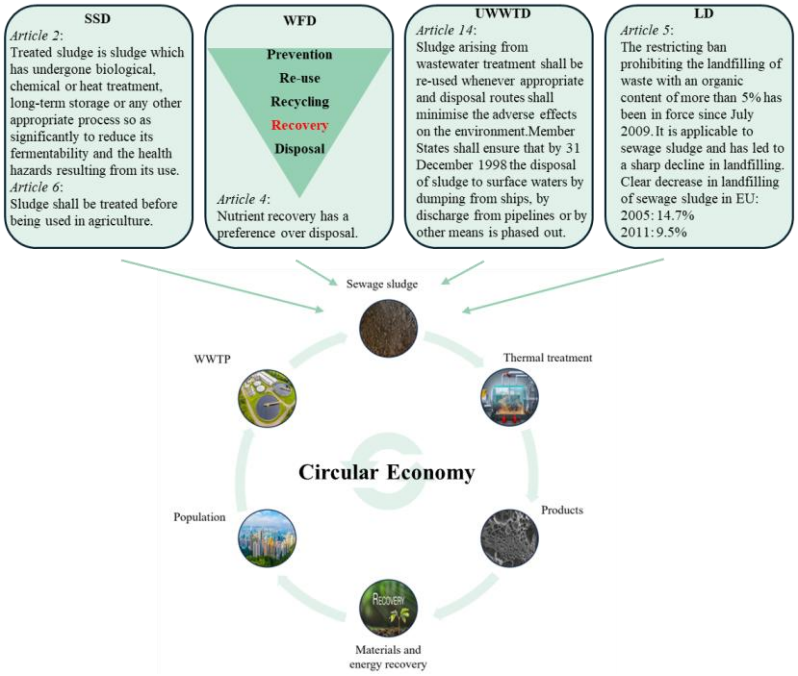


Figure 15 Legislative Drivers and Circular Economy Pathways for Sewage Sludge Management in the EU

2.6.2 Economic aspects

The economic viability of pyrolysis implementation remains one of the key constraints to largescale application of pyrolysis technology for sustainable SS management. Indeed, it is commonly acknowledged that the technological and economic viability of any pyrolysis systems depends on the correlation between the required capital, energy, and operational costs and the value of products obtained [48]. As a result, techno-economic performance is considered one of the main criteria that determine the transition from piloting to industrial implementation of pyrolysis technology.

Traditionally, it is possible to divide the cost structures of the pyrolysis plants into two main categories. On the one hand, there are capital costs – the reactor systems themselves, the facilities related to raw material handling, pretreatment (if necessary), product separation, and auxiliary equipment for construction, transport, etc. Although reactors represent the main part of the equipment, they make up only 10-15 percent of all capital expenses, while the rest is spent on feedstock handling, preparation, and subsequent operations [62]. On the other hand, operational costs cover feedstock collection, pretreatment, maintenance, labor force, utilities, grinding and drying, product transport and storage [62].

Table 4 Classification of Capital and Operational/Variable Costs in Pyrolysis Systems

Capital Costs	Operational / Variable Costs
Reactor / pyrolysis module	Biomass harvesting or feedstock
Feed handling and storage systems	Maintenance
Drying and pretreatment infrastructure	Labour

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Product collection and storage systems	Utilities
Transportation infrastructure	Drying and pretreatment
Auxiliary buildings and facilities	Transportation

Various factors may influence economic viability of different pyrolysis installations. For instance, they are related to type and quality of raw material; pyrolysis method; installation scale; design of a reactor; the need for the quality increase of produced products; and energy consumption. Plant size is considered as one of the crucial elements. As numerous papers prove, the cost per unit of a product in larger installations is significantly lower because of economies of scale compared to smaller facilities, which results in high costs per unit. Thus, financially viable operation requires inexpensive feedstock and sufficient scale [68].

In the case of SS pyrolysis, economic efficiency is influenced by several important factors. First of all, the variability of sludge as the feedstock is considered as one of the main disadvantages of its economic feasibility. High moisture content and high ash content result in increased costs for pre-treatment and/or drying. Furthermore, the heating value of produced product will decrease, and the quality of bio-oil will worsen. Thus, sludge pre-treatment can be considered as one of the main barriers for economically efficient SS pyrolysis [62].

Still, there are some economic benefits associated with this innovative technology compared to conventional biomass pyrolysis. For example, sludge as a resource has no significant price and is often even free of charge (although the gate fee should be paid). Moreover, the SS pyrolysis allows obtaining various types of products (biochar, bio-oil, syngas, etc.). Therefore, the operator may receive additional profits as he/she can sell some of those by-products [48].

Of the above-listed products, biochar is the most economically promising. According to technological and economic assessment, selling biochar can greatly contribute to the overall economic efficiency of the SS pyrolysis. Specifically, positive NPVs are mostly related to successful marketing of biochar obtained from SS pyrolysis. Finally, increased attention to carbon farming and creation of carbon credits may positively affect the efficiency through providing additional income for producers of carbon-containing products [70-72].

Moreover, bio-oil is quite an intriguing product, which may find use not only as energy carrier, but also as source material for different chemicals production. However, it is known, that due to oxygen and nitrogen content, and inherent instability, further treatment of bio-oil is required, causing large additional costs in upgrading bio-oil [73].

The other byproduct of pyrolysis is syngas, whose role in the economics of the process is that it may be used to produce energy. As a rule, syngas is not sold on the market but rather used internally to reduce dependence from other sources of energy [69]. Advanced configurations based on gas turbine generators and energy recovery systems can recover up to half of process energy [69].

It should also be mentioned as potential economic value of SS pyrolysis that, being a relatively rich source of such elements like phosphorus, SS contains some number of other elements, thus pyrolysis products may contain some amount of nutrients which can be reused in a cycle [74].

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However, it is necessary to mention several limitations of pyrolysis systems regarding their economic feasibility, namely high costs (both capital and operational), variability of feedstock, uncertainties concerning potential markets, difficulties in obtaining stable product quality, as well as immature regulatory basis. Inefficiency of environmental control system increases operating cost as well [48].

Table 5 Economic feasibility factors and optimization strategies in thermochemical sludge treatment

Factor	Challenges	Optimisation Strategies
Capital and Operational Costs	High equipment investment, high energy consumption, complex design, expensive catalysts	Develop low-cost catalysts, improve process parameters, and adopt modular designs
Process Complexity and Pretreatment Needs	High moisture and ash content require costly drying or pretreatment	Co-processing with biomass, introducing energy recovery systems, and using integrated processes
Energy Recovery Efficiency	Gasification offers high efficiency but requires a larger investment; pyrolysis is more flexible but slightly less efficient	Optimize gasification parameters (ER, temperature, steam ratio), and adopt hybrid systems (e.g., pyrolysis + gasification)
Byproduct Management and Environmental Impact	Production of tar, NOx, and other pollutants increases purification costs	Use catalysts to reduce tar and NOx formation, and design byproduct recovery systems
Commercialization and Scale-up	Lack of large-scale investments, market uncertainties, insufficient policy support	Conduct comprehensive techno-economic assessments, implement demonstration projects, and strengthen policy integration

Based on Table 5, the main economic issues of thermochemical sludge treatment are associated with capital and operational costs, complexity of pretreatment, the environmental management of byproducts, and problems with commercialization and scaling. Meanwhile, several approaches have been proposed in order to solve the problem, including the co-processing of sludge with biomass, improved heat integration, creation of low-cost recyclable catalysts, optimization of operating conditions, and modular design of reactors.

Thus, the economic efficiency of SS pyrolysis systems depends heavily on the possibility of the proper integration of these technologies. It can be stated that economic attractiveness greatly increases in case of cheap or even waste raw materials, larger scale of operation, internal heat integration, and utilization of valuable products such as biochar or recovered nutrients.

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3 Experimental methodology and system description

3.1 Description of the pyrolysis system

Within the framework of Task 7.5 of the THESEUS project, an experimental methodology was developed to investigate the thermochemical valorisation of sewage sludge produced in the Attica region. The methodology focuses on the controlled pyrolysis of dried sewage sludge under laboratory-scale conditions, with the aim of evaluating product formation, product recovery and the applicability of the selected analytical protocols. This chapter describes the pyrolysis system installed and operated at the Sanitary Engineering Laboratory of NTUA, the main operating principles of the setup, the feedstock preparation procedure, the experimental protocol and the analytical strategy followed for the preliminary characterization of the produced fractions.

3.1.1 Reactor configuration and setup

The experimental system is based on a laboratory-scale horizontal tube furnace (Carbolite Gero TF1/3, 450 mm heated length, 60 mm internal diameter), designed for high-temperature processing of materials under controlled atmospheres. The furnace operates with a maximum continuous temperature of 1100 °C and a maximum power output of 2 kW, enabling the controlled thermal conversion of solid feedstocks such as SS under pyrolytic conditions. The core component of the system is the work tube, positioned within the heated zone of the furnace, where the sample is placed and thermally treated. Also the furnace is equipped with electrical heating elements embedded within the refractory insulation surrounding the work tube. These elements are accessed through dedicated heating element access panels and are responsible for generating heat through electrical resistance. The supplied power is dynamically regulated by the temperature controller, allowing precise control of heating rates and setpoint temperatures.



Figure 16 Carbolite TF3 12/125/1200 pyrogasifier

The temperature inside the furnace is monitored using thermocouples and controlled via a touchscreen-based CC-T1 controller, which operates using PID (Proportional–Integral–Derivative) algorithms to adjust the power supplied to the heating elements and maintain the desired thermal profile. The controller allows the user to define programmable temperature profiles consisting of sequential segments, including controlled heating ramps (rate segments defined by target temperature and heating rate), isothermal holding periods

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(dwell segments), and termination steps (end segments), enabling fully automated operation of the pyrolysis process (Figure 17).

The work tube is sealed at both ends using dedicated end seal assemblies, which ensure airtight operation and allow the establishment of a controlled atmosphere within the reactor. These assemblies consist of sealing plates, O-rings, sealing sleeves, and clamps, forming a gas-tight enclosure around the tube. When operating under inert gas conditions, the internal pressure is maintained at low levels and should not exceed 0.07 bar to ensure safe operation of the sealing system. To enhance thermal performance and protect the sealing components, insulation plugs are inserted at both ends of the work tube. These elements, made of refractory insulating materials, reduce heat losses, improve temperature uniformity within the heated zone, and minimise thermal gradients between the hot central region and the cooler tube extremities. Additionally, they protect the end seals from excessive thermal exposure and reduce the risk of thermal shock within the system.

