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Master's Degree in Energy Engineering

# **Comparison of energy performance of different biomass conversion processes**

Master's Degree Thesis

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# List of Abbreviations

GHG	Greenhouse Gases
GHE	Greenhouse Effect
H <sub>2</sub> O	Water Vapour
CO <sub>2</sub>	Carbon Dioxide
H <sub>2</sub>	Hydrogen
N <sub>2</sub> O	Nitrous Oxide
CH <sub>4</sub>	Methane
O <sub>3</sub>	Ozone
SF <sub>6</sub>	Sulphur Hexafluoride
HFCs	Hydrofluorocarbons
NH <sub>3</sub>	Ammonia
PFCs	Perfluorocarbons
NF <sub>3</sub>	Nitrogen Trifluoride
GWP	Global Warming Potential
IEA	International Energy Agency
ESG	Environmental, Social and Governance
SSPs	Shared Socioeconomic Pathways
IPCC	Intergovernmental Panel on Climate Change
UNFCCC	United Nations Framework Convention on Climate Change
COP	Conference of the Parties
CHP	Combined Heat and Power
RED	Renewable Energy Directive
FPBO	Fast Pyrolysis Bio-oil
HTL	Hydrothermal Liquefaction

SVO	Straight Vegetable Oils
AD	Anaerobic Digestion
EGD	European Green Deal
ICE	Internal Combustion Engines
CNG	Compressed Natural Gas
LPG	Liquified Natural Gas
FT	Fisher-Tropsch
MSW	Municipal Solid Waste
LCFA	Long Chain Fatty Acids
VFA	Volatile Fatty Acids
SCFA	Short-Chain Fatty Acids
TS	Total Solids
VS	Volatile Solids
COD	Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
BMP	Biomethane potential or Biochemical Methane Potential
OLR	Organic Loading Rate
CSTR	Countinous Stirred Tank Reactors
UASB	Upflow Anaerobic Sludge Blanket
AFB	Anaerobic Fluidized Bed
FB	Fluidized Bed Reactor
IC	Internal Circuit Reactor
EGSB	Expanded Granular Sludge Blanket
PFR	Plug-flow reactor
ASBR	Anaerobic sequencing Batch Reactor
HSAD	High Solids Digestate
HVV	Higher Heating Value
SOFC	Solid Oxide Fuel Cell



# Abstract

The growing problem of greenhouse gas (GHG) emissions and global warming makes replacing fossil fuels with sustainable energy sources, such as biomass, a crucial priority for the global energy transition.

This master's thesis aims to collect, standardize, and compare the operating parameters and performance results from the most recent and relevant scientific literature for two of the main biomass conversion technologies: Anaerobic Digestion (AD) and Pyrolysis. The aim was to create an organized database to highlight the correlations between operating conditions, feedstock characteristics, and yields obtained, with the intention of supporting the formulation of policy and industrial guidelines.

The methodology involved a systematic review of the literature, selecting different process setups for AD and Pyrolysis, most of which were laboratory-scale experiments. The data were manipulated and standardized to allow for consistent comparison, focusing on feedstock properties, process parameters (temperature, scale, and residence time), and final product yields (biomethane, biochar, bio-oil, and gas).

The results showed that, for anaerobic digestion, mesophilic processes (35-37 °C) and a retention time of approximately 30-35 days are the norm. In summary, mesophilic processes ( $\approx 35\text{--}37$  °C) are more widely used than thermophilic processes ( $\approx 50\text{--}55$  °C), mainly for reasons of stability, robustness, and operating costs. In fact, mesophilic microbial consortia (methanogenic bacteria and archaea) are more resistant to fluctuations in temperature, pH, and organic load. Average biomethane yields were highest for animal feedstock and agricultural waste (approximately 350 L<sub>bioCH<sub>4</sub></sub>/kg<sub>DM</sub> in the case of animal feedstock), with commercial-scale plants demonstrating a significantly higher average yield (240 L<sub>bioCH<sub>4</sub></sub>/kg<sub>DM</sub>) than laboratory experiments (177 L<sub>bioCH<sub>4</sub></sub>/kg<sub>DM</sub>). Despite the variability of biomass (complex organic molecules) and the diversity of plants,

commercial-scale plants can benefit from more stable and well-established microbial consortia and longer adaptation times.

For pyrolysis, agricultural waste is the most commonly used feedstock (approximately 51% of cases studied). The average biochar yield was highest for sewage sludge due to the higher content of inorganic matter (ash) (biochar yield over 50 % by weight), while AD digestate was the most efficient in maximizing gas production (approximately 35% by weight of the products), which is useful for the subsequent production of biomethane or hydrogen.

This work provides a database and comparative analysis that can guide strategic choices for optimizing biomass use, helping to select the most suitable conversion technology and feedstock for the desired energy objective.

# Chapter 1

## Introduction

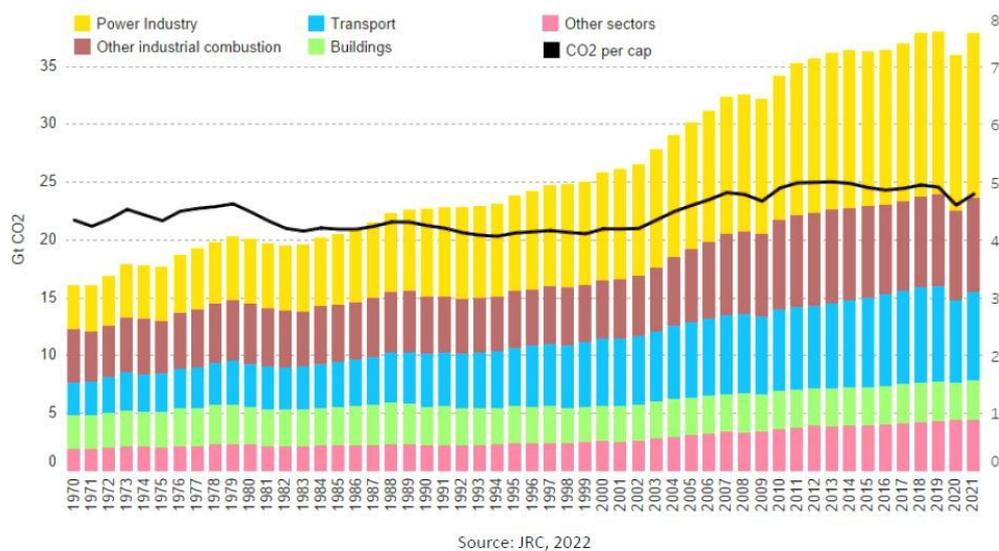
### 1.1 Greenhouse gas emissions and global warming

Greenhouse gases (GHG) are gaseous present in the atmosphere, both of natural and anthropogenic origin, that absorb the sun's heat, under the form of radiation that has a specific wavelength within the spectrum of thermal infrared radiation, that radiated from the Earth's surface, trapping it in the atmosphere not allowing it to exit into space. This property causes the greenhouse effect (GHE) [1]. As a consequence of the GHG effect, as mentioned above, heat cannot escape from the atmosphere, causing a rise in temperatures with effects on the climate of the planet, resulting in increasingly extreme and severe weather phenomena, on the lives of people, animals and vegetation.

Carbon dioxide ( $\text{CO}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), methane ( $\text{CH}_4$ ), water vapour ( $\text{H}_2\text{O}$ ), and ozone ( $\text{O}_3$ ) are the primary greenhouse gases in the Earth's atmosphere. Besides  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_4$ , the Kyoto Protocol, an international agreement signed in 1997 dedicated to set targets for reducing GHG emissions, deals with gases such as the fluorinated greenhouse gases (F-gases) that include sulphur hexafluoride ( $\text{SF}_6$ ), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and nitrogen trifluoride ( $\text{NF}_3$ ). Despite greenhouse-gases have a high global warming potential (GWP), they are used as a substitute for substances that

damage the atmospheric ozone layer because they do not harm this layer. [1]

All the gases cited before contribute to the GHE but some of them are emitted in larger quantities with respect to the others. As it is possible to see from the Figure 1, the larger share in GHG emitted is covered by the CO<sub>2</sub> that can have different sources as industrial processes and the process of production and consumption of the fossil fuels (coal, natural gas, oil) [2]. Figure 1 also shows that, from 1970 to 2021, the two sectors with the largest increase in CO<sub>2</sub> emissions are the power industry and transport. It should also be noted that CO<sub>2</sub> production per capita has not experienced significant variations (in 2021 it was 4,8 tCO<sub>2</sub>/cap) despite a significant increase in global CO<sub>2</sub> emissions. This trend can be explained by an increase in population as well as technological improvements leading to the use of more efficient technologies.



**Figure 1 Origins of GHG emission by sector [2]**

A lower share is represented by the CH<sub>4</sub> ( CH<sub>4</sub> has a significantly higher GWP value, ranging between 27 and 30.) produced in particular by the agricultural sector, the energy sector and in particular related to fossil fuels [3] and the N<sub>2</sub>O emitted during agricultural, land use, and industrial activities, in addition to the combustion of fossil fuels and solid [4].

Observing the trend in global greenhouse gas emissions (expressed in Gt of carbon dioxide equivalent, Gt CO<sub>2</sub>eq) from 2000 to 2022, organized by source (Figure 2), emissions in general have increased from around 25 Gt to over 35 Gt in 2022. The main sources of emissions remain fossil fuels, particularly coal, which accounts for the largest share of the total, followed by oil and natural gas. Non-CO<sub>2</sub> emissions, such as methane and nitrous oxide, although smaller, are also on the rise. The graph therefore highlights how the growth in global emissions is closely linked to the consumption of fossil fuels, despite contributions from other sources [4].

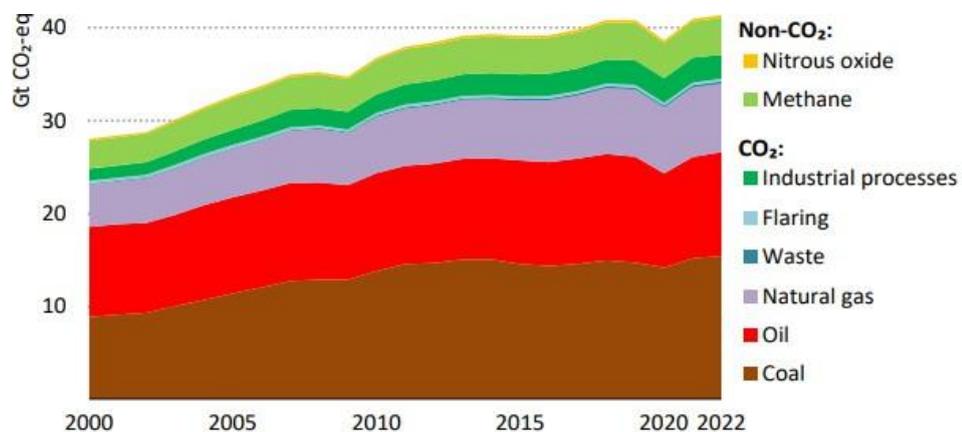
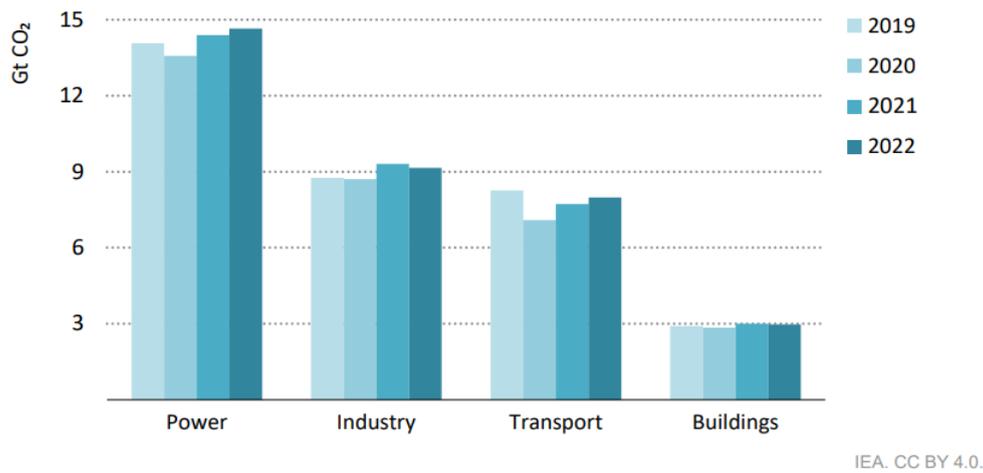


Figure 2 Origins of GHG by gases [4]

IEA. CC BY 4.0.

As reported in the annual report “CO<sub>2</sub> Emissions in 2022” published in 2022 by the International Energy Agency (IEA), after a decrease in 2020 caused by Covid-19 pandemic, GHG bounced back almost to the levels of the years before the pandemic. Most of the emissions are produced by the power sector followed by industry, transport and buildings as it is possible to see in Figure 3 [5, 6].

In Figure 3 the trend of growth in the CO<sub>2</sub> emission in the power sector and in particular in the fossil fuel field is represented. This analysis is focused on the period from 2015 to 2022, and it is therefore possible to detect the behavior of the use of fossil fuels in the last years and especially during the Covid pandemic [5].



**Figure 3 CO<sub>2</sub> emitted in different sectors in the years 2019-2022 [5]**

Industrial activities have led to an increasing level of carbon emissions in the atmosphere because of the growing level of industrialization and urbanization in many developing countries. This has also led to a significant increase in the global atmospheric concentration of anthropogenic GHGs, such as CO<sub>2</sub>, leading to global warming and therefore climate change [7]. Another source of anthropogenic CO<sub>2</sub> are the direct human activities on forestry and other kind of land use such as soil degradation, land clearing and deforestation [8].

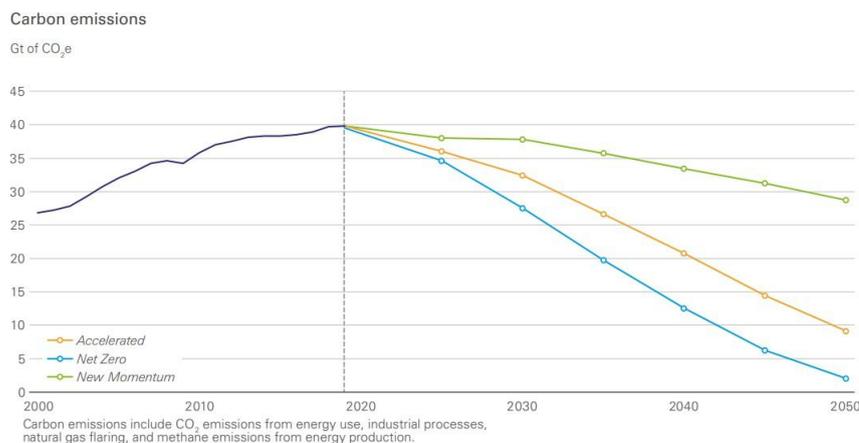
Greenhouse gas emissions, mainly CO<sub>2</sub> from fossil fuel combustion, are the main factor contributing to climate change. Understanding the sources and patterns of these emissions is critical to developing effective mitigation strategies, such as transitioning to renewable energy, improving energy efficiency, and developing carbon capture technologies. Forecasts, such as the BP outlook, provide future projections of emissions based on policy scenarios, technological innovations, and cost-effectiveness, helping to assess the likelihood of achieving global climate goals. A better understanding of emissions allows for more targeted measures to be implemented, accelerating emissions reductions and increasing the chances of success [9].

A projection of CO<sub>2</sub> equivalent emissions is provided by BP in the latest version of its annual Outlook 2023. Three possible scenarios are assumed in this report that take into consideration different trends in the reduction of CO<sub>2</sub>

equivalent in atmosphere [9]. The three global scenarios considered are:

- Accelerated: this is a hypothetical scenario created to evaluate what elements energy system might need to change if the world collectively takes action on CO<sub>2</sub>-equivalent emissions (CO<sub>2</sub>e) to fall by around 75 % by 2050 (relative to 2019 levels) in Accelerated. This reduction is assumed as a consequence of more tightening climate policies [9].
- Net Zero: this scenario is similar to the Accelerated one, but it envisages a reduction of 95 % by 2050 (relative to 2019 levels) in CO<sub>2</sub> equivalent emissions. In this scenario the emissions drop is because of both tightening climate policies and a shift in societal behavior and preferences, which further supports gains in energy efficiency and the adoption of low-carbon energy [9].
- New Momentum: is designed to represent the trajectory along which the global energy system is currently travelling. It is influenced by the actual legislation in energy emissions and the actual trend in global decarbonization [9].

These three possible scenarios are reported in Figure 4. It is immediately apparent that there is a need for more effective measures and strategies than those currently used to reduce CO<sub>2</sub>e production.



**Figure 4 CO<sub>2</sub> equivalent emissions in three different scenarios [9]**

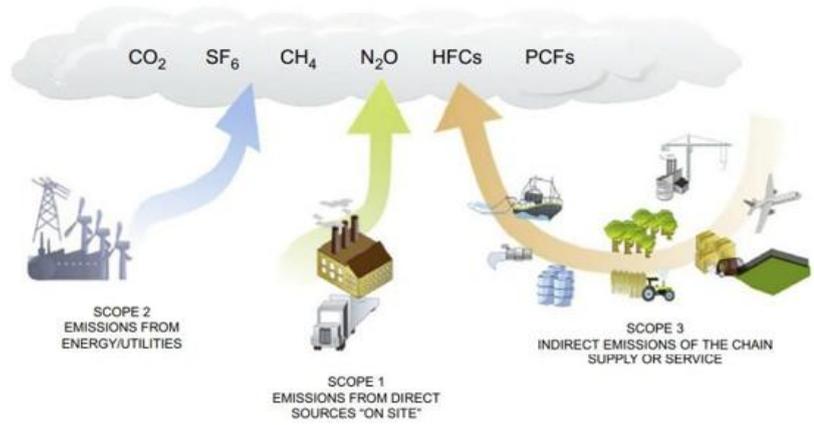
The emission scenarios outlined by BP Energy Outlook, such as Net Zero or Accelerated, provide a fundamental framework for understanding global decarbonization trajectories. To effectively and accurately assess the paths needed to achieve these scenarios, it is essential to adopt the Scope (1, 2, and 3) emissions reporting methodology. This detailed classification allows us to map and quantify the reductions required in each of the contexts envisaged by BP Outlook.

CO<sub>2</sub> emission scopes are a standardized classification used to measure and manage the environmental impact of organizations. They are defined by the Greenhouse Gas Protocol (GHG Protocol) and divided into three main categories as it is reported in Figure 5.

- Scope 1 includes all direct emissions produced by sources owned or controlled by the company, such as boilers, company vehicles, or industrial processes.
- Scope 2 covers indirect emissions from purchased energy generation, such as electricity, heat, or steam used in the organization's activities.
- Scope 3 includes all other indirect emissions along the value chain, such as those related to suppliers, transportation, business travel, and the use and disposal of products sold.

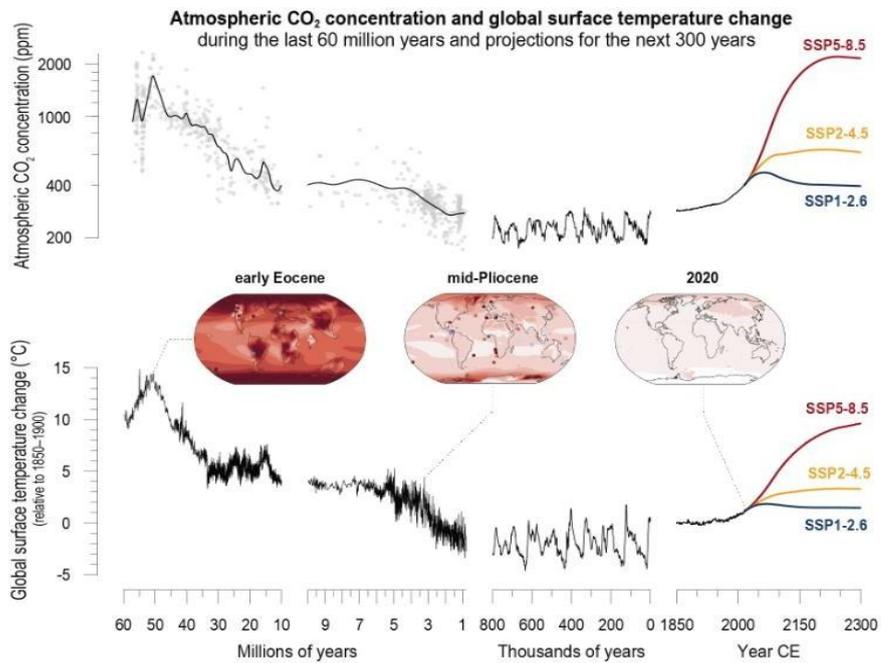
The distinction between the three scopes is essential for identifying the main sources of impact and developing targeted reduction strategies.

Scope 3 often accounts for the largest share of total emissions. Measuring and managing emissions across all three scopes enables more ambitious sustainability goals, such as carbon neutrality, to be achieved. This classification is now essential for ESG reporting, to comply with environmental regulations, and to improve corporate reputation.



**Figure 5 Classification of emission into scopes**

Global warming can be evaluated as the global surface temperature and its increment. Figure 6 shows how the CO<sub>2</sub> emissions and the Earth surface’s temperature are strictly connected both in the past from many millions of years ago in the present and in the future. [10]



**Figure 6 Changes in atmospheric CO<sub>2</sub> and global surface temperature (relative to 1850–1900) from the deep past to the next 300 years. [6]**

The figure shows the trend in atmospheric CO<sub>2</sub> concentration and global average temperature over the last 60 million years, together with projections up to 2300 based on different Shared Socioeconomic Pathways (SSPs). In earlier periods, such as the Eocene, CO<sub>2</sub> concentrations exceeded 1000 ppm, while in recent millions of years they have gradually decreased, stabilizing at around 280 ppm in the pre-industrial era. Global temperature followed a similar trend, with values up to +12 °C compared to the 1850 – 1900 period during the Eocene and a general cooling towards the modern era. The early Eocene, about 50 million years ago, was characterized by very high CO<sub>2</sub> and temperatures, while in the middle Pliocene, about 3 million years ago, CO<sub>2</sub> levels were similar to today's (~400 ppm), but temperatures were about 2–3 °C higher. Today, in 2020, CO<sub>2</sub> concentrations are around 415 ppm and temperatures have already risen by about +1 °C compared to pre-industrial levels. Today, in 2020, CO<sub>2</sub> concentrations are around 415 ppm and temperatures have already risen by about +1 °C compared to pre-industrial levels. Future projections vary depending on the scenario: the SSP1-2.6 scenario, with strong mitigation measures, predicts stabilization of concentrations and a limited temperature increase; the SSP2-4.5 scenario, which is intermediate, would lead to warming of around 2–3 °C by 2300; the SSP5-8.5 scenario, characterized by high emissions, could exceed 1000 ppm of CO<sub>2</sub> and cause an increase of more than +6 °C, returning the planet to conditions similar to those of tens of millions of years ago. The figure therefore highlights the close historical correlation between CO<sub>2</sub> and global temperature and shows how today's choices on emissions will determine whether the future climate will be relatively stable or extremely hot.

Climate change can manifest itself under different forms that can be related to human activities. In addition to global warming, climate change triggers interconnected phenomena such as melting ice and rising sea levels. Excess CO<sub>2</sub> absorbed by the oceans causes water acidification, damaging marine ecosystems such as coral reefs. Rising temperatures, combined with changes in precipitation patterns, cause extreme droughts that combine with heat waves to trigger more frequent and intense forest fires. These fires not only destroy biodiversity but also release large amounts of stored carbon into the atmosphere. Therefore, the

impacts are not isolated but combine to exacerbate crises, particularly those related to food security and human health. [6].

Over the years, in order to reduce global warming, commitments have been signed by governments on the reduction of climate-altering gas emissions.

An important organization has been created in 1995, the United Nations Framework Convention on Climate Change (UNFCCC). Nowadays the UNFCCC is composed of 198 Parties. Its final aim is preventing dangerous human interferences with the climate system [11]. Since the foundation, the adhering nations meet annually at the so-called Conference of the Parties (COP). At the COPs, the results achieved as an example in terms of reduction of GHG emissions or increase of the Earth's surface temperature are verified. In addition, these targets are adjusted, and new ones set.

At the 1997 Conference of the Parties, CoP3, held in Kyoto, Japan, the first major binding international agreement to combat climate change was signed. It was named the Kyoto Protocol and came into force in 2005. Its main aim was to reduce greenhouse gas emissions, which are responsible for global warming and climate change.

The agreement required 37 industrialized countries and the European Union to commit to cutting their overall emissions by 5.2% compared to 1990 levels between 2008 and 2012. The United States, despite initially signing, did not ratify the agreement, while developing countries such as China and India had no binding obligations. A new feature introduced by the protocol was the use of market-based instruments, including emissions trading and sustainable development projects, designed to facilitate the achievement of the targets. Despite these innovations, the treaty was criticized for its limited effectiveness, due to the lack of participation by some major polluters and the absence of real sanctions.

In 2012, the protocol was extended with a second commitment period until 2020, but it was then superseded by the Paris Agreement in 2015, which involved almost all the world's nations in a new commitment to combat climate change. The Paris Agreement involves almost all countries in the world, both developed and developing, requiring each to submit their nationally determined

contributions. The agreement does not impose binding targets that are the same for everyone, but is based on a system of flexible commitments, transparency, and periodic review. Every five years, countries must update their own goals, with the aim of progressively increasing climate ambition. A monitoring and transparency mechanism is in place to verify progress and compare national efforts.

One of the key elements of the agreement is the recognition of the need for international financing, especially to help developing countries mitigate the effects of climate change and strengthen their resilience.

The Paris Agreement also promotes the use of clean technologies, international cooperation, environmental education, and civil society involvement in the fight against climate change. In addition, for the first time in a climate agreement, the concept of “loss and damage” is formally recognized, the irreversible damage caused by global warming, particularly in the most vulnerable countries.

## **1.2 Sustainable technologies for the mitigation of GHG effect**

In order to reduce climate-altering gas emissions, there is therefore a need to replace fossil fuels in various sectors such as heat and power production, transport and industry.

Biomass plays a fundamental role in this energy transition towards defossilization and the achievement of climate targets.

The use of biomass allows waste materials from other processes such as agriculture or livestock farming, organic waste, or waste from certain industrial sectors to be exploited, transforming them into an energy resource and thus giving them economic value. Furthermore, from the point of view of electricity and heat distribution networks, they can guarantee stability as they are a programmable and modifiable energy source that is not subject to variations like wind and solar

sources. They offer a wide range of possible solutions through their use in different sectors and to generate different energy carriers. In particular, the main applications of biomass in the process of decarbonization and replacement of fossil fuels are:

- Electricity and heat: burning biomass in combined heat and power (CHP) plants allows electricity and heat to be produced simultaneously, reducing energy waste;
- Biogas and biomethane: anaerobic digestion can be used to generate biogas, which in turn can be purified into biomethane and fed into the gas grid, helping to defossilize the industrial and transport sectors;
- Biofuels: through processes such as anaerobic digestion, pyrolysis and gasification, biomass can be converted into biofuels (bioethanol, biodiesel, biomethane) that can be used in transport sector;
- Biohydrogen: mainly produced by purifying gases generated by thermochemical processes such as gasification and pyrolysis, or biochemical processes such as anaerobic digestion.

Biogas is a gaseous fuel, consisting of  $\text{CH}_4$  and  $\text{CO}_2$  produced from biomass. One of the main applications of biogas is its use in the combined production of electricity and heat through cogeneration. The combustion of biogas in cogeneration engines to produce electricity and use the heat generated by combustion to maintain the temperature of the digester or supply it to users such as district heating systems, farms, and industries [3].

Biogas can also be used through upgrading processes (water scrubbing, chemical absorption, adsorption, membrane technology and biological methods) to produce biomethane (also known as 'renewable natural gas'), which consists mainly of methane [13]. Biomethane can then be fed into the pipeline network following the removal of contaminants or directly for purposes such as heating and electricity generation, transportation [12]. Biomethane can also be produced

by the process of gasification of biomass followed by methanation but is currently produced 90% of the time by biogas upgrading. Biomethane combines all the advantages of natural gas without the associated net emissions. Another advantage is that it does not require the development of new infrastructure, increasing its versatility and cost-effectiveness [12].

In the transport sector, the use of biofuels plays a crucial role in defossilizing the sector. Biofuels are the most widely used renewable source product in the sector, accounting for 9% of the demand for road transport fuels in EU in 2021 and showing a growing trend [14]. Bioethanol, the most common, can be used in gasoline engines. It guarantees an 87 % to 96% reduction in emissions compared to regular gasoline. It is used in combination with fossil gasoline according to directives that vary from country to country. Biodiesel, unlike diesel, contains some oxygen in its chemical structure. Biodiesel can be used in normal diesel engines only if mixed with fossil diesel [15].

In the Renewable Energy Directive RED II, bioliquids are defined as 'liquid fuels for energy purposes other than for transport, including electricity, heating and cooling, produced from biomass', which, unlike biofuels, are used for static energy production. They are fast pyrolysis bio-oil (FPBO), hydrothermal liquefaction biocrude (HTL biocrude), liquefied wood and straight vegetable oils (SVO). In contrast to fossil fuels, bioliquids provide similar efficiency, reduced stability due to pressure and temperature fluctuations of the exhaust gas, but a large reduction in particle and NO<sub>x</sub> emissions [16]. Also inside RED II advanced biofuels are defined as renewable fuels obtained from sustainable raw materials, such as agricultural, forestry, and urban waste, and from raw materials such as algae.

The use of bio-hydrogen to produce energy is an innovative and very promising solution. Hydrogen (H<sub>2</sub>) is an energy carrier for storage that can store large amounts of energy, releasing it without producing CO<sub>2</sub> emissions during combustion, but only emitting water. Hydrogen can be produced from different raw materials and according to different processes. In order to obtain a substance

that makes a contribution to decarbonization, it will have to be produced through the electrolysis of water using electricity from renewable sources such as wind or solar energy, through methane cracking [17], or steam methane reforming through carbon capture [18] [19]. A well-established technique for using biomass as a sustainable solution for hydrogen production involves a water-gas shift reaction with the syngas generated by biomass gasification to obtain hydrogen. However, at present H<sub>2</sub> cannot be considered as a clean fuel (low carbon emission) because in 2021 it is produced 47 % from natural gas, 27 % from coal and 22 % from oil, and only 4 % from electrolysis [20].

There are a substantial number of papers in the literature dealing with anaerobic digestion and pyrolysis processes and their various specific aspects. However, since these are two biomass conversion processes, it would be useful to have a review of the two technologies in order to compare them. The literature review focused primarily on AD and pyrolysis due to their technological maturity and widespread commercial use. These are two biomass conversion processes based on proven and commercially developed technologies.

### **1.3 Scope of the work**

The main objective of this MSc. thesis is to collect parameters and results from different papers published in the most recent years about anaerobic digestion (AD) and pyrolysis. After collecting the aforementioned data, it is intended to organize them in order to be able to comment in a subsequent step operational difference related to the results obtained. The data of parameters and process results collected can be either from laboratory tests, from medium-scale tests or even from existing and operating large-scale plants.

The state of the art of two of the main developed processes for the biomass conversion, the AD and the Pyrolysis, are presented. The focus of this MSc. thesis is to present a full description of the operative parameters that characterize every

single process of biomass, the type of reactors that are used currently and the ones under development, the used feedstock and the pretreatment process that are widely used nowadays to maximize the processes, providing recommendations for European bioenergy policies and how they are being updated over the years. The structure of the manuscript is reported below.

Chapter 2 provides an overview of the legislative process at the European level regarding energy from renewable sources. Particular attention will be paid to the RED directives and measures regarding biofuels. Also in this chapter, the main regulations and regulatory changes concerning biomass, biofuels and other fuels produced from renewable sources are reported.