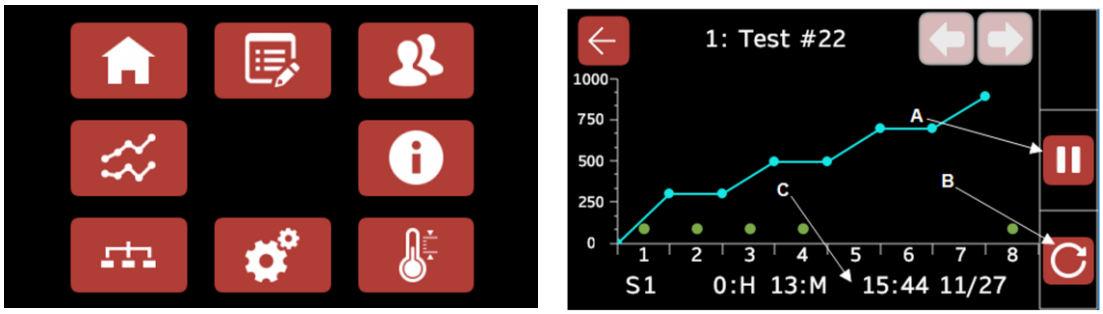


Figure 17 Programmable Temperature Control and Process Monitoring

Lastly the furnace is coupled with an inert gas supply system to enable operation under oxygen-free conditions. The inert gas package is designed to introduce non-flammable gases into a sealed vessel that is subjected to heating. In the present setup, **nitrogen (N_2)** is used as the inert gas. Gas flow is controlled via a flowmeter equipped with an adjustment knob, allowing regulation of the flow rate within the range of 1–10 L min^{-1}. The system ensures continuous purging of the reactor, preventing oxidation reactions and maintaining the required pyrolytic environment.

3.1.2 Operating conditions

The operating conditions applied in the present study were selected based on both literature evidence and system-specific constraints, with the aim of ensuring experimental reproducibility while systematically investigating the most critical parameters affecting the pyrolysis process.

- The **particle size** of the feed material was kept constant during all tests in order to provide uniformity and to minimize the effect of any limitations concerning heat and mass transfer processes. Thus, drying of SS material was followed by mechanical treatment of the feed material and its sieving up to particle size of 0.25-1 mm.
- Any attempt to alter the **moisture** level was not carried out during the course of the experiment, rather the emphasis was laid on attaining stability in the moisture level for all the tests performed. Drying of the sample was performed before conducting the test under controlled conditions and storage in sealed containers to avoid absorption of moisture from the surrounding environment.

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- Reagents were introduced to the apparatus under an inert atmosphere of **N_2 gas**. This was set at a flow rate of 1 L per minute; this is the lowest level that can be set using the flowmeter to prevent excess effects of flow rate on product distribution.
- **Reaction time** is one of the important parameters studied during the process. In order to have different temperatures ranges covered, including torrefaction, pyrolysis, and slow pyrolysis, the reaction time ranged from 15 minutes to 4 hours.
- The **heating rate** was chosen based on the furnace system operational capability. Because of certain limitations of the equipment, very high heating rates, which are usually used during fast pyrolysis, could not be reached. Thus, the heating rate range was chosen within 20-120 $^oC\ min^{-1}$ for the analysis of its impact.
- **Temperature** was one of the primary parameters investigated, given its dominant role in determining product distribution and reaction pathways. The experimental temperature range was set between 300 and 900 ^oC, covering conditions from mild thermal treatment (torrefaction range) to high-temperature pyrolysis.
- The **feeding rate** was kept constant in all experiments to ensure comparability of results. A fixed mass of 40 g of dried SS was introduced into the reactor for each experimental run.
- **Catalytic** and activation effects were also explored within the experimental framework. Chemical agents such as HCl, KOH, and $FeCl_2$ were considered for pre-treatment of the feedstock or post-treatment of the produced biochar, aiming to modify its physicochemical properties. In addition, CO_2 was investigated as a physical activation agent rather than a conventional catalyst. Its use is associated with gasification-type reactions that enhance pore development and surface area in carbonaceous materials. These agents have been widely reported in the literature for improving the quality and functionality of pyrolysis-derived products, particularly in applications related to adsorption and environmental remediation.

Table 6 Summary of operating conditions for pyrolysis experiments

Parameter	Value/Range	Description
Particle size	0.25-1 mm	Obtained via shredding and sieving to ensure homogeneity
Moisture content	Controlled (constant)	Samples dried and stored to minimise variability
Inert gas	N_2	Oxygen-free atmosphere
Gas flow rate	1 L min^{-1}	Constant, lower limit of flowmeter
Temperature	300-900 ^oC	Main parameter under investigation
Heating rate	20-120 $^oC\ min^{-1}$	Limited by furnace capabilities
Residence time	15 min - 4 h	Covers torrefaction to slow pyrolysis
Feedstock mass	40 g	Constant for all experiments
Catalysts/activation agents	HCl, KOH, $FeCl_2$, CO_2	Pre- or post-treatment for product enhancement

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3.2 Feedstock description and pre-treatment

The feedstock used in this study consists of dried SS originating from Psyttalia WWTP, which serves the greater Athens metropolitan area. The material represents a stabilised and processed sludge stream derived from a sequence of treatment steps, including the combination of primary and secondary sludge, followed by thermal hydrolysis, anaerobic digestion, mechanical dewatering, and final thermal drying. This treatment chain results in a relatively stable, low-moisture solid suitable for thermochemical conversion processes.

In addition to the Psyttalia sludge, dewatered SS from Metamorfosis WWTP was also considered within the scope of the project. However, this sludge was not utilised in the present experimental work due to its high moisture content, typically exceeding 80%. Given that the operation of the pyrolysis reactor requires feedstock with significantly lower moisture levels (generally below 30 wt.%), the use of such material would necessitate an additional drying step at laboratory scale. Therefore, its investigation is reserved for future experimental work.

Prior to pyrolysis, the Psyttalia sludge underwent basic pre-treatment to ensure consistency and reproducibility of the experiments. The material was mechanically shredded and subsequently sieved in order to obtain a uniform particle size fraction in the range of 0.25–1 mm. This step is essential to minimise variability associated with particle size effects and to ensure homogeneous heat transfer during thermal processing.

For a comprehensive evaluation of the feedstock and its behaviour during pyrolysis, a set of physicochemical properties must be determined. These include proximate analysis (moisture content, ash content, volatile matter, and fixed carbon), as well as ultimate analysis (elemental composition in terms of C, H, N, S, and O, along with higher and lower heating values, HHV and LHV). In addition, thermogravimetric analysis (TGA) is employed to assess the thermal decomposition behaviour of the material under controlled conditions. The analytical procedures and methodologies applied for these characterisations are described in detail in Section 3.4.

3.3 Experimental procedure

3.3.1 Pyrolysis experiments

The pyrolysis experiments were conducted using dried SS as feedstock, with a fixed sample mass of 40 g introduced into the work tube for each experimental run (Figure 18). The material was placed centrally within the tube to ensure uniform exposure to the heated zone. The reactor was then assembled and sealed using the appropriate end seals and insulation plugs, ensuring airtight conditions and enabling operation under a controlled atmosphere.

Following reactor preparation, nitrogen (N_2) was introduced as the carrier gas at a constant flow rate of 1 L min^{-1} in order to establish an inert environment and prevent oxidation reactions during thermal treatment. Once stable gas flow was achieved, the programmed thermal profile was initiated via the touchscreen controller. The experimental conditions, including target temperature, heating rate, and residence time, were defined according to the selected operating parameters for each run.

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The gaseous stream exiting the reactor, consisting of a mixture of carrier gas, condensable vapors, and non-condensable gases, was directed through a series of three impingers placed in an ice-cooled bath. Each impinger contained a suitable organic solvent, selected based on its ability to efficiently capture condensable compounds. Solvents such as acetone, isopropanol, ethyl lactate, and hexane were considered and tested for this purpose. The impinger system was maintained at low temperature (approximately −10 °C) in order to promote the condensation of volatile compounds and maximize the recovery of the liquid fraction. The use of low temperatures is critical, as it enhances vapour condensation efficiency, reduces losses of light organics, and improves the overall accuracy of bio-oil collection.

The non-condensable fraction of the gas stream, consisting mainly of permanent gases produced during pyrolysis along with the carrier gas, was subsequently collected in gas sampling bags for further analysis. This configuration allows for the separation of condensable and non-condensable products and facilitates their independent quantification and characterization.

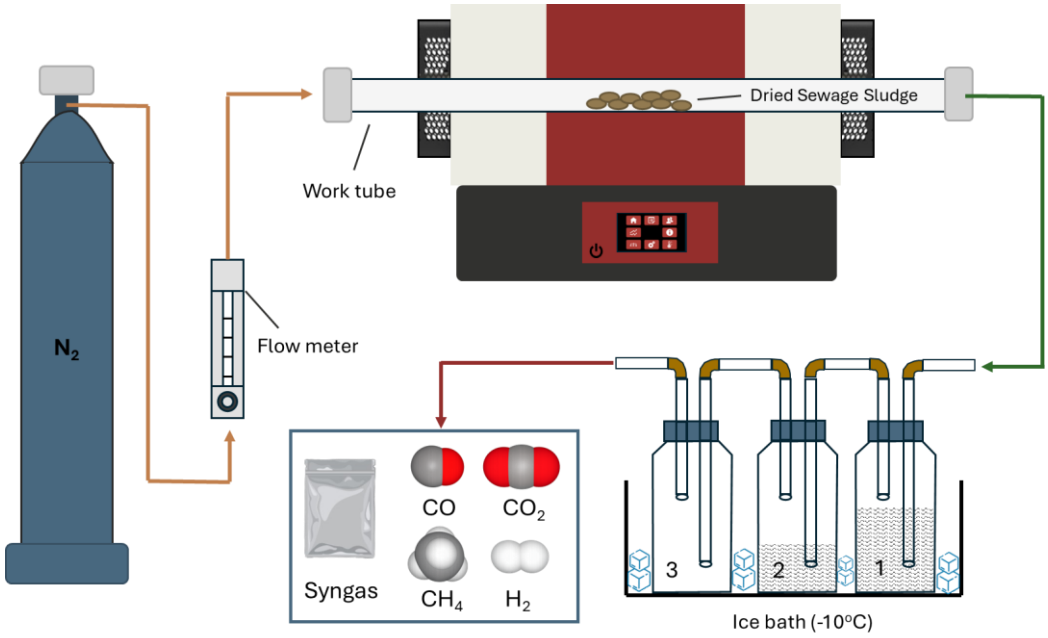


Figure 18 Experimental setup for sludge pyrolysis and product collection system

3.3.2 Mass balance approach

The amount of both the solid and liquid phases obtained at the end of the experiment was measured gravimetrically. The weight of biochar was determined based on the weight of the solid phase isolated at the end of the experiment from the work tube. For the liquid phase, since it is collected in impingers containing solvent, the isolation of bio-oil required the use of a rotary evaporator to remove the solvent.