Chapter 3 focuses on presenting the state of the art of different technologies for biomass conversion. To this end, the main operating parameters of the process and digesters, the characteristics of the biomass used are presented. Reference will also be made to some of the practices adopted in biomass preparation for what are referred to as pre-treatment or mixing works.

Chapter 4 reports on how the bibliographic research on anaerobic digestion and pyrolysis processes was carried out. In particular, it reports all the parameters that were taken into consideration for the two processes and the calculations and assumptions made during this phase in order to standardize the data and make them comparable.

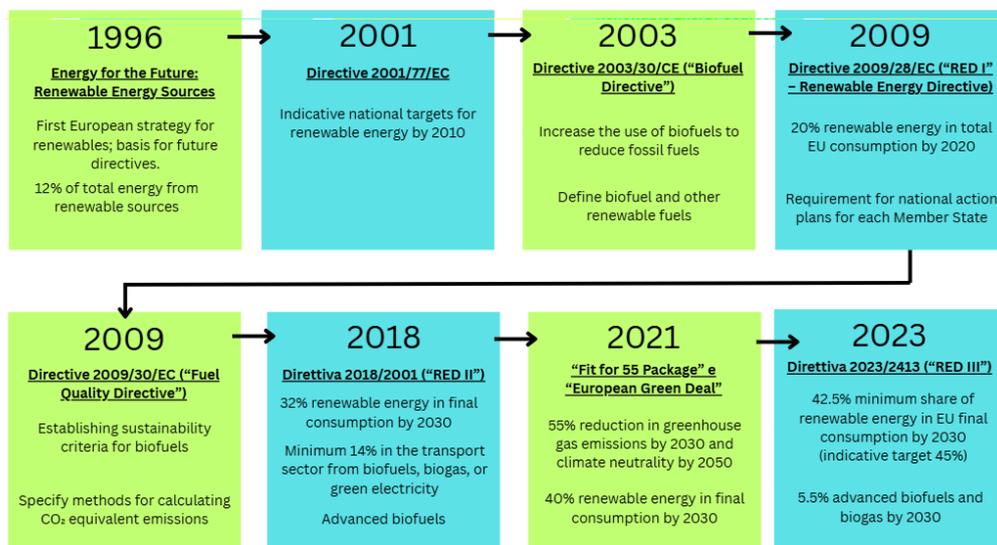
Chapter 5 presents the results obtained by comparing the data collected from the various papers analyzed. The comparison was carried out using Power BI software, which allows graphs to be generated that provide useful information on the two biomass conversion processes analyzed.

Chapter 6 contains the conclusions of the work, which seeks to provide policy recommendations on future developments and the maximum yield conditions of the two technologies based on the findings and discussion in the previous chapter.

# Chapter 2

## European Policy for Environmental Sustainability

The topic of energy is one of the most discussed and evolving topics in recent years. It is therefore up to the European Union to set rules on energy, renewables, organic products and climate-altering gas emissions in Europe. Figure 7 shows some of the most significant actions taken by the European Union in terms of reducing emissions to combat climate change.



*Figure 7 Principal European actions and targets*

The legislative path that has been taken so far overtime and how this has changed according to the new situations that the European Union is facing are useful for understanding what the current regulations are. They are also indicative of the regulatory and technological trend that will be encountered in the near future. The directives listed below are measures that come into force in the immediate future, even if the effects on the climate and the planet are not immediate. The implementation of these directives also requires a timeframe for the various states to enact laws with instructions on permits, suitable areas and possible incentive measures. They must therefore be extremely forward-looking and capable of providing guidance for the development of renewable technologies that can then be followed. Over the years, the European Union has set itself increasingly stringent climate targets in order to meet the targets set by international agreements on the subject, in which it plays a leading role worldwide. The updating of climate targets and the EU directives listed below are also seen as an economic strategy, encouraging, stimulating, and regulating the development of new clean technologies.

The first report of the European Union in this sector was the “Energy for the Future: Renewable Energy Sources “that has been published in 1996 where the objective of reaching the 12% of energy in gross inland energy produced from renewable energy was defined as an ambitious but realistic objective. [21]

In 2001, the Directive 2001/77/EC, the directive on electricity production from renewables has been released. This Directive gives National indicative targets for the European countries in terms of the percentage of energy derived from renewables by 2010. In addition, this document states how often member states must submit reports with the values obtained and the measures taken to achieve them [22].

The Biofuel Directive published in 2003 (Biofuel Directive 2003/30/CE) has the purpose of enlarging the use of biofuels or other renewable fuels in the transport sector instead of the widely used fossil fuels. gives important and useful definitions for what concern bio-products. Biofuels are defined as liquid or

gaseous fuel for transport produced from biomass while the other renewable fuels mean other fuels originated by renewables and used for transport purposes [23].

Directive 2001/77/EC and Biofuel Directive 2003/30/CE have both been repealed by the Directive 2009/28/EC, the Renewable Energy Directive (RED). The aim of this directive is to promote the use of energy from renewable sources by means of guidelines for individual member states. New targets are set for individual states regarding the use of energy from renewable sources in 2020. It is also stated that the overall objective of the European Community is to achieve 20% of energy from renewable sources by 2020. It also refers to the fact that each member state must provide a national plan with measures that will lead to the achievement of the target [24].

In the same year, the European Community issued a directive on fossil fuels and how to decrease the emission of GHGs. This was the directive 2009/30/EC, known as the Fuel Quality Directive. It reports the sustainability criteria for biofuels both in terms of biomass used and how it is produced and the reduction of greenhouse gas emissions by using biofuels instead of fossil fuels. The directive contains the specifications of biofuels required to be used as a substitute for fossil fuels for diesel and gasoline-powered engines. In addition to this, the methodology for calculating CO<sub>2</sub> equivalents in the case of biofuels is given [25].

The package of measures concerning the subject is the so-called RED II (Renewable Energy Directive - Directive 2018/2001) published by the European Council in 2018. This directive is designed primarily to promote the development of clean energy production from renewable sources, considering the Paris Agreement. The push for the use of renewable energy sources is dictated through new minimum values of energy consumption from renewable sources for the Member States. New specifications are also given for the transport sector in general, its emissions and for the supply of biomaterials for the creation of biofuels for the transport sector [26].

In 2021, there was a proposal by the European Parliament and the European Council following the targets that had been set in the "Fit for 55 package"

contained in the European Green Deal (EGD): reduction of greenhouse gas emissions by 55 % by 2030 as a preparatory but mandatory step toward achieving carbon neutrality in 2050. According to what is stated in the EGD itself, these goals are achievable only through an increase in the use of renewable sources for electricity production and biofuels. Thus, following this green line comes the above-mentioned proposal to increase the share of energy produced from renewable sources from the previous 32 % of RED II to a value of 40 % [27] [28].

The second revision of the Renewable Energy Directive (RED III), 2023 / 2413 was discussed and voted on in 2023. It includes as minimum overall targets the increase of the share of energy from renewable sources in the energy mix of member states to 42.5 % but member states will have to aim for a 45 % result overall. New lines for phasing out the use of woody biomass are also indicated. One issue addressed by this revision of the directive is the acceleration of the permitting processes for approving new installations of renewable sources, such as solar and wind, and the promotion of retrofitting of existing installations [29].

Articles from RED II, implementing acts, and RED III where topics related to biofuels and biomass utilization, their origin, and their use will be discussed in the following paragraphs.

## **2.1 Renewable Energy Directive 2018/2001 (RED II)**

The second revision of the RED Directive outlines a scheme for the promotion of renewable sources and sets a minimum utilization amount of 32 % in gross final energy consumption by 2030 by providing schemes for achieving such a development of renewable sources and national targets for each of the member State. In the case of Italy, the target to be reached of share of renewables in the national energy mix by 2020 was 17%. Criteria are also established for biofuels, bioliquids and biomass fuels in terms of sustainability in production and reduction of greenhouse gas emissions. [26] RED II requires each member state, in order to

promote renewable sources in the transportation sector to impose obligations on fuel suppliers so as to ensure a minimum share of 14 % of fuel from renewable sources such as biofuels, biogas. The GHG emissions savings from the use of renewable liquid and gaseous transport fuels of nonbiological origin shall be at least 70 % from 1 January 2021. For the calculation of the percentage of biofuels, bioliquids, and biomass fuels obtained from food and feed crops consumed in the transportation sector, it must be less than one percentage point greater than the share of such fuels in the final consumption of energy in the transport sectors in 2020 in that Member State. This limit is established in order to avoid using land exclusively for the purpose of producing these fuels. [26]

In RED II is also recommended that:

*“For the calculation of a Member State's gross final consumption of energy from renewable sources referred to in Article 7 and the minimum share referred to in the first subparagraph of Article 25(1), the share of high indirect land-use change-risk biofuels, bioliquids or biomass fuels produced from food and feed crops for which a significant expansion of the production area into land with high-carbon stock is observed shall not exceed the level of consumption of such fuels in that Member State in 2019, unless they are certified to be low indirect land-use change-risk biofuels, bioliquids or biomass fuels pursuant to this paragraph.” [26].*

The source of the biomass of agricultural and non-forest origin used to then produce biofuels, bioliquids, and biogas must be land with a low level of biodiversity and generally not of high value so as not to detract from other more valuable crops. [26] Any soil is assumed to be unsuitable if it has been at least for a period since January 2008 primary forest or forest land with no visible human activity, forest with recognized high biodiversity, protected areas for rare species and ecosystems, and natural grassland greater than one hectare with high biodiversity. In the case of forest biomass, on the other hand, in order to avoid carrying out an unsustainable process, the directive requires that such land meet land use, land use change, and forestry (LULUCF) criteria such as whether the

country or region of origin of the biomass has regulations on LULUCF and whether carbon sink management systems have been adopted [26].

Advanced biofuels in the European Union are defined by the specific feedstocks used in their production, a classification detailed in Annex IX of the Renewable Energy Directive II (RED II). In particular advanced biofuels are renewable fuels obtained from non-food biomass, such as agricultural, forestry, and urban waste, and from raw materials such as algae. This directive aims to reduce the negative impacts of biofuels on land use and biodiversity. These eligible feedstocks include a wide variety of waste, residues, and lignocellulosic materials such as used cooking oils, animal manure, sewage sludge, straw, and algae [26].

RED II also provides minimum GHG emission reduction levels for biofuels, biogas in the transportation sector, and bioliquids ranging from a 50 % reduction for pre-2015 plants and 65 % for plants operating from 2021.

## **2.2 Implementing act**

Implementing acts are measures in the form of regulations or implementing decisions useful for the implementation of the RED II and the achievement of its objectives by providing tools and guidelines. The implementing acts are adopted by the European Commission, after consultation with a committee composed of representatives of the Member States. The RED II requires the Commission to adopt implementing acts in several areas, including:

- the modalities for the calculation of the share of energy from renewable sources in gross final energy consumption and in the transport sector;
- the definition of modalities for the monitoring and verification of sustainability and traceability criteria for biofuels, bioliquids and biogas;

- the definition of modalities for the issue and recognition of guarantee of origin certificates for energy from renewable sources;
- the definition of modalities for cooperation between Member States and with third countries for the development and integration of renewable energy markets;
- the definition of criteria for the identification and support of projects of common European interest in the field of renewable energy.

Starting from April 2022, several regulations have been published for the introduction of various voluntary schemes. These are "an organization that certifies the compliance of economic operators with criteria and standards, including but not limited to the sustainability and greenhouse gas reduction criteria set out in Directive (EU) 2018/2001 and Delegated Regulation (EU) 2019/807" [30].

The term "economic operator" refers to producers of raw materials, waste collectors, and operators of plants for the production of final fuels, intermediate products or energy production. Voluntary systems have the function of monitoring and certifying the work of the various economic operators in the chain, of establishing useful procedures for collecting data from economic operators and then publishing them on a website. Those who carry out the checks must do so in accordance with the ISO 19011 standard when carrying out checks on greenhouse gas emission calculations but also on mass balance [31].

Some of the voluntary schemes that have been introduced and recognized through implementing acts by the European Union are:

- the "Sustainable Biomass Program", a certification scheme designed for woody biomass used for large-scale industrial energy production plants;
- the 'Biomass Biofuels Sustainability voluntary scheme (2BSVs)';-the "KZR INiG".

All certified operators, that can be from all over the world, can be seen on their respective websites [32] [33] [34].

## **2.3 Renewable Energy Directive 2023/2413 (RED III)**

The new Renewable Energy Directive III (RED III) was published in the Official Journal of the European Union on 31 October 2023, as a part of the “Fit for 55” package. This new Directive amends the previous RED II for Member States. In line with the European Green Deal of December 2019, which sets the goal for the European Union to achieve climate neutrality by the year 2050, the directive draws a line for achieving this goal in a widespread manner. The general objectives introduced with this regulation are that Member States shall ensure that the share of energy produced from renewable sources in 2030 represents at least 42.5 % of the Union's gross final energy consumption. In order to promote the development of new energy production technologies, an indicative target is also set whereby at least 5% of the new renewable energy capacity installed by 2030 must be of an innovative type [29].

In order to ensure that low-value materials are carried out, Member States are prohibited from providing incentives to plants using saw logs and veneers, industrial-grade round wood, stumps and roots, or to waste incinerators unless strict waste collection requirements are met.

Article 15 is amended to invite Member States to update their laws, regulations and bureaucratic procedures concerning the authorization, certification and licensing of plants for the production of energy (electricity or heat) from renewable sources.

In the RED III, Member States are instructed to map the territories suitable for the construction of certain types of renewable energy plants. This mapping must lead to the definition of Acceleration Zones by 21 February 2026 in which the installation of renewable source plants of certain types is favored [29].

Standards are set for the transport sector. A 29% share of renewable energy in final energy consumption in the transport sector by 2030 or a reduction of at least 14.5% in greenhouse gas emissions compared to reference values. To stimulate technological innovation in this sector, a target of 1% in 2025 and 5.5% in 2030 of advanced biofuels and biogas produced from raw materials listed in Annex IX, an excerpt of which is given below, and renewable fuels of non-biological origin in the energy mix of the transport sector is set. The system of credits for producers of electricity from renewable sources for recharging electric vehicles is also promoted. These credits can then be sold to producers who do not meet these standards, thus creating a market that leads to increased effort for electricity production from renewable sources [29].

With regard to the use of electricity from renewable sources in industry, an increase of at least 1.6 percentage points must be achieved as an annual average calculated for the periods 2021 to 2025 and 2026 to 2030. In this sense, there is a push for electrification of industrial processes where possible and especially for replacing fossil fuels for heating at a temperature below 200 °C. Thus, it is stipulated that the contribution of renewable fuels of non-biological origin (except those used as intermediate products for the production of conventional fuels) used for energy and non-energy end purposes shall be at least 42 % of hydrogen used for energy and non-energy end purposes in industry by 2030 and 60 % by 2035.

Biofuels, bioliquids and biomass fuels are considered to meet the renewable energy shares of the targets if they are:

- obtained starting from waste if the greenhouse gas reduction quantities specified in the legislation are met, based on when the plant started operating. Restrictions can be introduced in order to have better waste separation; [29]
- derived from waste not from forestry but from agriculture if the competent authorities have monitoring or management plans in place in order to address the impact on soil quality and soil carbon. They must derive from land that was peatland in January 2008 if it can be demonstrated that the

soil of origin; [29]

- derived from forest biomass provided that the harvesting of such biomass does not undermine the nature protection, biodiversity and habitat destruction of areas designated by national laws or competent authorities. The harvesting of stumps, roots, and the maximum harvesting thresholds set by the competent authorities must also be avoided [29].

# Chapter 3 State of the art

The sustainable management of organic waste is a major challenge for modern society, as it involves reducing environmental impact and valorizing renewable resources. Among the different technological options available, AD and pyrolysis are two processes that can be integrated in a sequential biorefinery to obtain high value-added products such as biogas, biochar and bio-oil.

This chapter will present the state of the art of anaerobic digestion and pyrolysis, analyzing the operating principles, operating conditions, control parameters and products obtained. Furthermore, possible synergies and complementarities between the two processes will be discussed, highlighting the advantages and challenges of a sequential biorefinery based on anaerobic digestion and pyrolysis.