Calculation of the total mass balance was based on the starting weight of dried SS and weights of the biochar and bio-oil obtained. As no attempt was made to directly measure the amount of gaseous products, the weight of the gas phase was estimated using the equation:

$$M_{SS} = M_{biochar} + M_{bio-oil} + M_{syngas} \quad (3.1)$$

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Where M_{SS} is is the initial mass of dried SS introduced into the reactor, $M_{biochar}$ is the recovered solid product, $M_{bio-oil}$ is the recovered liquid product after solvent evaporation and M_{syngas} is the calculated gas fraction.

The percentage yield of each product was calculated as the ratio between the mass of the collected product and the initial mass of dried SS used in the experiment:

$$Yield_i = \frac{M_i}{M_{SS}} \times 100 \quad (3.2)$$

Where M_i corresponds to the mass of each product fraction. For the gaseous fraction, the yield was calculated by difference using the measured solid and liquid yields. Duplicate experiments were carried out for each set of operating conditions, and the reported values correspond to the average of the duplicate runs.

3.4 Analytical methods and characterization strategy

3.4.1 Characterization strategy of pyrolysis products

The characterization of the products derived from SS pyrolysis is a key component of the present study, directly aligned with the overarching objective of the project, which focuses on the development of novel valorisation pathways for both material and energy recovery. Within this framework, the analytical strategy is designed to evaluate not only the distribution of pyrolysis products (biochar, bio-oil, and syngas), but also their physicochemical and compositional properties, with the aim of assessing their suitability for downstream applications and integration into existing industrial processes.

As illustrated in Figure 19, the characterization framework encompasses the analysis of all three product fractions, with a defined set of target parameters for each stream. These parameters have been selected based on their relevance to specific valorisation routes and their ability to capture both compositional and functional characteristics. For the liquid fraction (bio-oil), key parameters include density, viscosity, water content, and chemical composition, with particular emphasis on compounds such as volatile fatty acids (VFAs) and fatty acid methyl esters (FAMEs), which are of interest for their potential use in fuel production and their compatibility with petroleum refining processes. Parameters like pH, ash content, elemental analysis, surface area, and CEC have been taken into account in the solid phase due to its significance for future applications in fields like environmental remediation, adsorption, and soil amelioration. In contrast, for the gaseous phase, emphasis has been laid on the determination of gas composition (CH_4, CO_2, CO, and H_2) and estimation of higher and lower heating values (HHV and LHV).

At the current stage of the project (v1), analytical efforts have primarily focused on the solid fraction (biochar), for which a comprehensive set of laboratory protocols has been largely established and applied. These include both basic physicochemical characterization (e.g. proximate and ultimate analysis, pH,EC) and more advanced techniques related to surface properties and functionality. In contrast, the characterization of the liquid and gaseous fractions is still under development, mainly due to challenges associated with product recovery, solvent handling, and the dilution of the gas stream by the carrier gas. Thus, while the analytical parameters for both bio-oils and syngases have been defined, the methodology is still undergoing optimization and will be subject to further refinement throughout the course of this project.

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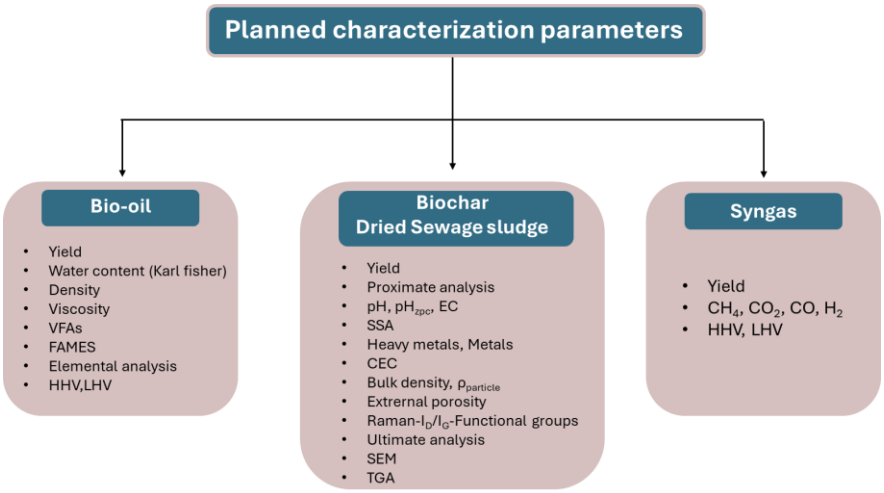


Figure 19 Planned characterization parameters for pyrolysis products

To fulfill the demands of analysis required for the study, an apparatus involving gas chromatography equipped with a barrier ionization discharge detector (GC-BID) has been purchased and is ready for use in the Sanitary Engineering Laboratory. The instrument will now be calibrated to allow precise analyses of gases and liquids collected during pyrolysis experiments. In particular, it is expected that the apparatus will contribute to the characterization of syngas composition, including those with trace amounts, and the detection and quantification of organic compounds in bio-oil, such as VFAs and FAMEs.



Figure 20 Gas chromatography (GC-BID) instrument for syngas and bio-oil analysis

3.4.2 Biochar characterization methods

The analytical methods described in this section were applied for the characterization of both the initial feedstock (dried SS) and the produced biochar, allowing for a comparative assessment of material properties before and after pyrolysis. The selected techniques aim to determine key physicochemical and compositional parameters, providing insight into the transformation of the material during thermochemical conversion. The analytical protocols applied for each parameter are presented in the following sections.

Following this approach, the characterization of the material begins with the determination of its basic compositional properties through proximate analysis.

The proximate analysis of the produced biochar was performed in order to determine its basic physicochemical composition, including moisture content, ash content, volatile matter, and fixed carbon.

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These parameters are essential for evaluating the thermal behaviour of the material, its stability, and its potential applications in both energy recovery and material valorisation.

Moisture content was found by using ASTM D2216-98 standard method [75]. In this process, sample taken for analysis was dried in an oven kept at 105 – 110 °C until reaching constant weight. Moisture content was calculated as:

$$Moisture(\%) = \frac{W_1 - W_2}{W_1} \times 100 \quad (3.3)$$

where W_1 is the initial mass of the sample (as received) and W_2 is the mass after drying.

The total solids (TS) content was determined as the complement of moisture content, representing the dry fraction of the sample.

The content of ash was determined using ASTM E1534-93 [76]. A quantity of about 2 g of the dried sample was put inside an oven and burnt at temperatures between 580 to 600 oC till there is complete incineration of the organic content. The sample was allowed to cool in a desiccator and then weighed.

$$Ash(\%) = \frac{W_2}{W_1} \times 100 \quad (3.4)$$

where W_1 is the dry mass of the initial sample and W_2 is the mass of the remaining inorganic residue (ash).

Volatile matter was measured using the method described in the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WPCF, 1992). An amount of the sample after drying was then subjected to heating to 500 ± 50 oC for a specific time reriod. The weight loss represents the amount of volatiles, which is represented as:

$$Volatile\ Matter(\%) = \frac{W_1 - W_2}{W_1} \times 100 \quad (3.5)$$

where W_1 is the initial dry mass and W_2 is the mass after thermal treatment.

Finally, the fixed carbon content was calculated by difference, using the relationship:

$$Fixed\ Carbon(\%) = 100 - [Ash(\%) + Volatile\ Matter(\%)] \quad (3.6)$$

After the determination of the basic compositional properties through proximate analysis, additional physicochemical parameters were evaluated in order to further characterize the material, particularly in relation to its behavior in aqueous systems. The **pH** and **EC** of both the produced biochar and the initial dried SS were measured as key indicators of alkalinity and soluble salt content. These parameters provide useful information on the interaction of the material with water and are commonly used to assess its suitability for environmental applications.

The measurements were carried out using a solid-to-solution ratio of 1:10 (w/v), employing deionized water (DIW) as the extraction medium. Specifically, 2.0 g of air-dried sample (ground to <2 mm) were weighed into a 100 mL centrifuge tube, and 20 mL of DIW were added. The suspension was shaken manually and then mechanically agitated for 1 hour at approximately 25 °C to allow equilibration between the solid and liquid phases. After agitation, the suspension was allowed to settle for approximately 30 minutes.

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The pH was measured using a calibrated pH meter, and the value was recorded once stabilization was achieved. Calibration was performed using appropriate buffer solutions depending on the expected pH range. The electrode was rinsed with deionized water between measurements to avoid contamination.

EC was measured using the same extract, ensuring consistency between the two measurements. The EC values provide an indication of the concentration of dissolved ionic species in the solution.

In addition to pH and EC, the **point of zero charge (pH_{pzc})** of the biochar was determined in order to evaluate its surface charge characteristics. The pH_{pzc} corresponds to the pH value at which the net surface charge of the material is zero. At solution pH values below the pH_{pzc}, the surface is positively charged, while at pH values above the pHpzc, the surface becomes negatively charged. This property is particularly important for understanding the adsorption behaviour of the material and its interaction with ionic species in aqueous systems. The determination was carried out using the pH drift method. A series of 0.1 M NaCl solutions were prepared and adjusted to initial pH values ranging from 2 to 11 using 0.1 M HCl and 0.1 M NaOH. Subsequently, 0.1 g of biochar was added to each solution, and the suspensions were sealed and agitated at 160 rpm for 4 hours to allow equilibration.

The final pH of each solution was then measured, and the pHpzc was determined by plotting the initial pH against the change in pH (ΔpH = pH_final − pH_initial). The point at which ΔpH equals zero corresponds to the pHpzc. All measurements were performed in duplicate to ensure reproducibility.

Following the determination of pH, EC, and pHpzc, the **total alkalinity (TA)** of the biochar samples was evaluated in order to further assess their acid-neutralising capacity and buffering behaviour. This parameter is particularly important for understanding the potential impact of the material on pH regulation in environmental applications.

The TA was determined using an acid–base titration method adapted from established protocols. Briefly, 0.5 g of dried and homogenised biochar sample were weighed into centrifuge tubes, and 25.0 mL of 0.05 M HCl were added. A blank solution containing only the acid (without biochar) was prepared in parallel. The suspensions were agitated for 24 hours at approximately 25–26 °C to ensure sufficient interaction between the solid phase and the acid solution.

After equilibration, the suspensions were filtered through 0.45 µm filters, and a fixed aliquot (10.0 mL) of the filtrate was collected for titration. The aliquot was titrated with standardised 0.05 M NaOH solution until reaching the endpoint at pH 8.2, and the volume of NaOH consumed was recorded. The same procedure was applied to the blank solution.

The biochar alkalinity was determined by comparing the volume of NaOH used in the blank titration with that needed for the biochar titration, since it is the quantity of acid neutralized by the biochar. The total acidity (TA) was represented in millimoles of H^+ per gram of biochar as:

$$TA\ (mmol\ H^+/g) = \frac{(V_b - V_{used})[ml] \times\ C_{NaOH}\ [mol\ L^{-1}] \times \frac{V_{total}}{V_{aliquot}}}{m\ [g]} \qquad (3.7)$$

where $\mathbf{V_b}$ is the volume of NaOH used for the blank (mL), $\mathbf{V_{used}}$ is the volume of NaOH used for the sample (mL), $\mathbf{C_{NAOH}}$ is the concentration of the NaOH solution (mol L^{-1}),$\mathbf{V_{total}}$ is the total volume of HCl added to the sample (mL), $\mathbf{V_{aliquot}}$ is the volume of the titrated aliquot (mL), and **m** is the mass of biochar (g). The scaling factor $\mathbf{V_{total}}$/ $\mathbf{V_{aliquot}}$ accounts for the difference between the total extraction volume and the analysed aliquot.

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For practical interpretation, the alkalinity values were also converted to mg $CaCO_3$ per gram of biochar using the relationship:

$$TA\ (mgCaCO_3/g) = 50 \times TA\ (mmol\ H^+/g) \tag{3.8}$$

All measurements were performed in triplicate in order to ensure the reliability and reproducibility of the results.

Following the evaluation of the chemical properties of the biochar further analysis was conducted to assess the surface characteristics of the material, which play a key role in its interaction with contaminants and its adsorption behaviour. In this context, the **SSA** of the biochar samples was determined using the methylene blue (MB) adsorption method, based on equilibrium isotherm analysis. The method relies on the adsorption of MB molecules onto the surface of the biochar, allowing the estimation of available surface sites through the determination of the maximum adsorption capacity.

Briefly, a series of MB solutions with different initial concentrations (20–120 mg/L) were prepared and contacted with a known mass of biochar (0.100 g) in a fixed solution volume. The suspensions were agitated for 24 hours at ambient temperature to ensure adsorption equilibrium. Following equilibration, the supernatant was analysed using a UV–Vis spectrophotometer at 664 nm, and the equilibrium concentration of MB was determined using a previously established calibration curve.

The amount of MB adsorbed at equilibrium (q_e, mg/g) was calculated from the difference between initial and final concentrations, taking into account the solution volume and the mass of the biochar. The adsorption data were fitted to the Langmuir isotherm model in its linearised form, allowing the determination of the maximum adsorption capacity (q_m), which corresponds to monolayer coverage of the surface.

The SSA was then calculated from q_m, taking into account the surface area occupied by a single methylene blue molecule, according to:

$$SSA = \frac{q_m \times N_A \times A_{MB}}{1000} \tag{3.9}$$

where SSA is the specific surface area (m^2/g), q_m is the maximum adsorption capacity (typically expressed in mmol/g), N_A is Avogadro's number (6.023×10^{23} mol^{-1}), and A_{MB} is the surface area occupied by a single MB molecule (typically ~130 $Å^2$). All experiments were conducted in duplicate, and the results are reported as mean values.

Following the assessment of the surface characteristics of the biochar, additional physical properties were determined, including **particle density**, **bulk density**, and **external porosity**. These parameters provide important information regarding the structure of the material at the macroscopic scale, as well as its behaviour in applications involving packed beds, filtration systems, and adsorption columns.

The particle density of the biochar was determined using a water displacement method based on a modified pycnometric approach. A known mass of oven-dried biochar was introduced into a pre-weighed volumetric flask, followed by the addition of deionised water. The suspension was gently boiled under agitation to remove entrapped air and subsequently allowed to cool to room temperature before being filled to a fixed volume. The particle density was calculated by accounting for the displaced water volume, according to:

$$\rho_{particle} = \frac{\rho_w * (W_s - W_b)}{(W_s - W_b) - [(W_{sw} - W_b) - (W_w - W_a)]} \tag{3.10}$$

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where ρ_w is the density of water at the measured temperature, Wa is the mass of the empty flask, Ww is the mass of the flask filled with water, Wb is the mass of the dried flask, Ws is the mass of the flask containing the dry sample, and Wsw is the mass of the flask containing the sample and water.

Bulk density was determined by measuring the mass and volume of the settled sample of biochar. First, the fixed amount of oven-dried material was placed in a graduated cylinder and the cylinder was tapped for a specific period until settling was completed. Then the total volume of the sample was measured, and the bulk density was computed by dividing the dry weight of the material by its volume.

Particle density and bulk density were used to determine external porosity, which refers to the fraction of interstitial space in a packed material. External porosity is essential in describing transport phenomena associated with packed beds or columns. The external porosity (ε) was determined using the following formula:

$$\varepsilon = 1 - \frac{\rho_{bulk}}{\rho_{particle}} \tag{3.11}$$

All measurements were performed on oven-dried materials to minimize effects due to water content, with results reported as means of multiple replicates.

Once the analysis of physical and surface properties was completed, the CEC was determined to assess the ability of the biochar to retain and exchange cations, which is significant for its potential use in environmental applications, such as soil improvement or adsorption, where the ability to provide an ion exchange process is desirable.

CEC was determined based on NH4OAc extraction at neutral pH (pH = 7) according to a modified technique used for biochar. Prior to extraction, pretreatment procedures were performed to diminish the effect of salt ions that might overestimate the number of exchangeable cations in the samples. Pretreatment entailed rinsing the samples with deionised water followed by adjusting pH to neutrality using dilute HCl.

Subsequently, a known mass of oven-dried biochar was extracted 4 times with 1 M NH_4OAc solution. The suspensions were agitated under controlled conditions to ensure sufficient contact between the extracting solution and the solid phase, followed by centrifugation and collection of the supernatants. Successive extractions were performed to ensure complete removal of exchangeable cations from the biochar matrix.

The collected extracts were analyzed for the predominant exchangeable cations, that is Ca2+, Mg2+, K+ and Na+, along with some chosen metals, e.g., Fe, Al, Mn, using flame atomic absorption spectroscopy (FAAS). Cation Exchange Capacity (CEC) was calculated from the sum of the extracted exchangeable cations. All values were normalized to dry mass content, and results reported are averages of triplicate measurements.

Apart from determining exchangeable cations, analysis of total metal content in solid samples (feedstock and the resultant biochar) was carried out to know more about their composition and possible effects on environment. The procedure involved microwave-assisted digestion of solid samples according to EPA method 3015A, where HNO3 was used to digest the sample.

Subsequently, concentrations of major elements, namely Ca, Mg, Na, K, Cu, were determined by FAAS. However, trace elements such as Ni, Cd, Cr, Pb, Zn and Mn, whose concentrations can be harmful to health, required more sensitive instrument due to smaller concentration ranges and low detection limits. They were measured via graphite furnace atomic absorption spectroscopy (GFAAS).

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3.5 Experimental limitations and assumptions

There are a few assumptions and limitations to make when discussing the experimental process described above for this research. The limitations mentioned in this report concern the small-scale laboratory set-up of the reactor device as well as some aspects related to measurement process.

The first limitation associated with the quantification of liquid products, namely, bio-oil, is related to its losses due to evaporation of organic compounds due to their volatile nature. In addition, there could be cases when some condensable components have managed to escape the reactor system due to incomplete capturing of such components. Besides, there can also be losses of liquid substance within the work tube and other parts of the apparatus, which may influence the results significantly.

Secondly, when considering measurement of the solid residue or biochar, there may be an issue of some solid components sticking to the walls of the work tube or other reactor components. Thus, the amount of biochar obtained can be slightly smaller than the actual amount.

Thirdly, it is also difficult to measure the amount of syngas produced. Indeed, the amount of gas produced was determined based on mass calculations of the initial sample and final samples of liquid and solid residues. Consequently, any mistake in determining the amount of the latter two substances would negatively affect the calculation of syngas yield.

Fourthly, it is also important to consider certain limitations associated with composition of syngas. Namely, there is always a constant nitrogen (N2) flow through the system with the volume of 1 L min−1. Nitrogen gas represents a considerable part of gas mixture produced, and it may result in gas mixture dilution. Yet, it is partially solved by employing gas chromatography with barrier ionization discharge detector (BID).

Lastly, there are several limitations related to operational parameters of the reactor. Low pressure (0.07 bar) and strict temperature gradient within the reactor can restrict the heat transfer.

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4 Preliminary experimental results

4.1 Overview of conducted experiments

At the current stage of the research, the experimental work should be considered preliminary and exploratory, aiming primarily at the optimization of the experimental protocol and the overall pyrolysis setup. In particular, the first series of tests was intended not only for studying the performance of dried SS under pyrolysis conditions but also for checking the validity of the experimental procedure per se. In other words, special attention was paid to achieving more stable reactor performance, improving the workflow, decreasing experimental uncertainties, and maximizing the accuracy of total mass balance calculations.

In more detail, the main focus of the pilot experiments was put on testing the effect of operating conditions, such as pyrolysis temperature, heating rate, residence time, and solvent choice for bio-oil capture. At the same time, there were also performed other experiments for assessing the effect of pretreatment techniques on sludge pyrolysis and biochar properties. Thus, the above-mentioned experiments allowed for gaining basic insights into product distribution and recovery performance.

The experiments conducted can be classified into four main categories:

- temperature variation experiments,
- residence time and heating rate variation experiments,
- solvent comparison experiments for bio-oil recovery,
- and chemically pretreated sludge experiments.

For clarity and easier reference throughout the following chapters, each experimental condition was assigned a unique experimental code.

Temperature Variation Experiments: In the first experimental series, pyrolysis temperature was investigated while maintaining constant heating rate (40 °C·min^{-1}), residence time (30 min) and solvent type. These experiments aimed to evaluate the influence of temperature on product distribution, biochar yield and bio-oil recovery.

Table 7 Toluene-based experiments

Experimental Conditions	Experimental Code
500 °C – 40 °C·min^{-1} – 30 min – Toluene	SS500-H40-R30-T
600 °C – 40 °C·min^{-1} – 30 min – Toluene	SS600-H40-R30-T
700 °C – 40 °C·min^{-1} – 30 min – Toluene	SS700-H40-R30-T
800 °C – 40 °C·min^{-1} – 30 min – Toluene	SS800-H40-R30-T
900 °C – 40 °C·min^{-1} – 30 min – Toluene	SS900-H40-R30-T

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Table 8 Ethyl lactate-based experiments

Experimental Conditions	Experimental Code
500 °C – 40 °C·min^{-1} – 30 min – Ethyl Lactate	SS500-H40-R30-EL
600 °C – 40 °C·min^{-1} – 30 min – Ethyl Lactate	SS600-H40-R30-EL
700 °C – 40 °C·min^{-1} – 30 min – Ethyl Lactate	SS700-H40-R30-EL
800 °C – 40 °C·min^{-1} – 30 min – Ethyl Lactate	SS800-H40-R30-EL

These experiments allowed the evaluation of temperature effects under otherwise identical operating conditions, while simultaneously enabling a preliminary comparison between two different solvents used for bio-oil trapping.