## 3.1 Anaerobic Digestion

AD is a widely used technology whereby organic material is converted into energy-rich biogas and a plant nutrient- rich residue, the digestate [35]. Biogas is a mixture of CH<sub>4</sub> and CO<sub>2</sub> and small traces of nitrogen (0-3 %), water vapor (5-10 %), oxygen (0-1%), hydrogen sulfide (0-10,000 ppm), ammonia (0–200 mg/m<sup>-3</sup>) and siloxanes (0-40 mg/m<sup>-3</sup>) [36]. The percentage content of these two gases, however, depends on the composition of the biomass used as feedstock and certain operational parameters [37]. Biogas has several possible applications, such as separation of biomethane (bio CH<sub>4</sub>) for use as renewable natural gas, used in processes such as combined heat and power generation from biogas (CHP), trigeneration (highly efficient energy system that simultaneously produces electricity, heat, and cooling from a single fuel source) [38]. Biogas fuel can be

used in both spark-ignition (gasoline) and compression-ignition (diesel) engines with varying degrees of modification on conventional internal combustion engines (ICE). In this type of engine the dual-fuel mode can be used with little or no modification compared to full gas engine conversion, which may require major modifications. Other uses are to produce Fisher-Tropsch (FT) fuels through cleaning and conversion actions to form syngas or methanol [38].

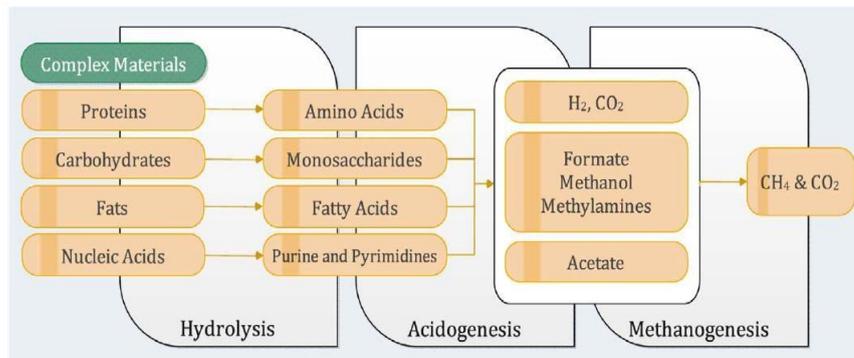
Besides biogas, the other product of AD is digestate. Digestate can be defined as the undecomposed residue from the anaerobic digestion process. It is composed of water, undecomposed organic compounds and minerals [39]. As the biogas its composition is strictly related to the type of feedstock used in the digester and how it is pretreated [40]. Digestate is widely used as fertilizer due to its high content of nutrients and in particular phosphorus, potassium and the nitrogen fraction, included  $N-NH_4$ ,  $N-NO_3$  [40]. The main use to date of digestate from AD is as a biofertilizer in agricultural soils precisely because of the aforementioned presence of useful nutrients to increase soil yield [41]. It is also a widely used practice as it is economic beneficial as digestate being in many realities considered a waste material from biogas production. However, this is not the only possible use of digestate: it could be used as feedstock for biochar, bio-oil and syngas production through pyrolysis, liquefaction, HTC and gasification, respectively [42].

Some of the most used biomass feedstock for AD are organic fraction of municipal solid waste (OF-MSW), sludge from wastewater treatment, waste from food processing industries, energy crops and agricultural wastes such as manure and plant residues [43].

### **3.1.1 Biological Reactions**

During AD, the breakdown of organic compounds is achieved by a combination of many types of bacteria and archaea (microorganism). The biomass

added to the digester is broken down into sugars, amino acids and fatty acids (hydrolysis), fermented to produce volatile fatty acids and alcohols (acidogenesis) followed by the conversion into ( $H_2$ ),  $CO_2$  and ammonia ( $NH_3$ ) and, finally, methanogenesis produce biogas from acetic acid and  $H_2$  (Figure 8).



*Figure 8 Scheme of the steps involved in anaerobic digestion [84]*

The four main reactions that occur in an anaerobic digestion process are:

- **Hydrolysis:** Hydrolysis is the first step of anaerobic digestion, in which the bacteria transform the organic complex substrate (carbohydrates, proteins, lipids, etc.) into polymers and monomers such as amino acids, long chain fatty acids (LCFA) and simple sugars [45]. Moreover, at low temperature hydrolysis may limit the overall process and thereby determining the required reactor design [45]. The products of hydrolysis are the substrates for acidogenic bacteria.
- **Acidogenesis:** In the second stage of the process, the products obtained from hydrolysis (amino acids, LCFAs and simple sugars) into smaller compounds such as volatile fatty acids (VFAs) as acetate propionate, butyrate, alcohols (methanol and ethanol) as well as  $H_2$ ,  $CO_2$  and ammonia [45].
- **Acetogenesis:** In the next step, acetogenesis, short-chain fatty acids (SCFA) are generated and then converted to acetic acid, carbon dioxide

and hydrogen by acetogenic bacteria [45].

- Methanogenesis: The last step in anaerobic digestion is methanogenesis of which there are two types: acetoclastic and hydrogenotrophic methanogenesis. It is at this stage that acetic acid is converted into CH<sub>4</sub> and CO<sub>2</sub> [45]. Acetoclastic methanogenesis is responsible for two-thirds of the final amount of methane while the last third is due to hydrogenotrophic methanogenesis where CH<sub>4</sub> is generated from dissolved H<sub>2</sub> and CO<sub>2</sub> [45].

### **3.1.2 Factors affecting the reactions**

As a first step, it should be pointed out that the operating parameters of anaerobic digestion do not have universally optimal values but rather depend on what product is intended to be obtained and enhanced by this process and what are the conditions and properties of the biomass used as feedstock.

#### **3.1.2.1 Temperature**

In an AD process, temperature is recognized as one of the most important parameters that influence both the AD microbial ecosystem and thus all the reactions of the process, due to the fact that the various microorganisms vary their effectiveness in processes in relation to temperature, and the performance of the digester [46] [47].

The process of anaerobic digestion can be classified into three categories depending on the temperature inside the reactor:

- psychrophilic (< 20 °C); [47]
- mesophilic (20 – 43 °C but most commonly between 35 and 37 °C); [47]

- thermophillic (50 - 60 °C, with optimum temperature at 55 °C) [47].

### 3.1.2.2 Characterization of the feedstock

Feedstocks from different sources with therefore different characteristics and different possible yields in terms of biogas produced can be used for the AD process. The choice of biomass type is mostly dictated by the conditions of local production activities, their possible useful waste, and the possibility of having access to possible waste or wastewater. The choice therefore to start biogas production from anaerobic digestion is a consequence of the availability of feedstock whatever it may be.

The main parameters to define biomass are:

- **Total Solids (TS):** The amount of solids remaining after heating the sample at 105 °C for 24 hours until a constant weight is obtained [48]. It is also called Dry Matter (DM) and is composed of both suspended solids and an inert part.
- **Volatile Solids (VS):** the fraction of dry matter that evaporates in the heating process at a temperature of 550 °C to constant weight. It can be evaluated as the difference between total solids (TS) and total fixed solids, which is the inert fraction formed by inorganic compounds [49]. VS can be expressed either as a percentage of the total biomass or as a percentage of the solid fraction.
- **Ash:** are the inert part of the total solids that remain after heating to 550 °C.
- **Chemical Oxygen Demand (COD):** Proportion of oxygen required for the oxidation of the organic matter contained within a liter of water. It is expressed in milligrams of oxygen per liter (mg of O<sub>2</sub>/L) that measures the concentration of dissolved oxygen in a liquid, usually water. It is a key indicator of water quality [50].

- **Biochemical Oxygen Demand (BOD):** is the amount of oxygen consumed, under controlled conditions, for the biological oxidation of the organic matter contained within the sample.
- **C/N ratio:** The carbon-nitrogen ratio of the matrix entering the digester is one of the most important parameters to control in order to achieve optimal biological activity. Too little nitrogen and therefore too high a C/N ratio leads to a fast consumption of nitrogen and a low yield in terms of biogas produced. Conversely, too high an amount of nitrogen, too low a C/N ratio, will cause an increased risk of ammonia inhibition, which is toxic for biogas production. An optimal C/N ratio value has been shown to be between 20 and 30 and most commonly used 25 [51].
- **Biomethane potential or Biochemical Methane Potential (BMP):** the maximum amount of biomethane that can be produced by AD of a given substrate, it is defined through a laboratory test, the BMP test [52] [53]. In real plants, efficiencies of 80-90 % in the biogas production, calculated as the biogas effectively produced with respect to the biomethane potential, indicates a properly conducted process [54].

There are certain parameters that must be considered and controlled during the AD process to ensure a stable process.

- **Organic Loading Rate (OLR):** it is the quantity of volatile solids fed into a digester per day under continuous feeding that can be properly digested by the digester itself. Increasing the amount of biomass entering the digester will also increase the amount of biogas produced up to a certain limit, beyond which, however, the activity of certain bacteria may be inhibited, leading to a non-optimal AD. OLR is expressed in  $\text{kg VS/m}^3/\text{d}$  [55].
- **Retention Time:** in general, it can be defined as the time required inside the bioreactor to complete the degradation of organic matter [56]. Two types can be defined: SRT (solid retention time), the average residence

time of a solid bacterium in a digester, and HRT (hydraulic retention time), the time liquid and dissolved material remains inside the reactor, [57] obtained with the formula:

$$HRT = \frac{V}{Q}$$

(Equation 1)

where,

V: is the volume of the digester

Q: the flow rate in time of the incoming matter.

It depends on the type of biomass input and its OLR and is one of the most influential parameters for CH<sub>4</sub> yield. Its typical value lies between 15 and 30 days under mesophilic conditions. HRT that is too low leads to an accumulation of VFA whereas if the HRT is too high, the digester components will not be utilized effectively [58].

- **pH**: its value reflects the variation of the digestion process in the reactor. it is therefore important to assess its change over time rather than its absolute value [59]. In general, the optimal pH value is between 6.8 and 7.4. The pH value influences the bacterial population species within the reactor [56].

### 3.1.3 AD reactors

In recent years there has been evolution in the technologies used for the AD process. In particular, the main differences regard the type of AD reactor chosen. The selection of the type of reactor regards both the kind of substrate available with its chemical and physical properties and techno-economic reasons. The two main parameters for the classification of anaerobic digesters are the number of stages, which influences the conditions under which reactions can take place

within the reactor, and the percentage of total solids within the feedstock, which determines how it is fed into the reactor. In accordance with this the classification of bioreactors can be done:

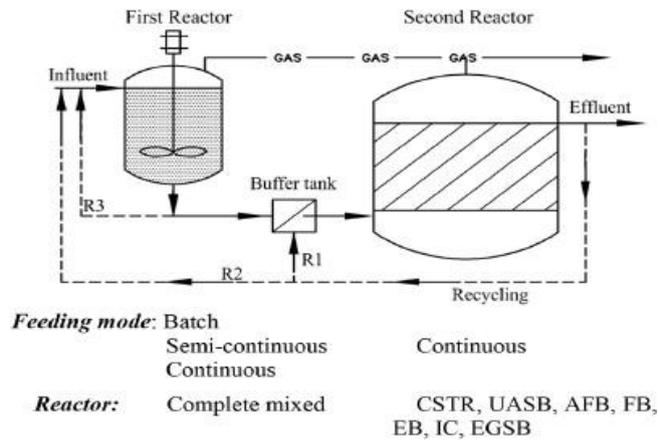
- With respect to the number of stages: one, two or three stages
- With respect to the TS content in the feedstock: wet or dry digestion and therefore batch, continuous, attached and suspended reactors.

The multistage systems, batch, continuous one- stage systems, and continuous two-stage systems are the most common types of digesters used in the industry [60]. It also reports the main features that a bioreactor needs to satisfy like reducing the reactor's volume by having a short hydraulic retention time, managing a high organic loading rate continuously and consequently produce a large amount of high-quality biogas [60]. In the following pages an overview of the different design of AD reactors is developed.

AD in general has always been carried out in a single reactor in which all the first mentioned reactions forming part of the process therefore took place. However, since each individual step in AD needs special operating conditions of pH, temperature, etc. in order to obtain an optimal environment for the bacterial populations to operate, the idea was developed to subdivide the digestion within several reactors. These reactors have different operating parameters to ensure more congenial conditions for each individual stage of digestion. Several different configurations such as two-stage or three-stage AD were therefore conceived in this direction [61].

Two-phase systems consist of a first reactor or phase in which optimal conditions are created for the hydrolysis and acidogenesis bacteria to work, while in the second, acetogenesis and methanogenesis are favored. In the first reactor, the substrate is moistened with recirculated water from the second reactor, which provides better pH control due to its high alkalinity and in order to ensure a better mix in the case of extremely dry input material. The second phase can be either wet or dry. The reactor types that can be used as the first reactor are continuous

stirred tank reactors (CSTR), while CSTR, Upflow Anaerobic Sludge Blanket (UASB), Anaerobic Fluidized Bed (AFB), Fluidized Bed (FB), Internal Circuit (IC), and Expanded Granular Sludge Blanket (EGSB) reactors can be used as the second reactor [62] (Figure 9).



**Figure 9** The configuration of the two-stage digestion system [62]

The three-stage configuration, on the other hand, presents some critical economic issues due to the cost of investment, maintenance and operation. This is therefore not yet a viable solution. On the other hand, from the point of view of reactor organization, the first is used for hydrolysis, the second for acidogenesis and acetogenesis, while the last reactor has optimal conditions for methanogenesis.

In both configurations, since optimal conditions for the bacteria are guaranteed, it is possible to achieve higher VS reduction values, shorter HRT and higher OLR. However, despite the higher conversion efficiency of the two-reactor configuration, the most widely developed solution in large-scale plants today is the single-reactor configuration [60].

The TS content in the feedstock strongly influences the type of process and therefore the type of reactor used. For feedstock that have a TS content above 20% are treated by a solid digestion while with total solids under 15% the digestion is considered as wet. The TS content is strictly related to the moisture

content and to the lignin content in the biomass. These factors affect the time that the biomass needs to be digested inside the reactor and therefore the HRT. HRT is not important only for technical aspects but also for economic reasons because it influences the rate with which the biomass can be supplied inside the reactor.

These beforementioned distinctions of biomass and plant configuration result in different biomass treatment and AD reactors:

- Conventional reactors:

- Plug-flow reactor (PFR): this kind of reactor is mainly applied to semisolid flow of raw materials, such as sludge, vegetable waste, cow dung. The material flows from one end of the reactor to the other without any mixing in that direction [63]. The reactor in question can be positioned horizontally or vertically. PFRs have higher efficiency, better bioconversion of biomass input, and better volume exploitation than CSTR reactors. Furthermore, it can be defined as a simple configuration with a relatively low cost of installation as well as operation costs. Typically, the HRT varies between 20 and 50 days, the OLR of PFRs is usually a value between 1-6 kgCODm<sup>-3</sup>d<sup>-1</sup> [64]. The major drawbacks of PFRs are the low mass transfer due to lack of mixing, thermal stratification and solid sedimentation, or floating/scum-formation problems [65].
- Continuous stirred tank reactor (CSTR): this is the most widely used type of bioreactor for AD due to its simple operation, continuous operation, and simple configuration. This type of reactor provides for feedstocks to be constantly and continuously mixed by mechanical means, keeping the reactor contents homogeneous with a theoretically constant composition and temperature over the entire reactor. Such mixing may occur continuously or intermittently. In such circumstances, best inoculum substrate interaction and mass transfer could be obtained. It has a simple principle of operation, but it is less efficient in terms of effluent quality. Due to its working principle, it causes a low concentration of microorganism inside the reactor but if it is combined with a membrane

reactor (MBR) could lead to better results. In most of the cases it is used in the vertical configuration [56]. CSTR can be used to treat wastewater with high quantity of solids.

- Anaerobic sequencing Batch Reactor (ASBR): is a single reactor in which both the treatment and the fermentation occur. These reactors have demonstrated parameter control capability and process efficiency in many cases greater than continuous systems. However, the need for larger volumes is an obstacle in its development [56].

#### - Sludge Retention Reactors

- Up-flow anaerobic sludge bed reactor (UASB): this reactor is widely used due to its simplicity and cost-effectiveness for the treatment of effluents. It is composed of a dense sludge bed positioned at the bottom of the reactor to ensure optimal contact between wastewater and biomass. It requires a small volume and is able to achieve high values of biogas produced as well as being able to handle high OLR values [56].

#### - Anaerobic membrane reactors

- Anaerobic Fluidized Bed Reactor (AFBR): the AFBR uses fluidised bed technology, which is also used in reactors for other types of processes such as pyrolysis or gasification. It consists of the use of small particles of sand, zeolite, alumina or activated carbon to promote the formation of populations of microorganisms. Particularly used for biological wastewater treatment. These particles are held in suspension by the upward flow of incoming wastewater. A biofilm is created around these particles that allows the biomass to cling and enable good mass transfer [56][66]. It has a high efficiency in COD removal, the production of a CH<sub>4</sub>-rich biogas, reduced production of waste sludge and easy process control. However, it requires periodic cleaning of the particles in the reactor to remove excess biomass [67].

## 3.2 Pyrolysis

Pyrolysis is a thermochemical decomposition process, achieved at high temperatures and in the complete absence of an oxidizing agent (normally oxygen). If the material is heated in the presence of oxygen, combustion takes place, generating heat and producing oxidized gaseous compounds in what is complete combustion. If, on the other hand, the same heating is carried out under anoxic conditions (total absence of oxygen), the material undergoes the splitting of the original chemical bonds with the formation of simpler molecules.

Pyrolysis can be used in various sectors, including energy production, the transformation of organic materials into chemicals, waste treatment, the characterization of fuels and the synthesis of advanced materials. Depending on the type of material, temperature and reaction time, pyrolysis can produce a variety of solid, liquid and gaseous products with different properties and uses. Gaseous products such as CO, H<sub>2</sub> and CH<sub>4</sub>, short hydrocarbon chain gases, and CO<sub>2</sub> are generated. Liquid products such as bio-oil and tars consists of aliphatic and aromatic compounds, phenols, aldehydes, and levoglucosan, hydroxy acetaldehyde, hydrocarbon chains, and water. Bio-oil and tars are similar, but bio-oil differs from tars in being composed of organic compounds of lower molecular weight, in being less viscous, and in being more viscous. The third product of pyrolysis is the solid product, the biochar, is a carbon-rich solid that can be widely used in agriculture because it is useful for reducing CO<sub>2</sub> emissions into the air and reducing GHG emissions, as will be detailed later.

There are different parameters that characterize and influence pyrolysis and its products, such as the possible feedstocks, the types of plants used, and possible developments.

### 3.2.1 Feedstock

Different types of biomasses can be used for pyrolysis. In general, some macro- categories can be distinguished:

- Woody biomass: also called lignocellulosic biomass. It is the most widely used biomass material. Wood contains lignin (20-30%) [ $C_9H_{10}O_3$ ], cellulose (40-45 %) [ $C_6H_{10}O_5$ ], and hemicelluloses (25-35 %). Lignin has a high resistance to chemical decomposition and therefore biomass with a low level of lignin and a higher percentage of cellulose and hemicelluloses is generally preferred [68].
- Non-woody biomass: has a lower lignin content than woody materials. It typically has a lower energy content and is typically derived from waste from agricultural processes, animal waste or herbaceous plants. They therefore represent a material that may be less interesting energetically but is very abundant and consequently low cost, also because they are waste materials [69].
- Municipal Solid Waste (MSW): this is an ever-growing waste due to people's lifestyles and needs. It generates a problem both in terms of the occupation of large areas to be used for disposal (*i.e.* landfills) and the contamination of soil and groundwater by the gases emitted if not properly controlled and managed. It is therefore necessary to find a possible strategy for its further utilization instead of disposal, which could clearly be pyrolysis. MSW represents a mixture of different materials with different compositions and physical and chemical properties [70], [71], as Table 1 briefly describes.

Type of countries	Organic (%)	Paper (%)	Plastic (%)	Metals and glass (%)	Others
Low-income group	64	6	9	6	15
Middle income group	56	12	13	7	12
High income group	28	30	11	13	18

*Table 1 Average waste composition in various income group countries [71]*

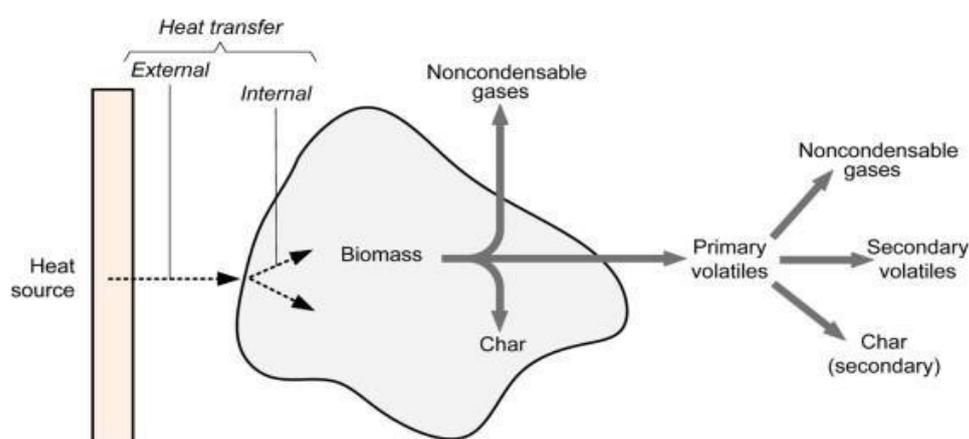
- Plastic waste: this is a subcategory of MSW. In recent years, pyrolysis has attracted industries because of the possibility of converting plastics into high-value resources such as biofuels. In general, there are many types of plastics but a good number of them have a calorific value above 40 MJ/kg which is considered a high value for energy purposes.
- AD Digestate: pyrolysis of digestate from anaerobic digestion represents a valuable opportunity to optimize energy efficiency and improve the sustainability of the process. In order to pyrolyze it, the digestate must contain a low amount of water and must therefore be dried to obtain a high solids digestate (HSAD). Digestate obtained from anaerobic digestion is also used directly as fertilizer in agriculture, but this generates some negative effects such as emissions of greenhouse gases, odors, pathogens and heavy metals. However, this is a product with high energy and nutrient potential. The possible options are therefore either to produce energy via biological or thermal processes or to convert it into products such as biochar, activated carbons or composite materials [72].

### **3.2.2 Pyrolysis' process**

The pyrolysis process is characterized by a high degree of complexity resulting from the different nature of the feedstock used. In the best-known case of woody biomass, the interactions between its three main components (lignin, cellulose and hemicellulose) during pyrolysis are very difficult to predict. It can be said that during pyrolysis a large number of reactions occur simultaneously or one in succession to the other. For example, dehydration, depolymerization, isomerization, aromatization, decarboxylation, and charring. A rough distinction of the pyrolysis process phases can be carried out by dividing them into three main phases:

- evaporation of the moisture present in the feedstock;
- primary decomposition;
- secondary decomposition (oil cracking and repolymerization) [73].

In the first phase, the water present in the substrate is eliminated by means of temperature growth ranging from 150 °C to about 200 °C. In addition to the elimination of water, CO, CO<sub>2</sub> and some light hydrocarbons (formic acid, acetic acid) begin to be released.



*Figure 10 Scheme of the phases of the pyrolysis [74]*

During primary decomposition, between 200 and 400 °C, the actual decomposition of the substance occurs, resulting in a reduction in mass and volume to form solid biochar. Further gases such as CO and CH<sub>4</sub> are also formed.

At higher temperatures, secondary decomposition reactions take place where the products of primary decomposition react with each other to form cracked bio-oil.

### 3.2.3 Pyrolysis' operative parameters

Even in the case of pyrolysis, it is necessary to keep in consideration various parameters that determine its operation. The first fundamental aspect that must be mentioned is the type of substrate used; this will give rise to solid, liquid and gaseous products with different compositions and in different quantities. Furthermore, one type of substrate rather than another implies certain pre-treatment procedures. Also, with regard to feedstock, particle size affects pyrolysis performance. As a thermal decomposition process, the temperature at which the conversion takes place, the speed at which this temperature is reached (heating rate) and the residence time within the reactor play a key role. The possible use of a catalyst to reduce temperatures or pyrolysis residence time [75].

	Intermediate pyrolysis	Fast pyrolysis	Flash pyrolysis
Operating temperature (°C)	500-650	850-1250	900-1200
Heating rate (°C/s)	1-10	10-200	>1000
Solid residence time (s)	0.5-20	0.1	<1
Particle size (mm)	1-5	<1	<0.5

*Table 2 Operating parameters of different pyrolysis [75]*

#### 3.2.3.1 Temperature

Temperature is the most important parameter in pyrolysis and can generally vary between 400 and 1200 °C. Pyrolysis will result in the same products but in different percentages. At lower temperatures, a limited amount of volatiles can be converted to gas, resulting in a higher biochar and liquid yield. Conversely, at

higher temperatures, cracking and volatilization reactions will be favoured and thus the amount of gas produced will be higher. However, the properties of the products are also influenced: at higher temperatures the bio-oil will have a higher calorific value [76] [77].

### **3.2.3.2 Heating rate**

Another parameter characterizing pyrolysis is the heating rate, expressed in °C/s, which can vary from less than 1 °C/s to more than 1000 °C/s. The heating rate indicates the speed at which the pyrolysis temperature is reached. Slow heating rates promote polymerisation of bio-oil components, particularly at low temperatures (< 500 °C), resulting in higher primary coke yields. Decomposition reaction was found to be pronounced at fast heating rates, causing decreases in the tar yields and abundance of light compounds. The increases in the yields of the secondary coke, the formations of more condensed aromatic structures and macromolecules were also promoted at fast heating rates via the secondary reactions.

### **3.2.3.3 Residence time**

The solid residence time (s) indicates the length of time for which the biomass remains inside the reactor. In general, the longer the residence time of the organic matter, the lower the yield in liquid fraction while the yield in gaseous or char species will increase. At low residence times, the production of bio-oil is favored due to the fast removal of organic vapors [78].

### **3.2.3.4 Particle size**

The particle size of the pyrolysis feedstock is another factor that can influence the yield of the process. Referring mainly to woody biomass, increasing the average biomass particle size decreases the yield of bio-oil due to the effect particle size has on the production of derived compounds. Smaller particles result in a better and more uniform heat transfer within the biomass leading to an improvement in pyrolysis performance. In order to increase the yield of bio-oil,

which is the most energetically relevant product of the pyrolysis process, it is advisable to provide for pre-treatments in which the size of the biomass is reduced such as milling or grinding [79].

The combustion process of biomass in the absence of oxygen, based on the parameters that characterize it such as operating temperature, heating rate, residence time, can be divided into a few categories:

- Slow pyrolysis
- Conventional pyrolysis
- Fast pyrolysis
- Flash pyrolysis

These categories do not have a strict definition and in fact the above-mentioned parameters characterizing each them can change. However, slow pyrolysis, also known as carbonization, can be defined as pyrolysis characterized by very high residence times of up to hours or days, with therefore a very low heating rate down to 1 °C/s rather low temperatures, i.e. less than 400 °C. Slow pyrolysis is used when the aim is to increase gas yield. Conventional or intermediate pyrolysis, lower residence times in the order of a few minutes, still low heating rates and temperatures that can vary between 400 and 500 °C. Fast pyrolysis is characterized by even higher temperatures around 500/600 °C, a very high heating rate (10-200 °C) and therefore a short residence time (2-10 s). This type of pyrolysis is used if one wants to maximise bio-oil production up to 50-70 wt%, which can then be achieved by rapid cooling of the pyrolysis vapours. The last type is flash pyrolysis, which is a pyrolysis carried out in a very short time of about 0.5 s with a very high heating rate of up to 103-104 °C/s. In flash pyrolysis, even higher bio-oil yields of up to 80 wt% can be achieved. The importance of having a small biomass particle size is even more important in the case of fast and flash pyrolysis where the heat exchange must take place in a very short time frame and must therefore be extremely effective.

### 3.2.1 Pre-treatments

Biomass needs to be pretreated in order to make the pyrolysis process more efficient. Pre-treatments are also used if one wants to increase a certain pyrolysis product over another. The four main types of biomass pre-treatment can be physical, thermal, chemical, biological and a combination of these. [80]

Physical pre-treatments involve milling or grinding to reduce particle size in order to promote heat exchange within the reactor and improve pyrolysis efficiency.

High-pressure extrusion of the biomass to form cylindrical pellets can also sometimes be performed to increase the volumetric energy density of biomass while decreasing the moisture content [80]. Thermal pretreatment allows biomass to be dried in order to improve pyrolysis efficiency and increase the quality of the bio-oil. In a virtuous and efficient pyrolysis system, the heat generated inside the reactor is reused to pre-heat to a temperature between 200 °C and 300 °C and dry the biomass that will then enter the reactor. This has several benefits such as higher energy density, it has enhanced grindability, lower hygroscopicity when stored in open air, lowers the risk of biological degradation and self-ignition, and improves feeding in the reactors. Therefore, if derived from otherwise wasted heat, this type of heat treatment can be highly advantageous also from an economic point of view. However, there are also innovative technologies for thermal pre-treatment such as ultrasound and microwave irradiation [80].

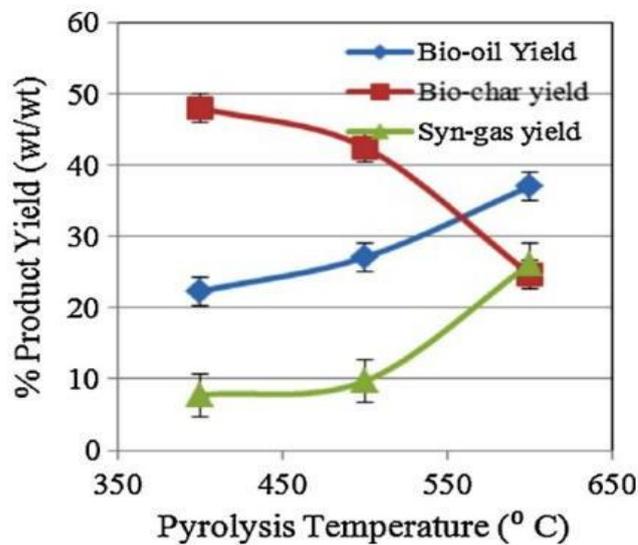
The most commonly chemical pretreatments used pre-treatments are acid ( $\text{H}_2\text{SO}_4$ ) and alkali (such as  $\text{NaOH}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{NH}_4\text{OH}$ ) pre-treatments, hydrothermal pre-treatment, ammonia fiber expansion and steam explosion. They are all used to compromise the lignocellulosic structure and promote its decomposition.

Biological treatments are more sustainable and less energy-intensive but slower processes, ranging from a few hours to several days. It is typically used to

increase biogas production by introducing natural microbes, fungi that are able to degrade lignin and hemicellulose in the biomass [80].

### 3.2.5 Products from pyrolysis

In the pyrolysis process, three different energetically interesting substances are obtained as outputs: bio-oil, biochar and gas. All of these products have interesting applications, and one type of pyrolysis may be preferred over another, depending on which product one prefers to maximize. However, the more one is able to exploit these products, the more energetically and economically virtuous pyrolysis becomes. In Figure 11 the production yield as function of the process temperature. It can be seen that the production yield of char and syngas behave in the same way, increasing as the temperature and thus the volatile substances rise. the opposite is true for bio-oil, which, having a generally higher yield than the other products, decreases production when temperatures rise.



*Figure 11 Production yields as function of the pyrolysis temperature [81]*

Bio-oil is generally a product of the thermochemical convection processes of

matter. It is a dark brown liquid substance, a compound of water (15-35 wt%) and a multitude of organic compounds, such as acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, alkenes, nitrogen compounds and miscellaneous oxygenates, as well as solid particles. The highest yield of bio-oil comes from fast (60-70 wt%) or flash (75 wt%) pyrolysis. Bio-oil is characterized by a high oxygen content, which leads to a reduction in the higher heating value (HHV).