Heating Rate and Residence Time Experiments: A second experimental series was conducted to investigate the effect of heating rate and residence time while maintaining constant temperature and solvent type. These experiments were designed to examine how changes in thermal severity and vapour residence conditions influence pyrolysis behaviour, product formation and mass balance closure.

Table 9 Effect of heating rate and residence time experiments

Experimental Conditions	Experimental Code
500 °C – 40 °C·min^{-1} – 15 min – Toluene	SS500-H40-R15-T
500 °C – 80 °C·min^{-1} – 15 min – Toluene	SS500-H80-R15-T
500 °C – 40 °C·min^{-1} – 60 min – Toluene	SS500-H40-R60-T

Solvent Comparison Experiments: An additional experimental series focused specifically on the influence of different condensation solvents on bio-oil recovery efficiency. In these experiments, all pyrolysis conditions remained constant (800 °C, 80 °C·min^{-1}, 15 min), while only the solvent used in the trapping system was varied. The purpose of this experimental group was to evaluate the ability of different solvents to capture condensable pyrolysis vapours and maximize bio-oil recovery. The experiments also provide insight into solvent polarity effects and potential selectivity toward different bio-oil fractions.

Table 10 Solvent Comparison Experiments

Experimental Conditions	Experimental Code
Toluene	SS800-H80-R15-T
Ethyl Lactate	SS800-H80-R15-EL
Ethyl Acetate	SS800-H80-R15-EA
Isopropanol	SS800-H80-R15-IPA

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Hexane	SS800-H80-R15-HX
Acetone	SS800-H80-R15-AC
No solvent	SS800-H80-R15-NS

Pretreated Sludge Experiments: Finally, a separate experimental series was conducted using chemically pretreated SS prior to pyrolysis. The aim was to investigate how pretreatment affects sludge structure, inorganic composition and ultimately pyrolysis product characteristics.

Acid pretreatment (HCl): For the acid pretreatment experiments, dried and sieved SS was treated with 0.5 M HCl at 60 °C for 1 h. Following treatment, the solid residue was filtered and repeatedly washed with deionized water until the filtrate pH approached neutrality. The material was subsequently dried at 105 °C prior to pyrolysis. The purpose of the acid pretreatment was primarily to partially remove inorganic components and modify the mineral composition of the sludge prior to pyrolysis.

Table 11 Acid pretreatment Experiments

Experimental Conditions	Experimental Code
500 °C – 40 °C·min^{-1} – 30 min – EL – HCl pretreatment	SS500-H40-R30-EL-HCl
600 °C – 40 °C·min^{-1} – 30 min – EL – HCl pretreatment	SS600-H40-R30-EL-HCl
700 °C – 40 °C·min^{-1} – 30 min – EL – HCl pretreatment	SS700-H40-R30-EL-HCl

Alkaline pretreatment (KOH activation): For the alkaline pretreatment experiments, KOH pellets were ground into powder and physically mixed with dried SS at a KOH:SS ratio of 1:4 prior to pyrolysis. After pyrolysis, the produced biochar was cooled under nitrogen atmosphere and subsequently washed with 0.1 M HCl followed by distilled water until neutral pH was achieved. The washed material was then dried at 105 °C for 5–6 h and stored in airtight containers. Biochar yield calculations were performed after the washing procedure in order to exclude residual activating agents and inorganic residues. These experiments aimed to investigate the effect of chemical activation on pore development, biochar structure and product yields, particularly regarding the enhancement of SSA and adsorption-related properties.

Table 12 Alkaline pretreatment Experiments

Experimental Conditions	Experimental Code
500 °C – 40 °C·min^{-1} – 30 min – EL – KOH pretreatment	SS500-H40-R30-EL-KOH
600 °C – 40 °C·min^{-1} – 30 min – EL – KOH pretreatment	SS600-H40-R30-EL-KOH
700 °C – 40 °C·min^{-1} – 30 min – EL – KOH pretreatment	SS700-H40-R30-EL-KOH

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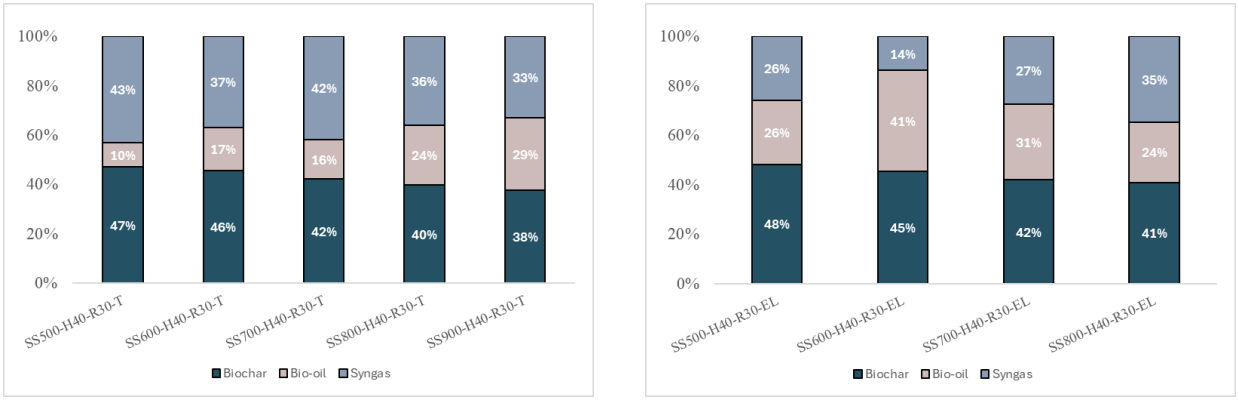
4.2 Product yields and mass balance

The preliminary product distribution results are presented in Figures 21–23. The mass balance calculation approach has been described in the previous methodological section. Since these experiments represent an initial experimental campaign, the results are interpreted as indicative trends, aiming to provide a first evaluation of the influence of pyrolysis temperature, condensation solvent and chemical pretreatment on the relative distribution of biochar, bio-oil and syngas.

As shown in Figure 21, pyrolysis temperature affected product distribution differently depending on the solvent used for the recovery of the condensable fraction. In the experiments conducted with toluene as the condensation solvent, biochar yield gradually decreased from 47% at 500 °C to 38% at 900 °C. This reduction can be attributed to the enhanced devolatilization and thermal decomposition of the organic fraction at higher temperatures, resulting in lower solid residue formation. At the same time, the recovered bio-oil fraction increased from 10% at 500 °C to 29% at 900 °C, suggesting that higher temperatures promoted the formation and/or recovery of condensable pyrolysis products under these conditions. The calculated syngas fraction showed a corresponding decrease from 43% to 33%, although this trend should be interpreted in relation to the increased measured liquid recovery.

A different trend was observed when ethyl lactate was used as the condensation solvent. In this case, biochar yield also decreased with increasing temperature, from 48% at 500 °C to 41% at 800 °C, confirming the general effect of temperature on solid residue reduction. However, the bio-oil yield reached a maximum at 600 °C, where it accounted for 41% of the initial dried sludge mass. Above this temperature, the bio-oil fraction decreased to 31% at 700 °C and 24% at 800 °C, while the calculated syngas fraction increased. This behaviour indicates that intermediate temperatures favoured the recovery of condensable vapours, whereas higher temperatures likely enhanced secondary cracking reactions, shifting part of the liquid-forming compounds toward non-condensable gases.

The comparison between the two solvents in Figure 21 also highlights the importance of solvent selection in the recovery of bio-oil. Ethyl lactate resulted in substantially higher bio-oil recovery than toluene at 500–700 °C, while at 800 °C the difference between the two solvents became less pronounced. This suggests that ethyl lactate may be more effective in trapping polar and oxygenated compounds present in sewage sludge-derived pyrolysis vapours, especially at lower and intermediate pyrolysis temperatures.



(a) (b)

Figure 21 Effect of Pyrolysis Temperature on Product Distribution Using Different Condensation Solvents: (a) Toluene and (b) Ethyl Lactate

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The effect of condensation solvent was further investigated under fixed pyrolysis conditions, namely 800 °C, 80 °C·min^{-1} and 15 min residence time, as presented in Figure 22. Under these conditions, biochar yield remained practically stable, ranging between 40.0% and 41.0%. The observed differences were mainly associated with the recovered bio-oil fraction. Ethyl lactate showed the highest bio-oil recovery, with a yield of 24.4%, followed by isopropanol, toluene and ethyl acetate. The lowest bio-oil recovery was observed in the experiment without solvent, where the bio-oil fraction reached 21.6%. Although the differences are not very large, the results confirm that the use of a condensation solvent improves liquid recovery and that solvent properties can influence the efficiency of bio-oil trapping.

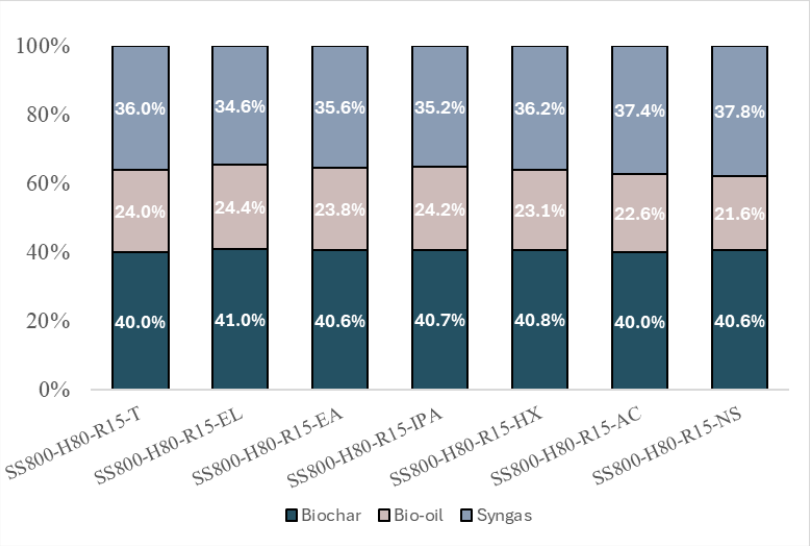


Figure 22 Influence of Condensation Solvent on Bio-oil Recovery

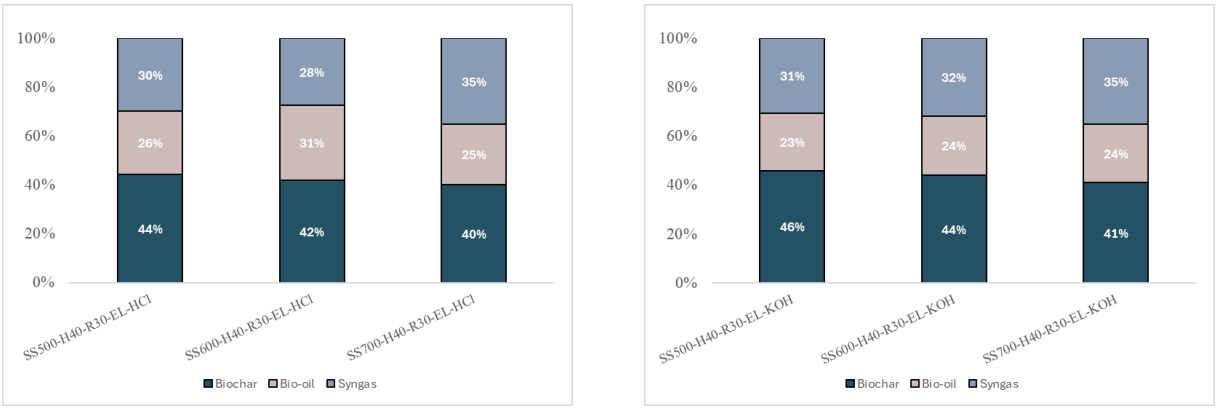
The influence of chemical pretreatment on product distribution is presented in Figure 23. For the HCl-pretreated SS, biochar yield decreased from 44% at 500 °C to 40% at 700 °C, following the expected trend of increased devolatilization with temperature. Compared to the corresponding non-pretreated experiments using ethyl lactate as condensation solvent (Figure 21b), the HCl-treated samples exhibited lower biochar yields and generally higher bio-oil recovery, particularly at 600 °C, where the liquid fraction increased from 41% in the untreated sample to 31% after pretreatment while the gas fraction increased substantially. This behaviour suggests that acid pretreatment alters the inorganic composition and mineral content of the sludge, potentially promoting the release of volatile compounds and modifying secondary cracking reactions during pyrolysis. The partial removal of inorganic phases prior to pyrolysis may also reduce catalytic char-forming reactions, favouring the formation of condensable products at intermediate temperatures.

For the KOH-pretreated samples, biochar yield decreased from 46% at 500 °C to 41% at 700 °C, while the bio-oil fraction remained relatively stable, ranging between 23% and 24%. Compared to the untreated ethyl lactate experiments, the KOH-pretreated samples showed slightly higher biochar yields and lower bio-oil recovery across the investigated temperature range. This difference was particularly noticeable at 600 °C, where the untreated sample exhibited the maximum liquid yield of 41%, whereas the KOH-pretreated sample remained at approximately 24%. At the same time, the calculated syngas fraction increased gradually from 31% to 35% with increasing temperature. The observed behaviour may be associated with the activation effect of KOH, which promotes structural rearrangement and carbon retention within the solid matrix during

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pyrolysis. Moreover, the combination of KOH with the organic structure of SS can cause carbonization reactions and affect the profile of volatiles being produced, thus helping to achieve the stable liquid products obtained after the pretreatment process.



(a) (b)

Figure 23 Effect of Chemical Pretreatment on Product Distribution: (a) HCl Pretreatment and (b) KOH Pretreatment

The results obtained thus far indicate that the main product is biochar, representing about 38% to 48% of all products. It was identified that the temperature had a major effect on the product yield. Specifically, the increased thermal intensity was associated with the decreased biochar formation. The bio-oil yield showed dependency on both temperature and solvent used; ethyl lactate appears to be promising for the range of moderate temperatures. The chemical pretreatment affected the product yield as well – while HCl pretreatment resulted in a higher bio-oil yield at 600°C, KOH pretreatment led to a stable bio-oil yield and higher biochar formation.

Overall, these results serve as a starting point for optimization of the process and choice of the appropriate parameters for further analysis. It is worth mentioning, however, that, since no gas product yields were directly measured, future experiments should include their estimation and analysis as well.

4.3 Biochar preliminary characterization

Following the evaluation of product yields and mass balance, the produced biochar samples were subjected to a preliminary characterization in order to assess their main physicochemical, structural and compositional properties. The preliminary characterization results are presented in Tables 13–14 and Figures 24–31. At this stage, the obtained results are used primarily to evaluate the applicability and reliability of the selected analytical protocols, identify first trends among the produced materials and assess the influence of pyrolysis conditions on the resulting biochar properties. In parallel, the analyses provide useful insights regarding experimental limitations, methodological uncertainties and parameters requiring further investigation and optimization in subsequent experimental phases. Since the characterization is still at an early stage, the results should be interpreted as indicative rather than definitive.

As an initial step of the biochar characterization, proximate analysis was performed in order to evaluate the main compositional changes occurring after pyrolysis and to obtain a first indication of the thermal conversion efficiency of the SS. Emphasis was given to the evolution of volatile matter, ash content and fixed carbon, since these parameters are directly related to devolatilization behaviour and the enrichment of

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inorganic constituents within the produced biochar matrix. The proximate analysis results of the raw SS and selected biochar samples are presented in Table 13.

The raw SS exhibited a moisture content of 8.3%, total solids of 91.7%, volatile matter of 60.4%, fixed carbon of 1.4% and ash content of 38.2%. After pyrolysis, a clear reduction in volatile matter was observed, confirming the thermal decomposition and devolatilization of the organic fraction during the process. In the produced biochars, volatile matter decreased substantially, ranging from 31.1% for SS500-H80-R15 to 20.2% for SS800-H40-R30. This decrease was generally more pronounced at higher pyrolysis temperatures, indicating more extensive removal of volatile compounds.

At the same time, ash content increased considerably after pyrolysis, reaching values between 67.9% and 79.4%, compared to 38.2% in the raw sludge. This increase is expected, as the organic fraction is progressively removed during pyrolysis, while inorganic constituents are retained and concentrated in the solid residue. The highest ash content was observed for SS800-H40-R30, suggesting that higher temperature treatment enhances the relative enrichment of mineral matter. Fixed carbon values remained low in all samples, ranging between 0.4% and 1.0%. This is consistent with the highly inorganic nature of sewage sludge-derived biochar, although fixed carbon determination in ash-rich materials should be interpreted cautiously, since inorganic oxidation and high mineral content may affect the accuracy of proximate calculations.

Table 13 Proximate Analysis of Sewage Sludge and Biochar Samples

	Moisture	Total solids	Volatile matter [a]	Fixed Carbon[a]	Ash[a]
SS	8.3%	91.7%	60.4%	1.4%	38.2%
SS500-H40-R15	9.8%	90.2%	28.6%	0.8%	70.6%
SS500-H80-R15	7.3%	92.7%	31.1%	1.0%	67.9%
SS500-H40-R60	11.0%	89.0%	26.0%	0.6%	73.4%
SS600-H40-R30	6.0%	94.0%	26.6%	0.9%	72.5%
SS700-H40-R30	6.0%	94.0%	24.3%	0.6%	75.1%
SS800-H40-R30	7.6%	92.4%	20.2%	0.4%	79.4%

[a]On a dry basis.

Following proximate analysis, additional characterization focused on the surface chemistry and electrochemical properties of the produced biochars, since parameters such as pH, EC and point of zero charge strongly influence the environmental behaviour, adsorption potential and interaction of the material with dissolved species. The corresponding results are presented in Table 14.

The raw SS showed a near-neutral pH of 7.42 and pHpzc of 7.55. After pyrolysis, the pH of the produced biochars generally increased, indicating the development of alkaline character. Samples produced at 500 °C exhibited mildly alkaline pH values around 8.0–8.5, while a sharp increase was observed at higher temperatures, with pH values reaching 11.11 at 600 °C and approximately 12.5 at 700–800 °C. This trend can

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be attributed to the decomposition of acidic organic groups and the concentration of alkaline inorganic phases, such as Ca, Mg, Na and K containing compounds, in the biochar matrix.

A similar trend was observed for pHpzc, which increased from approximately 8.1–8.4 in the 500 °C samples to around 12.0 for the 700–800 °C biochars. This indicates that the surface charge behaviour of the material is strongly affected by pyrolysis temperature. The determination of pHpzc is important because it defines the pH at which the net surface charge of the biochar is zero. Below this value, the surface tends to be positively charged, whereas above it, the surface becomes negatively charged. Figure 24 illustrates the determination of pHpzc through the ΔpH method, where the point of zero charge corresponds to the intersection of the curve with ΔpH = 0. This parameter is particularly relevant for adsorption applications, as it influences the interaction of biochar with ionic contaminants.

Electrical conductivity showed more variable behaviour. Compared to the raw SS, which exhibited an EC of 1736 µS/cm, most biochar samples produced at 500–600 °C showed lower EC values, between 557 and 660 µS/cm. However, a sharp increase was observed for the samples produced at 700 and 800 °C, with EC values of 9010 and 8320 µS/cm, respectively. This suggests an increased release or concentration of soluble inorganic salts at these temperatures. The decrease observed again at 900 °C may indicate changes in mineral speciation, volatilization or reduced solubility of certain inorganic compounds, although this trend requires further confirmation.

Table 14 pH, pHpzc and EC of Sewage Sludge and Biochar Samples

	pH	pHpzc	EC (mS/cm)
SS	7.42	7.55	1736
SS500-H40-R15	8.07	8.35	614
SS500-H80-R15	8.02	8.09	615
SS500-H40-R60	8.51	8.34	557
SS600-H40-R30	11.11	9.63	660
SS700-H40-R30	12.47	11.97	9010
SS800-H40-R30	12.46	12.01	8320
SS900-H40-R30	10.49	9.81	608

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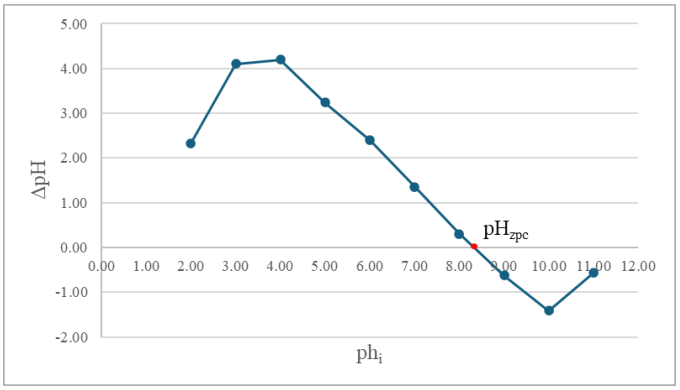


Figure 24 Determination of pHpzc of SS500-H40-R15

In addition to pH and surface charge measurements, total alkalinity was also evaluated in order to further assess the buffering capacity and alkaline nature of the produced biochars. Since sewage sludge-derived biochars contain high amounts of inorganic mineral phases, alkalinity constitutes an important parameter influencing both environmental behaviour and potential applications. The TA results are presented in Figure 25. The produced biochar samples exhibited high alkalinity values, generally ranging between approximately 850 and 1100 mg $CaCO_3$/g. A gradual increase was observed with increasing pyrolysis temperature, particularly from 600 °C onwards. This trend is consistent with the pH results and further confirms the increasing alkaline character of the biochar at higher treatment temperatures. The high alkalinity of sewage sludge-derived biochar is mainly associated with the concentration of carbonate, oxide and hydroxide mineral phases, particularly those containing Ca and Mg. From an application perspective, this property may be relevant for pH buffering and soil amendment applications, although it also indicates the need for careful evaluation before use in systems where strong alkalinity may be undesirable.