Bio-oil is considered a viable alternative to fossil fuels due to its still high energy density. However, bio-oil cannot be used directly in engines due to its high viscosity, high oxygen content, thermal instability and high corrosiveness. Some of the advantages of using bio-oil over fossil fuels lies in the lower NO<sub>x</sub> and SO<sub>x</sub> content, which therefore limits pollutant gas emissions into the air.

Biochar is the solid residue, the solid component among pyrolysis products, and its formation is favored in slow pyrolysis. It is a compound formed as a result of the re-condensation of cleaved molecules and volatiles biomolecules formed during biomass heating. It has a high carbon content and a porous structure due to hydrogen and oxygen being removed from the biomass during pyrolysis [75]. It is highly valued for its soil amendment and carbon storage capacity and is used as a soil amendment due to presence of elements such as N, P and K, in carbon capture and for the reduction of contaminants in water by adsorption [81].

The gaseous product of pyrolysis, the pyrolysis gas, is composed mostly of CO, CO<sub>2</sub> and to a lesser extent of H<sub>2</sub> and other hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub>). The composition of syngas can vary with temperature and in particular, at high temperatures CO<sub>2</sub>, CO, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> increases while the content of H<sub>2</sub> and CH<sub>4</sub> decreases. The production of this gas is favoured at high temperatures. This gas can be used for combined heat and power production (CHP) or be converted into higher molecular weight hydrocarbons by using catalysts in the Fischer-Tropsch synthesis (FTS) process [81]. One possible use of the gas is in combination with Solid Oxide Fuel Cell (SOFC) systems for power generation.

In the uses just mentioned, the presence of another pyrolysis product, tar, can be verified within the gas. It is a compound of aromatic hydrocarbons and thus consists of carbon, oxygen, hydrogen and in minor traces nitrogen sulphur and a few other elements and inorganic compounds with high viscosity [75]. It consists of different compounds depending on the pyrolysis temperature. It is also defined as all organics boiling at temperatures above that of benzene. Its presence results in damage or an unacceptable level of maintenance for the system [82]. In the case of SOFC cells, it generates both a deactivation of catalytic reactions (shift, reforming...) and a formation of solid carbon that leads to the break-down of the anode structure and thus the failure of the fuel cell.

# Chapter 4 Methods

Since these two technologies, anaerobic digestion and pyrolysis, are of considerable importance in the production of renewable energy and thus the reuse of basically waste materials, a considerable number of scholarly articles have been published over the years. Each of these articles, however, deals with different aspects of these technological processes. In order to be able to make conclusions, it is necessary to carry out a process of pre-selection of the relevant studies and a subsequent adaptation of the data and creation of useful indices. The details of this work are reported in this chapter.

## 4.1 AD parameters for the comparison

There is an extensive scientific bibliography on AD and its many aspects. Many papers have been read to understand which is the most used feedstock, the influence of some operative parameters and the typical results obtained. The work has been focused on the papers that are more recent and on the one that are mostly cited by other studies. The papers reviewed for the AD were published between 2007 and 2022.

These studies were conducted by different authors at different periods, in different locations around the world and with different objectives. All the data were presented in different typologies: with non-comparable unit of measurements or with different basis as reference. It was therefore necessary to make an effort in selecting the studies to be analyzed, choosing the data to be monitored, and in the subsequent process of standardization for comparison.

There are also a multitude of studies that present more than one experiment because, for example, with the same operative parameters the feedstock is

changed and therefore many results are obtained. In these situations, all the results are collected.

To compare the results some manipulations and simplified assumptions on the data have been necessary in order to obtain comparable reference data and results.

In the research phase, attention has been paid to the properties of the feedstock in input to the process. The collected informations are:

- the typology of feedstock: its origin that can be woody biomass, wastewater, waste materials, agricultural waste, animal origin;
- the ultimate analysis: its chemical composition and in particular the C, H, N, O quantities;
- The proximate analysis: composition in terms of Total Solids (TS), Volatile Solids (VS);

Other important parameters that were taken into account in order to make comparisons. They were related to the operating parameters and the characteristics of the reactors used in each study:

- The scale of the experiment (large scale, pilot, small scale or lab scale)
- The temperature of the process at which the study was conducted that allows to define two possible AD processes: the mesophilic and the thermophilic
- The time of duration of the experiment expressed in days that did not coincide with HRT in all experiments.

The parameters that were considered for the subsequent comparison regarding the process outputs are:

- The TS and VS content in the feedstock that in some cases have been obtained through manipulations and assumptions.
- The composition in terms of percentage of CH<sub>4</sub> and CO<sub>2</sub> of the biogas.
- The yield of bio CH<sub>4</sub> produced expressed in reference to the biomass

in input to the process and in particular to its dried mass. This parameter has been expressed in  $L_{bioCH_4}/kg_{DM}$  by making certain manipulations in several cases, which will be indicated below.

In some studies, there are also reported the results of the production of the other output of the AD process, the solid digestate.

All these data reported before are useful to make a valid and coherent comparison between different experiments, for example putting under comparison papers that report experiment with digester of the same scale. This is done also to understand how a different value of a certain properties can change the outcome of AD and to see if the results that can be obtained in the simulation process can be considered in accordance with the literature.

Hereinafter all the calculations done to have proper values are reported:

- Feedstocks were grouped under macro-categories in terms of provenance. Going more specific, however, in many cases they are a mixture of feedstock as the plant is often built to valorize excess or waste material from other production processes.
- the proximate analysis on dry basis (%wt) as reported.

$$\%_{moisture} + \%_{fixed\ carbon} + \%_{volatile\ matter} + \%_{ash} = 100\%$$

(Equation 2)

- the biogas composition (v/v) when is not expressed has been calculated as:

$$\%_{CH_4} + \%_{CO_2} = 100\%$$

(Equation 3)

- the scale of the experiment (experimental studies or large scale)
- the yield of biogas: it is given under different forms and with different unit of measurement.
- The temperature of the digestion can be subdivided into two big

categories: mesophilic conditions if the temperature is lower than 45 °C and otherwise thermophilic conditions.

## **4.2 Pyrolysis parameters for the comparison**

Many papers have been analyzed to understand which are the most used feedstocks, the influence of some operative parameters and the typical results obtained. The work has been focused on the papers that are more recent and on the ones that are mostly cited by other studies. The papers reviewed for pyrolysis were published between 2002 and 2021. As these studies were conducted by different people at different times, in different locations around the world and with different objectives all the data were presented in different typologies: with non-comparable unit of measurements or with different basis as reference.

There are also a multitude of studies that present more than one experiment because for example, with the same operative parameters the feedstock is changed and therefore many results are obtained. In these situations, all the results are collected. To compare the results some calculations and simplified assumptions on the data have been necessary in order to obtain comparable source data and results.

In the research phase attention has been directed on the properties of the feedstock inputs to the process. The collected informations are:

- the typology of feedstock: its origin that can be agricultural waste, woody biomass, AD digestate;
- the ultimate analysis: its chemical composition and in particular the C, H, N, O quantities;
- the proximate analysis: composition in terms of TS and therefore moisture content;

- the HHV expressed in MJ/kg.

Other important parameters that were taken into account in order to make comparisons were the operating parameters as well as the characteristics of the bioreactor used in the individual study:

- The scale of the experiment (experimental studies or large scale)
- The temperature of the process at which the study was conducted.
- The residence time of the experiment.

With regard to the outputs of the pyrolysis process (biochar, biogas and bio-oil), the following properties and data have been collected:

- the yield of biochar produced, expressed as a percentage of the products of the pyrolysis;
- the biochar surface expressed in  $\text{m}^2/\text{g}$ ;
- the ultimate analysis of the obtained biochar: its chemical composition and in particular the C, H, O, N quantities;
- the HHV of the biochar in MJ/kg;
- the yield of biogas produced, expressed as a percentage of the products of the pyrolysis;
- the yield of bio-oil produced, expressed as a percentage of the products of the pyrolysis;
- the HHV of the pyrolysis gas in MJ/kg;
- the HHV of the bio-oil in MJ/kg.

Similarly to what was done to AD, each study focuses on a particular aspect of pyrolysis rather than on all the data that could have been useful for this work.

Some studies focus exclusively on the biochar produced, others on all three products, and still others on the influence of temperature, and so on.

Since the main interest was focused on biochar production, the efficiency of the pyrolysis process in producing biochar was calculated. This parameter is obtained by comparing the energy potential of the biochar obtained with the energy potential of the biomass entering the process, according to the formula shown below:

$$\eta_{biochar} = \frac{yield_{biochar} \left[ \frac{kg}{kg_{DM}} \right] * HHV_{biochar} \left[ \frac{MJ}{kg} \right]}{HHV_{feedstock} \left[ \frac{MJ}{kg} \right]}$$

(Equation 4)

Hereinafter all the calculations done to have proper values are reported:

- feedstocks were grouped under macro-categories in terms of provenance. Going more specific, however, in many cases they are a mixture of feedstock as the plant is often built to valorize excess or waste material from other production processes.
- the HHV of the feedstock, when it is not given directly, is calculated through the following formula:

$$HHV_{biomass} = 0,2949 * C + 0,825 * H$$

(Equation 5) [84]

- the yield of biochar: it is given under different forms and with different unit of measurement.

# Chapter 5 Results

After reading multiple scientific articles and studies reporting on various aspects of AD and pyrolysis, only a few were selected that contained information useful for the purpose of this work. Specifically, for the AD, 58 different process setups were considered, some of which were contained within the same study, in which certain parameters were varied to observe changes in output. In the case of pyrolysis, there were 53 different cases. Problems were encountered in comparing the results and parameters of different studies, as these were not always expressed in the same unit of measurement. It was therefore necessary to make some approximations, as explained in chapter 4 of this work. A significant number of papers were not reported or taken into consideration because, although they contained some data that was important for this work, they did not present other parameters that had been decided to be considered in the discussion. It has been tried to prioritize and focus mainly on the most recent works, but also those most frequently cited in other studies.

It should be noted that most of these studies report experiments carried out in the laboratory, as it is difficult to find papers reporting cases of commercial-scale plants that are actually in constant operation.

They were sorted and the necessary calculations were carried out as indicated in Chapter 4. Subsequently, correlations between the operating parameters and the characteristics of the materials used were evaluated using the Power BI tool.

Before proceeding to the presentation of the results and their analysis, all the data taken into account and collected as a result of the reading of the documents are reported. All this work will be done for both anaerobic digestion and pyrolysis processes.

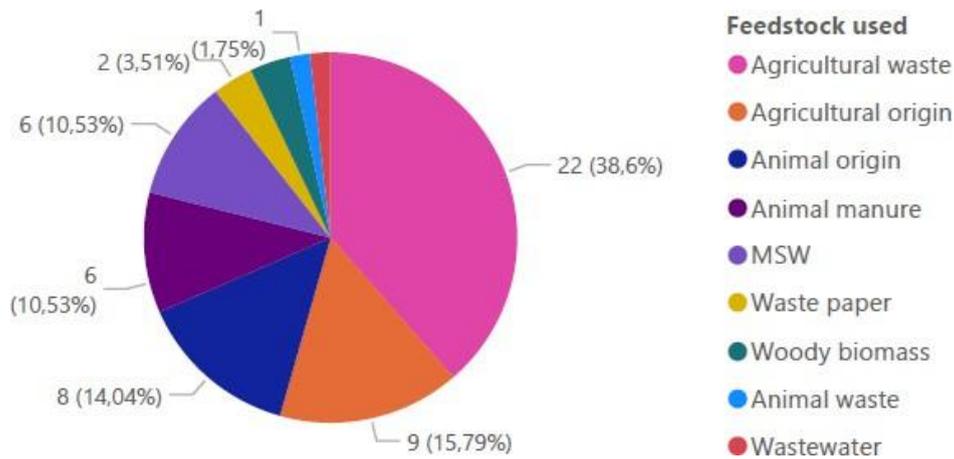
## 5.1 Anaerobic Digestion

Table 3 below presents summary data on AD processes obtained from the studies analyzed. This provides an overview of the main parameters and results obtained from the literature reviewed.

Feedstock used	Feedstock rate [kg/h]	TS [%wt]	VS [%wt]	Scale	Time [days]	T (°C)	Type of digestion	Yield [LbioCH <sub>4</sub> /kgDM]	Ref.
Agricultural waste		5,0	4,5	Experimental	120	37	Mesophillic	250,9	[85]
Agricultural waste		10,0	9,0	Experimental	120	37	Mesophillic	324,1	[85]
Agricultural waste		15,0	13,5	Experimental	120	37	Mesophillic	321,7	[85]
Agricultural waste		20,0	18,0	Experimental	120	37	Mesophillic	288,7	[85]
Agricultural waste	1858,33			Large Scale	83,72		Thermophillic	387,0	[86]
Agricultural waste	1537,50			Large scale	45,45		Mesophillic	360,0	[86]
Agricultural waste		25,9	24,0	Experimental	55	35	Mesophillic	182,5	[87]
Agricultural waste		23,5	22,0	Experimental	40	37	Mesophillic	207,6	[88]
Agricultural waste		7,7	4,1	Experimental	30	37	Mesophillic	70,2	[89]
Agricultural waste		7,7	4,1	Experimental	30	37	Mesophillic	62,2	[89]
Agricultural waste		7,7	4,1	Experimental	30	37	Mesophillic	66,0	[89]
Agricultural waste		7,7	4,1	Experimental	30	37	Mesophillic	40,1	[89]
Agricultural waste		7,7	4,1	Experimental	30	37	Mesophillic	26,3	[89]
Agricultural waste		7,7	4,1	Experimental	30	37	Mesophillic	25,0	[89]
Waste paper		7,7	4,1	Experimental	30	37	Mesophillic	8,1	[89]
Woody biomass		7,7	4,1	Experimental	30	37	Mesophillic	9,1	[89]
Agricultural waste		5,0	4,5	Experimental	30	37	Mesophillic	111,6	[89]
Agricultural waste		5,0	4,5	Experimental	30	37	Mesophillic	99,9	[89]
Agricultural waste		5,0	4,5	Experimental	30	37	Mesophillic	125,2	[89]
Agricultural waste		5,0	4,5	Experimental	30	37	Mesophillic	72,9	[89]
Agricultural waste		5,0	4,5	Experimental	30	37	Mesophillic	53,7	[89]
Agricultural waste		5,0	4,5	Experimental	30	37	Mesophillic	51,5	[89]
Waste paper		5,0	4,5	Experimental	30	37	Mesophillic	281,0	[89]
Woody biomass		5,0	4,5	Experimental	30	37	Mesophillic	48,9	[89]
Agricultural waste	56000,00	35,5	32,0	Large scale	62	45	Mesophillic	157,9	[90]
MSW		6,5	6,0	Experimental	60	55	Thermophillic	101,5	[91]
MSW		7,3	6,5	Experimental	60	55	Thermophillic	195,9	[91]
MSW		6,7	6,2	Experimental	60	55	Thermophillic	27,8	[91]
MSW		6,7	5,5	Experimental	60	55	Thermophillic	147,8	[91]
MSW		7,1	5,5	Experimental	60	55	Thermophillic	224,6	[91]
MSW		6,8	6,3	Experimental	60	55	Thermophillic	250,1	[91]
Wastewater	1666,67			Large scale	39,5	25	Mesophillic	96,3	[92]
Animal origin		15,0	6,9	Experimental	217	35	Mesophillic	126,2	[93]
Animal origin		15,0	9,3	Experimental	217	35	Mesophillic	195,9	[93]
Animal origin		15,0	10,8	Experimental	217	35	Mesophillic	252,4	[93]
Animal origin		15,0	27,7	Experimental	217	35	Mesophillic	194,0	[93]
Animal origin		15,0	8,9	Experimental	217	35	Mesophillic	265,4	[93]
Animal origin		15,0	12,9	Experimental	217	35	Mesophillic	244,6	[93]
Animal origin		15,0	12,3	Large scale	217	35	Mesophillic	326,8	[93]
Agricultural origin		15,0	10,0	Experimental		35	Mesophillic	402,1	[94]
Agricultural origin		17,8	17,2	Experimental		35	Mesophillic	349,4	[94]
Agricultural origin		11,1	10,5	Experimental		35	Mesophillic	294,4	[94]
Agricultural origin		9,2	8,7	Experimental		35	Mesophillic	321,9	[94]
Agricultural origin		13,1	12,4	Experimental		35	Mesophillic	162,0	[95]
Agricultural origin		40,9	30,5	Experimental		35	Mesophillic	178,0	[95]
Agricultural origin		40,9	30,5	Experimental		35	Mesophillic	208,0	[95]
Agricultural origin		40,9	30,5	Experimental		35	Mesophillic	198,0	[95]
Animal manure	2500,00	40,9	30,5	Large scale	35	35	Mesophillic	180,0	[96]
Animal Manure	1458,33	20,0	16,0	Large scale	35	35	Mesophillic	240,7	[96]
Animal Manure	3125,00	27,0	18,9	Large scale	35	35	Mesophillic	158,3	[96]
Animal Manure	458,33	12,0	9,5	Large scale	35	35	Mesophillic	162,9	[96]
Agricultural waste	1208,33	35,0	28,0	Large scale	35	35	Mesophillic	360,0	[96]
Animal waste	416,67	30,0	28,5	Large scale	35	35	Mesophillic	350,0	[96]
Animal Manure	10416,67	20,0	18,0	Large scale	35	35	Mesophillic	160,0	[96]
Animal Manure	7291,67	10,0	8,0	Large scale	35	35	Mesophillic	160,0	[96]
Agricultural origin	1666,67	10,0	8,0	Large scale	35	35	Mesophillic	308,6	[96]