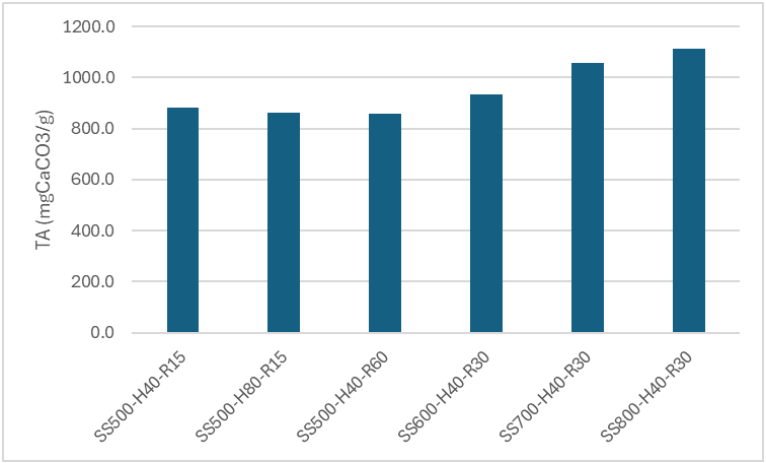


Figure 25 Total Alkalinity (TA) of the Produced Biochar Samples

Since surface-related properties play a critical role in adsorption processes and environmental applications, preliminary evaluation of the SSA of the produced biochars was also performed. In the present study, SSA was estimated using the methylene blue adsorption method combined with Langmuir isotherm analysis. The corresponding results are presented in Figures 26 and 27. The SSA of the produced biochars, determined using the methylene blue adsorption method, is presented in Figure 26. The results indicate that surface area was strongly affected by pyrolysis conditions and pretreatment. For the non-pretreated samples, the SSA

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increased from approximately 26 m²/g for SS500-H40-R15 to 67 m²/g and 75 m²/g for SS700-H40-R30 and SS800-H40-R30, respectively. This increase can be attributed to the progressive release of volatile compounds and the development of pore structure at higher temperatures. However, the sample produced at 900 °C exhibited a substantially lower surface area, around 20 m²/g, suggesting that excessive temperature may lead to pore collapse, sintering or structural rearrangement of the carbon-mineral matrix.

The effect of pretreatment was also evident. The HCl-treated sample showed a higher surface area than the corresponding untreated sample produced at 500 °C, while the HCl-UB sample, where the acid pretreatment was combined with ultrasonic bath treatment, reached one of the highest SSA values among the tested materials. This behaviour suggests that acid treatment may enhance surface development through partial removal of inorganic phases and increased pore accessibility, while the additional ultrasonic treatment may further promote structural disruption and opening of blocked pores, improving the exposure of internal surface sites.

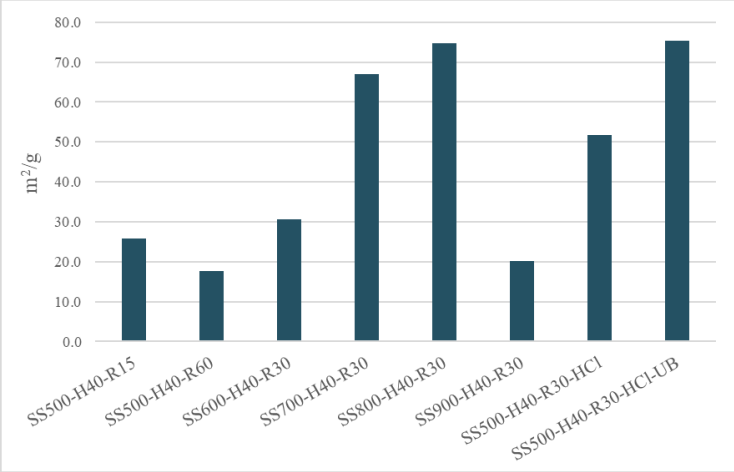


Figure 26 Specific Surface Area of the Produced Biochar Samples Determined by the Methylene Blue Method

Figure 27 presents an example of the Langmuir adsorption analysis used for the determination of the methylene blue adsorption capacity of the SS800-H40-R30 biochar. The linearized Langmuir plot was used to determine the maximum adsorption capacity, q_m, which was then used for the calculation of SSA. The good linear fit, with $R^2 = 0.9755$, indicates that the Langmuir model provides a satisfactory approximation for this sample. The corresponding isotherm also shows the typical tendency toward saturation, supporting the assumption of finite adsorption sites on the biochar surface.

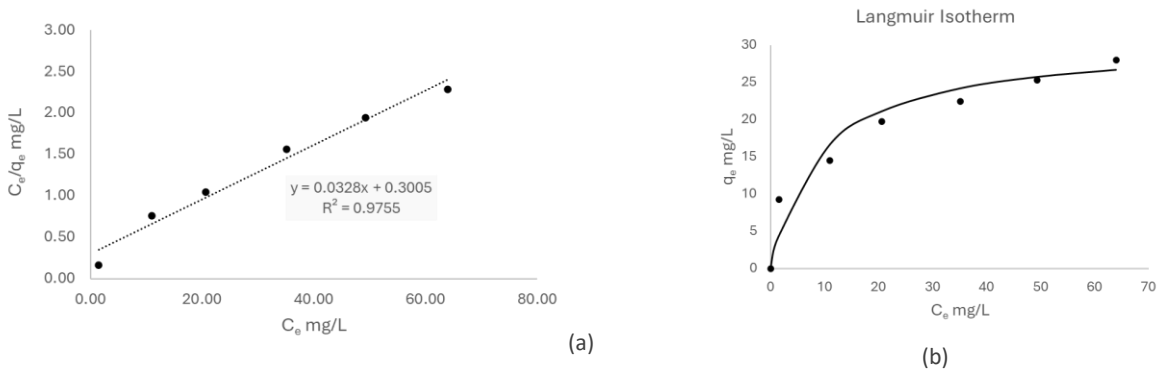


Figure 27 Langmuir Adsorption Analysis of SS800-H40-R30 Biochar: (a) Linearized Plot and (b) Langmuir Isotherm

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In addition to chemical and surface-related characterization, selected physical properties of the produced biochars were also evaluated, since parameters such as density and porosity strongly influence material handling, packing behaviour and potential adsorption performance. The corresponding results are presented in Figure 28. The physical properties of the produced biochars are presented in Figure 25, including bulk density, particle density and external porosity. Bulk density remained relatively stable among the samples, generally close to 600 kg/m³. In contrast, particle density was considerably higher, reflecting the mineral-rich nature of sewage sludge-derived biochar. External porosity values were also high, generally ranging around 0.69–0.75, indicating that the produced materials possess a porous structure. These properties are important for practical applications, as they influence packing behaviour, hydraulic performance, adsorption contact efficiency and handling characteristics. However, bulk density and porosity measurements can be affected by particle size distribution and sample packing, and therefore should be further validated in future tests.

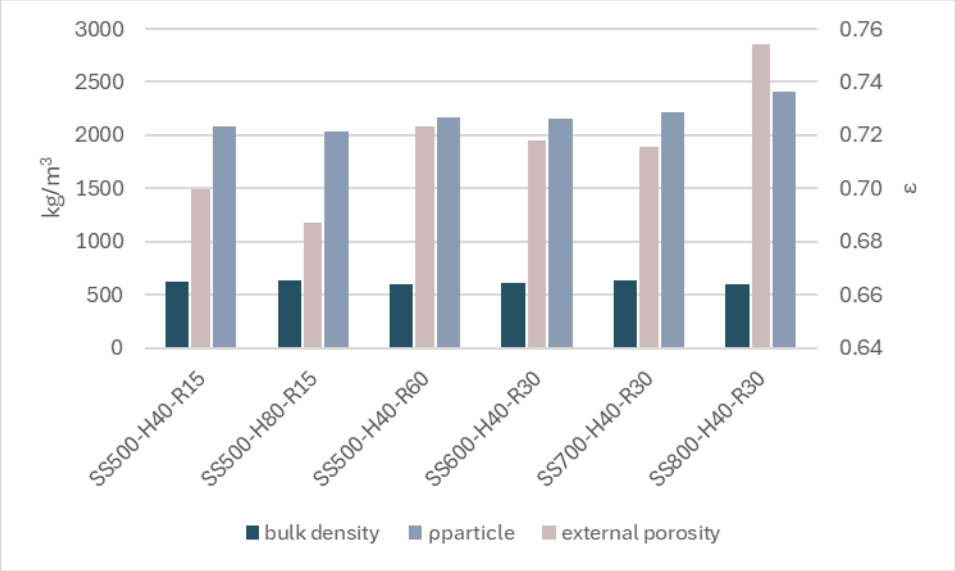


Figure 28 Bulk Density, Particle Density and External Porosity of the Produced Biochar Samples

To determine further surface reactivity and ion exchange properties of the synthesized biochars, the cation exchange capacity (CEC) was measured. As CEC values correlate directly with adsorptive properties, nutrient retention ability, and reactivity with other ionic compounds, they are considered an important parameter when assessing environmental applicability of the studied biochars. Figure 29 shows the relative influence of major exchangeable cations on the overall CEC value for the tested biochars.

Calcium was found to be the main exchangeable cation for all investigated biochar samples followed by magnesium and, to a lesser degree, potassium and sodium ions. The identified ratio corresponds to the mineral composition and high alkalinity value of biochar synthesized from sewage sludge. An insignificant increase in overall CEC can be detected depending on the increasing pyrolysis temperature, indicating the possible influence of temperature on the abundance of exchangeable sites and presence of alkaline minerals in the biochar matrix. As the dominant exchange cations are calcium and magnesium, the exchange process occurring at the biochar surfaces should primarily involve alkaline earth elements.

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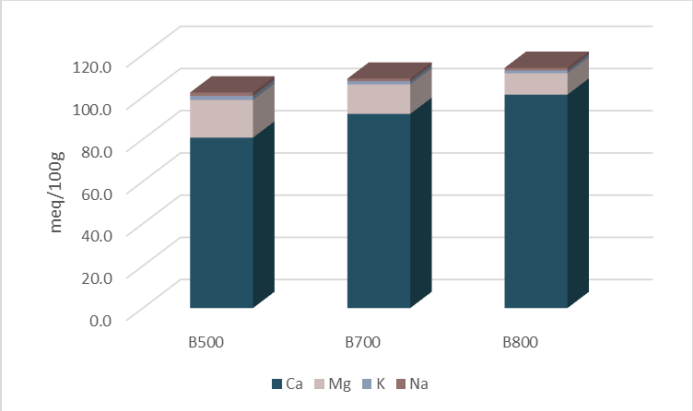


Figure 29 CEC Composition of the Produced Biochar Samples

Finally, the inorganic composition of the raw SS and biochar samples is presented in Figures 30 and 31. Figure 31 shows the major inorganic elements, including Ca, Mg, Na and K. The results indicate a clear enrichment of these elements in the biochar samples compared to raw SS, with calcium being by far the dominant component. This trend follows the increase in ash content and confirms the concentration of inorganic matter during pyrolysis. The increase in Ca and Mg is also consistent with the observed increase in pH, pHpzc and TA.

Heavy metal concentrations are presented in Figure 30. Compared to raw SS, most biochar samples showed higher metal concentrations, mainly due to the mass loss of organic matter during pyrolysis and the consequent concentration of inorganic elements in the solid residue. Zinc appeared to be the dominant heavy metal fraction, while Cu, Cr, Pb and Mn were also present in measurable quantities. This finding is particularly important for the potential application of sewage sludge-derived biochar, as the presence of heavy metals may restrict certain uses, especially direct soil application. At the same time, the retention of metals in the solid phase may also indicate immobilization during pyrolysis, which can be beneficial from a stabilization perspective, provided that leaching behaviour is properly assessed.

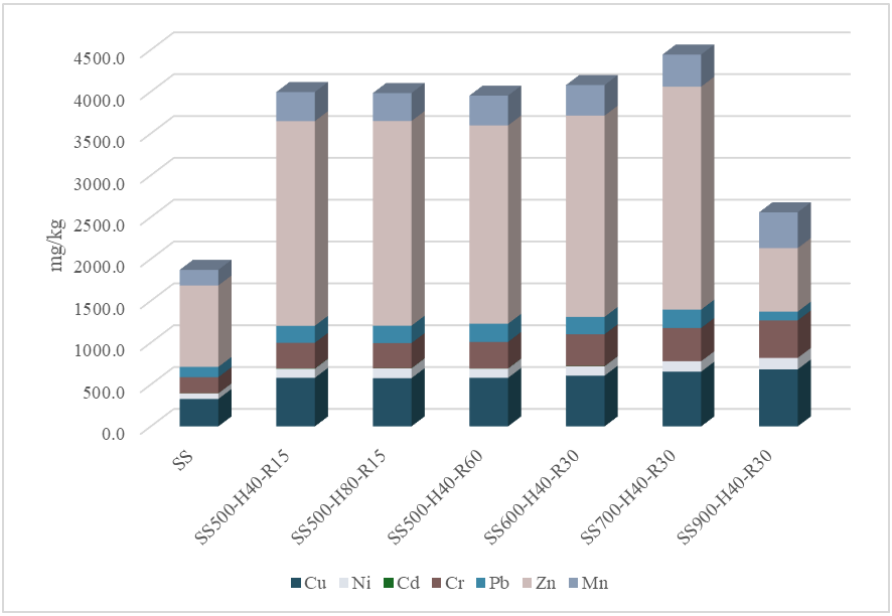


Figure 30 Heavy Metal Concentrations in Raw Sewage Sludge and Produced Biochar Samples

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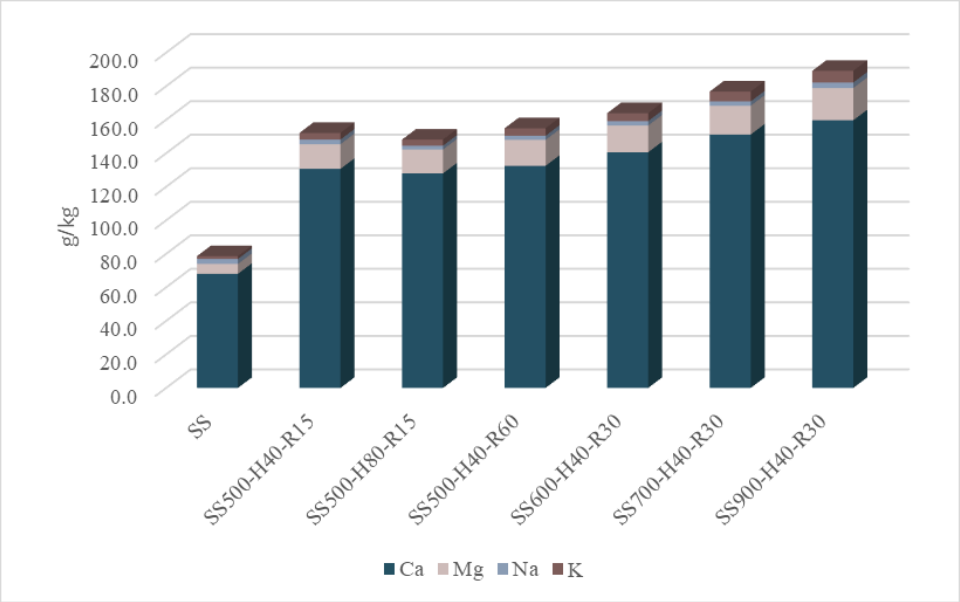


Figure 31 Major Inorganic Elements in Sewage Sludge and Biochar Samples

Taken together, the preliminary characterization results confirm that SS pyrolysis produces a highly mineral-rich, alkaline and structurally porous biochar. Increasing pyrolysis temperature generally reduced volatile matter, increased ash content, enhanced alkalinity and promoted surface area development up to an optimum range around 700–800 °C. However, very high temperature treatment may reduce surface area and modify soluble salt behaviour. The results also highlight the importance of inorganic composition and heavy metal content, which must be further evaluated through leaching tests and safety assessment before considering specific applications. Overall, the preliminary data provide useful first insights into the behaviour of sewage sludge-derived biochar and support the need for further characterization, including repeated measurements, direct comparison of pretreatment effects and more detailed assessment of adsorption performance and environmental safety.

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5 Conclusions

5.1 Conclusions & Next Steps

In this deliverable we present the preliminary results obtained in the course of our research on the valorisation of sewage sludge (SS) in the Attica region performed under the THESEUS project, in particular Task 7.5. In this part of the project, the first results on the valorisation of sewage sludge have been presented, based on which we were able to establish scientific foundations for carrying out studies in the field of thermochemical transformation of sewage sludge, in particular, pyrolysis.

Review of the literature indicates that SS could be viewed as a source of organic matter, nutrients, inorganic compounds, and even energy resources. Valorisation of SS faces various challenges associated with high variability of its composition, high moisture content, ash, etc. In light of this situation, thermochemical methods are considered promising alternatives to traditional management technologies for sewage sludge as they allow volume reduction, stabilisation, and obtaining multiple fractions – from biochar to syngas.

The review of pyrolysis characteristics demonstrates that the amount and quality of the end products vary considerably depending on the temperature, heating rate, time, feedstock, reactor type, and other factors. In particular, sewage sludge pyrolysis products, namely biochar, are attractive due to their high content of organic substances (carbon and mineral substances), alkaline pH and porosity. On the other hand, bio-oil and syngas can serve as valuable products as well. They require subsequent upgrading to be usable.

In terms of legislation and economic aspects, the European Union and different countries promote recovery and reuse of sewage sludge nowadays. However, there are no specific rules concerning products of pyrolysis of sewage sludge. They depend on the usage of the products obtained.

Our work discusses the experimental setup for pyrolysis of sewage sludge. Its goals include checking the feasibility of this procedure, optimizing the setup parameters and products collection, assessing the mass balance approach. In addition, we analyzed the influence of pyrolysis temperature, condensation solvent, heating regimes and pre-treatment by chemicals on this process.

It has been found that several fractions of products can occur during sewage sludge pyrolysis, and their amounts depend on the experimental conditions. It should be noted that biochar is generated predominantly compared to gas and liquid fractions. The liquid fraction dominates among liquids. The rise of the pyrolysis temperature leads to the reduction of biochar amount. Also, it influences considerably on the amounts of gas and bio-oil. The role of condensation solvent cannot be underestimated. In this study, ethyl lactate has proved itself very effectively.

Moreover, chemical pre-treatment has shown to affect considerably the amount of biochar and bio-oil produced. Depending on the used reagents, different trends in the change of the yields of the obtained products have been observed. Thus, this is a very important point which needs to be considered further.

First results on characterisation of sewage sludge derived biochar indicate its high potential. Namely, it should be noted that obtained biochar contains considerable amounts of ash, has high pH, and high alkalinity, and it is rich in minerals. With increasing temperature of pyrolysis, the amounts of volatile matter decrease, and the amounts of minerals increase, which also affects some other characteristic features of the obtained material, in particular, pHpzc, electric conductivity (EC), and specific surface area (SSA).

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The use of methylene blue adsorption method for the preliminary assessment of SSA demonstrated that the highest values can be reached using samples of biochar treated with acids at intermediate temperatures. Finally, it needs to be mentioned that high content of heavy metals in the produced solid fraction requires additional investigation, which should be performed for the sake of safety.

To summarise, pyrolysis emerges as a potentially promising technique for the valorisation of sewage sludge produced in the Attica region. As seen from the preliminary results presented, the process can produce multiple recoverable products from dried SS, whereas produced biochar has all the required characteristics and potential for application.

However, due to preliminary nature of the results, it is required to perform additional experiments for confirmation and repetition of the results and for more accurate analysis of the process and product characteristics. Moreover, it is required to investigate in detail the potential and safety of the products obtained in the process of pyrolysis.

The next steps in the task will involve conducting additional experiments with the setup. The goal will be the confirmation of repeatability of obtained results, their analysis in more details and optimisation of the process parameters. Mass balance calculations will include measuring and accounting of the gas produced during pyrolysis.

In addition, further analysis of the obtained fractions will be carried out, namely, bio-oil composition will be evaluated, and the contents of volatile matter will be estimated, and, finally, syngas composition will be determined via GC-BID. Moreover, the physical and chemical properties of the obtained biochars will be investigated in more details.

Further attention will be paid to investigation of the safety and applicability of the obtained products and their potential for various applications, in particular, assessment of their adsorbing ability and heavy metal content.

Finally, the results of the experiments will be connected with techno-economics and other related aspects to evaluate and compare different valorisation routes of SS in the Attica region.

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