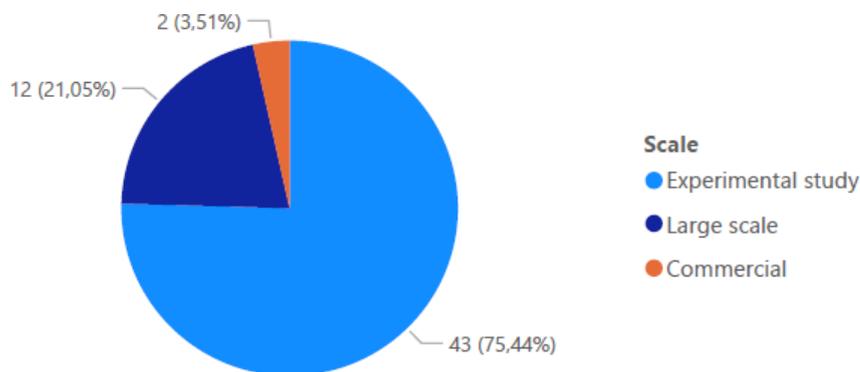
*Table 3 Comparison table of the studied Anaerobic Digestion cases*

The studies concerning AD, as can be seen in Figure 12, deal with processes in which the feedstock material used is waste material or waste from agricultural activities with around 54% of the studies analyzed. This is followed by animal waste material from livestock farms, MSW, wastepaper derived from municipal waste and finally wastewater.



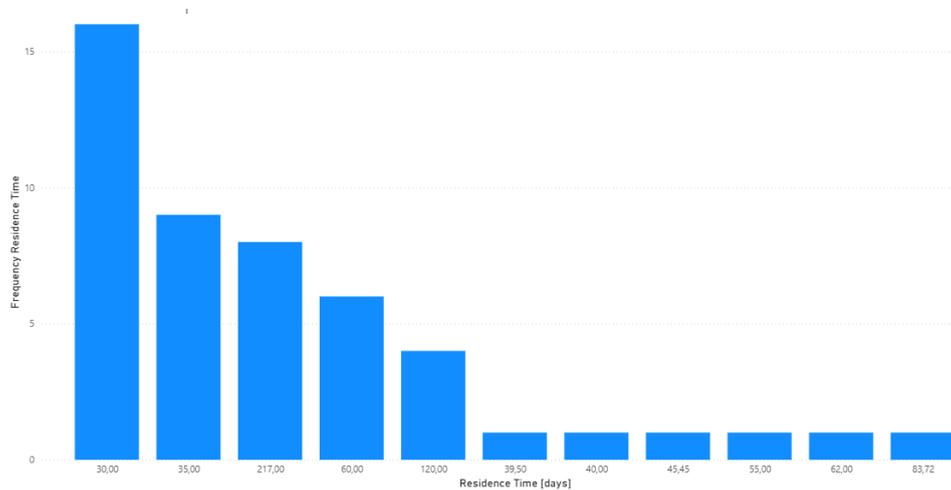
**Figure 12 Distribution of feedstock in different Anaerobic Digestion's cases**

Three quarters of the cases considered refer to installations concerning experimental studies. This testifies to the fact that information on large-scale, operating plants is not very user-friendly. In figure 13 the studies considered are organized according to their scale.



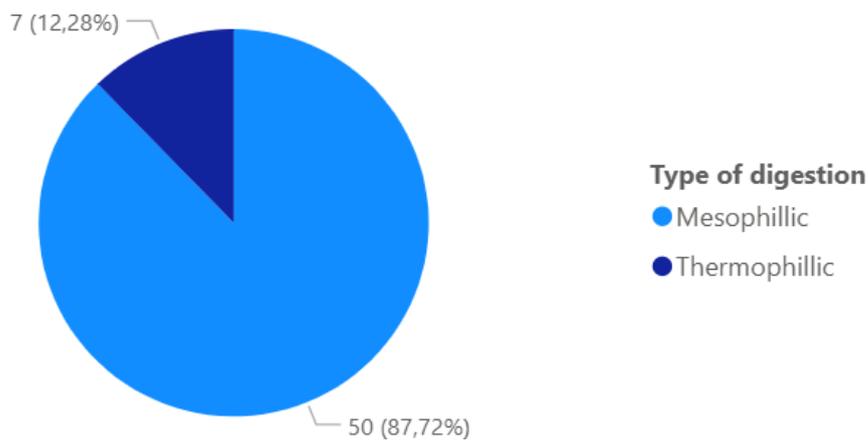
**Figure 13 Scale of Anaerobic Digestion's cases**

As mentioned above, one of the evaluated aspects of the AD process is the residence time the feedstock spends inside the reactor to complete digestion. Observing Figure 14 it can be argued that a large number of the cases considered predict a digestion residence time of around 30 to 35 days.



**Figure 14 Duration of Anaerobic Digestion's cases**

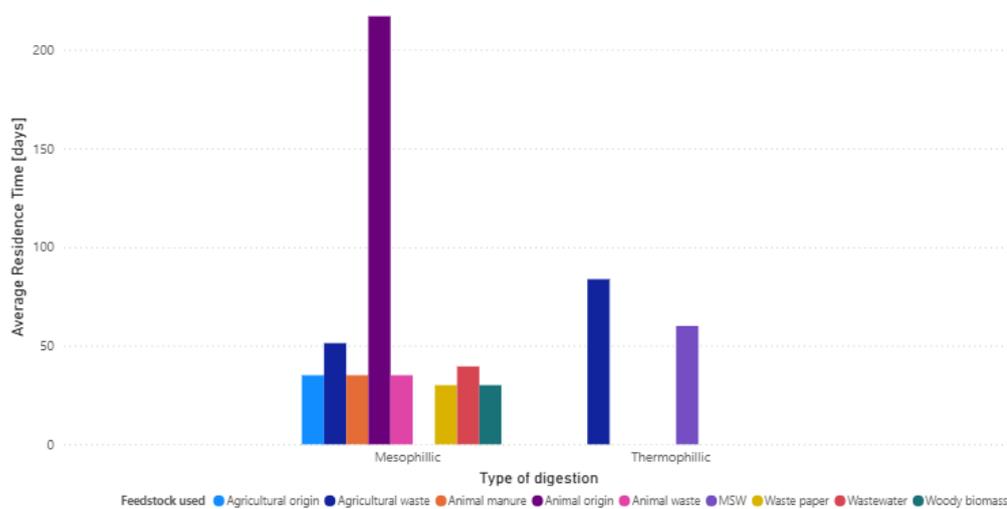
Concerning the temperature inside the digester, as shown in Figure 15, about 88 % of the studies analyzed concern mesophilic processes with temperatures typically between 35 °C and 37 °C.



**Figure 15 Type of disestion in Anaerobic Digestion's cases**

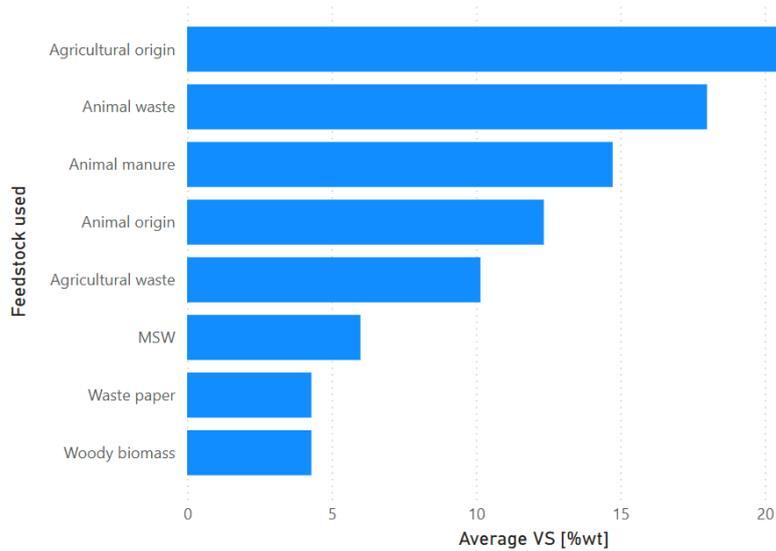
In Figure 16, analyzing the different residence times for the different

biomasses and for the two types of AD (mesophilic and thermophilic), it can be seen that with thermophilic digestion at higher temperatures, only two types of biomass are digested, MSW and agricultural waste. On the other hand, with the exception of MSW, all other biomasses are treated with mesophilic digestion at lower temperatures. With the exception of biomass of animal origin (which has an average peak of 217 days), biomass treated with a mesophilic regime has a lower average residence time (all biomass has an average residence time between 30 and 50 days) than that of the thermophilic regime (biomass has an average residence time between 60 and 85 days).



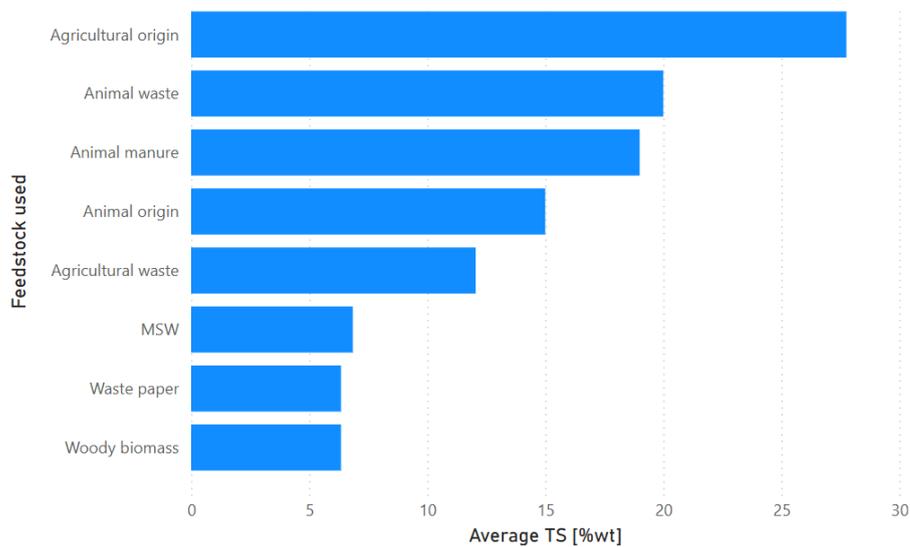
**Figure 16 Average residence time in different feedstock in AD**

The following Figures 17 and 18 show the amount of volatile solids within the feedstock entering the digester. Feedstock of agricultural origin has the highest volatile solids content (around 22,5%), while woody biomass and waste paper have around 4% VS.



**Figure 17 Volatile Solid concentration in feedstock**

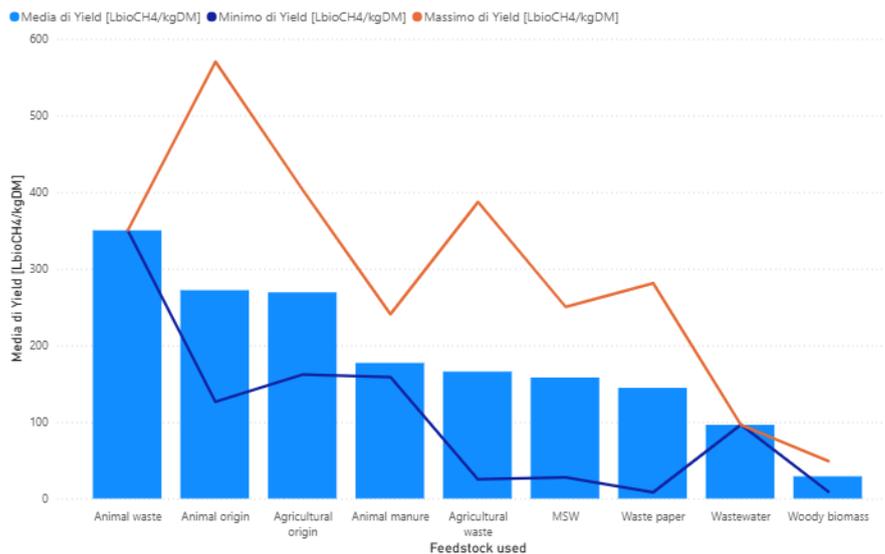
Feedstocks have an average TS content of between 6% and 28%. In particular, feedstock of agricultural origin has an average TS content of around 28%. A very low amount of TS and consequently a high degree of moisture is found within Animal manure, MSW, wastepaper and woody biomass. These results, however, are also since studies concerning these feedstocks were limited in number.



**Figure 18 Total Solid concentration in feedstock**

The main objective of the completed analysis is to see from which processes the greatest amount of biomethane can be generated. With this in mind, the following graphs show the trends in CH<sub>4</sub> production as the nature and origin of the digested biomass change, at the scale of the study considered.

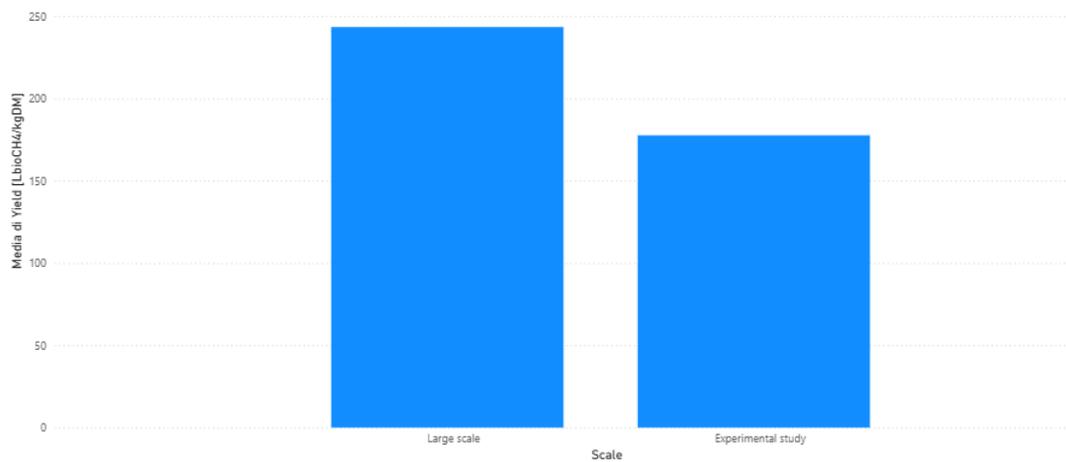
In particular, in Figure 19, CH<sub>4</sub> production, expressed in LbioCH<sub>4</sub>/kg<sub>DM</sub>, takes on higher values in the case of biomass of animal origin or waste from animals with values hovering around 350 LbioCH<sub>4</sub>/kg<sub>DM</sub>. Good average values are also obtained with agricultural waste materials. In contrast, the lowest yields are encountered using waste paper, wastewater and woody biomass. The feedstock capable of generating the lowest amount of bio CH<sub>4</sub> is woody biomass, which has an average production of approximately 29 LbioCH<sub>4</sub>/kg<sub>DM</sub>.



**Figure 19 Yield of Biogas produced for different feedstock**

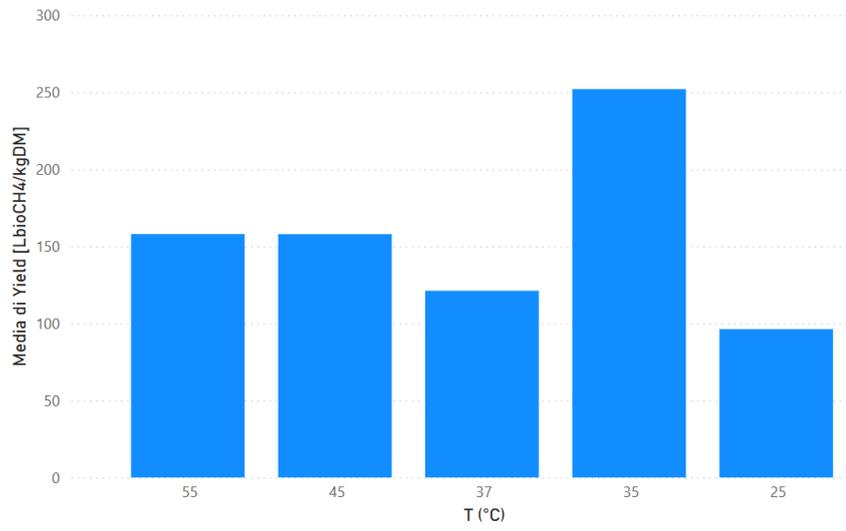
Instead, in Figure 20, the existing proportionality between experiment or large scale is shown. In general, on average, we see that large-scale and already commercially available plants return higher yields than those experiments conducted in the laboratory or on a small scale. Laboratory plants have an average yield of around 177 LbioCH<sub>4</sub>/kg<sub>DM</sub>, while commercial plants, although fewer in number, have a yield of around 240 LbioCH<sub>4</sub>/kg<sub>DM</sub>. Laboratory studies present a

certain degree of uncertainty regarding the possibility of obtaining the same results on a commercial scale. This stems from the difficulty in replicating laboratory conditions in terms of biological, chemical, physical, and operational factors. In experiments, mixing within the digester is optimal, whereas on an industrial scale, areas with varying densities of material or with different types of material are created. In addition, the microbial community within the reactor may behave differently. Furthermore, on a large scale, it is more complicated to control operating parameters such as temperature and its variations within the digester, which is less sensitive to changes than a laboratory experiment digester. Variations in large-scale plants can be caused by flow variations, failures, or power supply instability.



***Figure 20 Yield of Biogas for different scales of Anaerobic Digestion's cases***

Figure 21 shows the production of bio CH<sub>4</sub> in relation to the temperature of the digestion process. At temperatures ranging from 25° to 55°, production ranges between 100 LbioCH<sub>4</sub>/kg<sub>DM</sub> and 260 LbioCH<sub>4</sub>/kg<sub>DM</sub>. In particular, there is a peak in production at 260 LbioCH<sub>4</sub>/kg<sub>DM</sub> at a temperature of 35°, which corresponds to mesophilic conditions.



*Figure 21 Yield of Biomethane with respect to T [°C]*

## 5.2 Pyrolysis

The following Table 4 summarizes the main experimental data reported in the literature concerning the production of biochar, biogas and bio-oil through pyrolysis processes applied to different types of biomass. The studies analyzed differ in terms of the operating conditions adopted, such as process temperature and residence time, as well as the variability in the composition of the feedstocks used. In order to allow for a consistent comparison between the different contributions, the yields have been expressed in terms of biochar obtained relative to the initial dry mass of the starting material.

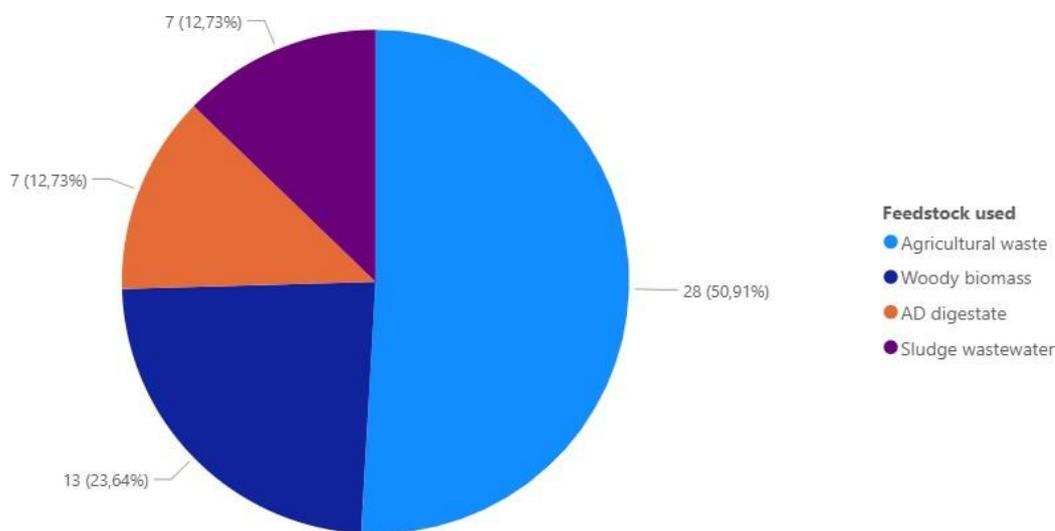
Hence, the Table 4 is therefore a useful summary tool for identifying the main yield trends and highlighting the correlation between feedstock composition, process parameters and biochar production. It also provides the basis for subsequent statistical and comparative assessments aimed at optimizing pyrolysis as a process for the energy and environmental valorization of waste and residual biomass.

Feedstock used	Feedstock quantity [kg/h]	Moisture [%wt]	TS [%wt]	VS [%wt]	C [%]	H [%]	O [%]	N [%]	HHV [MJ/kg]	Scale	Time [min]	T [°C]	Schar [m <sup>2</sup> /g]	Moisture [%wt]	TS [%wt]	VS [%wt]	C [%]	H [%]	O [%]	N [%]	Char HHV [MJ/kg]	Yield char [%]	Yield gas [%]	Gas HHV [MJ/kg]	Yield oil [%]	Oil HHV [MJ/kg]	η biochar	Ref.
Agricultural waste	1,0	7,6	92,4	66,2	41,6	6,1	51,6	0,7	17,3	Experimental study	60	400		6,2	93,8	4,7	76,2	4,5	19,2	0,2	26,2	29,8				44,0	0,45	[97]
Woody biomass	1,0	10,7	89,3	68,5	47,0	6,2	46,7	0,2	19,0	Experimental study	60	400		4,2	95,8	1,0	82,5	3,8	13,5	0,2	27,5	32,2				44,0	0,47	[97]
Agricultural waste	1,0	7,6	92,4	66,2	41,6	6,1	51,6	0,7	17,3	Experimental study	600		6,0	94,0	4,8	84,9	2,3	12,5	0,4	26,9	21,7				44,0	0,34	[97]	
Woody biomass	1,0	10,7	89,3	68,5	47,0	6,2	46,7	0,2	19,0	Experimental study	600		1,3	98,7	8,9	88,4	2,7	8,6	0,3	28,3	27,0				44,0	0,40	[97]	
AD digestate	996,1	70,3	29,7	21,4	42,5	6,1	50,0	1,4	17,5	Experimental study	10	400					42,5	6,8	49,3	1,4	18,1	35,7	53,0		11,3	23,5	0,37	[98]
AD digestate	279,2	0,0	100,0	89,0	43,0	6,2	39,5	1,3	17,8	Large scale	10	600					42,5	6,8	49,3	1,4	18,1	34,0	10,2		55,8	23,5	0,35	[98]
AD digestate					73,6	2,4	24,0		23,7	Experimental study	90	600	17,7				76,5	2,9	19,8	0,8	25,0	18,0				44,0	0,19	[99]
AD digestate					33,9	4,5	46,9	2,4	13,7	Experimental study	120	600					30,8	1,4	39,9	2,7	10,2	45,5	43,6		10,9	44,0	0,34	[100]
Agricultural waste					36,1	3,4	55,8	1,2	13,5	Experimental study	120	600					50,8	2,1	36,7	1,8	16,7	36,3	51,2		12,5	44,0	0,45	[100]
Agricultural waste	4,7	95,3			40,6	5,4	43,8	1,9	16,4	Experimental study	300	400	6,5				49,7	2,8	15,0	2,3	16,9	39,6				44,0	0,41	[101]
Agricultural waste	4,7	95,3			40,6	5,4	43,8	1,9	16,4	Experimental study	300	500	7,1				47,3	1,7	17,0	1,9	15,3	36,6				44,0	0,34	[101]
Agricultural waste	4,7	95,3			40,6	5,4	43,8	1,9	16,4	Experimental study	300	600	6,8				51,3	1,3	10,1	2,0	16,2	34,2				44,0	0,34	[101]
Agricultural waste	4,7	95,3			40,6	5,4	43,8	1,9	16,4	Experimental study	300	700	13,4				50,9	1,2	8,1	1,8	16,0	31,7				44,0	0,31	[101]
Agricultural waste	4,7	95,3			40,6	5,4	43,8	1,9	16,4	Experimental study	300	800	12,6				48,9	1,2	15,7	1,4	15,4	29,4				44,0	0,28	[101]
Agricultural waste	4,9	95,1			45,8	6,2	40,7	1,7	18,6	Experimental study	300	400	2,8				63,4	3,2	16,7	2,6	21,3	30,6				44,0	0,35	[101]
Agricultural waste	4,9	95,1			45,8	6,2	40,7	1,7	18,6	Experimental study	300	500	1,4				67,1	2,4	13,5	2,3	21,8	30,2				44,0	0,35	[101]
Agricultural waste	4,9	95,1			45,8	6,2	40,7	1,7	18,6	Experimental study	300	600	1,2				66,9	1,7	14,4	2,1	21,1	28,8				44,0	0,33	[101]
Agricultural waste	4,9	95,1			45,8	6,2	40,7	1,7	18,6	Experimental study	300	700	0,3				66,0	1,3	14,7	2,1	20,5	28,1				44,0	0,31	[101]
Agricultural waste	4,9	95,1			45,8	6,2	40,7	1,7	18,6	Experimental study	300	800	6,8				67,6	1,0	12,5	1,9	20,7	27,2				44,0	0,30	[101]
Agricultural waste	6,8	93,2			40,7	5,1	32,3	3,8	16,2	Experimental study	300	400	2,7				39,8	2,5	13,9	2,1	13,8	45,3				44,0	0,39	[101]
Agricultural waste	6,8	93,2			40,7	5,1	32,3	3,8	16,2	Experimental study	300	500	0,1				38,9	1,5	13,7	2,2	12,7	42,0				44,0	0,33	[101]
Agricultural waste	6,8	93,2			40,7	5,1	32,3	3,8	16,2	Experimental study	300	600	1,8				35,0	1,1	17,6	2,1	11,2	40,0				44,0	0,28	[101]
Agricultural waste	6,8	93,2			40,7	5,1	32,3	3,8	16,2	Experimental study	300	700	0,9				39,3	1,2	10,6	2,4	12,6	38,9				44,0	0,30	[101]
Agricultural waste	6,8	93,2			40,7	5,1	32,3	3,8	16,2	Experimental study	300	800	1,8				36,3	0,7	16,9	2,6	11,3	37,0				44,0	0,26	[101]
Sludge wastewater	84,5	15,5	11,4	37,9	5,5	50,4	6,2	15,7	Experimental study	90	300	4,0				39,7	4,1	49,1	7,1	15,1	64,2				44,0	0,62	[102]	
Sludge wastewater	84,5	15,5	11,4	37,9	5,5	50,4	6,2	15,7	Experimental study	30	300	90,0				22,5	2,2	73,0	2,3	8,5	60,5				44,0	0,33	[102]	
Sludge wastewater	14,2	85,8	64,8	38,1	5,0	15,0	5,8	15,4	Experimental study	40	450	39,6				16,7	0,9	80,2	2,2	5,7	57,0				44,0	0,21	[103]	
Agricultural waste	2330,0	10,0							14,5	Large scale	0,03	550		36,2			56,5	1,7	11,5		6,8	26,0	25,9		48,1	18,0	0,12	[104]
Agricultural waste	0,4				48,8	6,6	40,9	3,7	19,8	Experimental study		350									17,3	46,0	10,0	14,5	44,0	44,0	0,40	[104]
Agricultural waste	0,4				48,8	6,6	40,9	3,7	19,8	Experimental study		600									21,3	31,0	23,0	14,5	46,0	44,0	0,33	[104]
Agricultural waste	0,4				47,1	6,2	37,6	9,1	19,0	Experimental study		350									19,9	38,0	15,0	3,0	47,0	44,0	0,40	[104]
Agricultural waste	0,4				47,1	6,2	37,6	9,1	19,0	Experimental study		600									26,1	27,0	26,0	13,0	47,0	44,0	0,37	[104]
Agricultural waste	5,0	6,8	93,2	79,0	45,6	5,5	45,7	0,6	17,9	Experimental study	0,5	450		9,1	90,9	26,3	66,5	3,4	15,3	1,3	22,5	31,3				44,0	0,39	[105]
Agricultural waste	5,0	6,8	93,2	79,0	45,6	5,5	45,7	0,6	17,9	Experimental study	0,5	600		10,6	89,4	11,2	71,5	2,5	5,4	1,1	23,2	16,9				44,0	0,22	[105]
Agricultural waste	5,0	6,8	93,2	79,0	45,6	5,5	45,7	0,6	17,9	Experimental study	0,5	800		11,2	88,8	3,3	71,6	1,2	4,9	0,9	22,1	11,4				44,0	0,14	[105]
Woody biomass	5,0	4,7	95,3	83,8	48,5	5,9	45,2	0,1	19,2	Experimental study	0,5	450		5,1	94,9	44,7	71,8	3,9	22,7	0,2	24,4	26,6				44,0	0,34	[105]
Woody biomass	5,0	4,7	95,3	83,8	48,5	5,9	45,2	0,1	19,2	Experimental study	0,5	600		6,5	93,5	19,7	84,7	2,8	10,3	0,2	27,3	15,2				44,0	0,22	[105]
Woody biomass	5,0	4,7	95,3	83,8	48,5	5,9	45,2	0,1	19,2	Experimental study	0,5	800		10,4	89,6	2,6	89,7	1,2	3,6	0,3	27,5	9,5				44,0	0,14	[105]

Feedstock used	Feedstock quantity [kg/h]	Moisture [%wt]	TS [%wt]	VS [%wt]	C [%]	H [%]	O [%]	N [%]	HHV [MJ/kg]	Scale	Time [min]	T [°C]	Schar [m <sup>2</sup> /g]	Moisture [%wt]	TS [%wt]	VS [%wt]	C [%]	H [%]	O [%]	N [%]	CharHHV [MJ/kg]	Yield char [kg/kgDM]	Yield gas [%]	Gas HHV [MJ/kg]	Yield oil [%]	Oil HHV [MJ/kg]	η biochar	Ref.
Sludge wastewater	0,02	5,0	95,0		35,7	5,2	25,4	3,5	14,8	Experimental study		450	6,7	0,9		23,1	36,0	2,6	6,4	3,8	12,8	53,0	9,6		37,4	44,0	0,46	[106]
Sludge wastewater	0,02	5,0	95,0		35,7	5,2	25,4	3,5	14,8	Experimental study		450	5,4	0,4		18,4	29,9	1,8	6,5	3,2	10,3	47,0	13,0		40,0	44,0	0,33	[106]
Sludge wastewater	0,02	5,0	95,0		35,7	5,2	25,4	3,5	14,8	Experimental study		850	35,2	1,4		4,6	33,0	0,7	1,7	1,7	10,3	44,0	16,0		40,0	44,0	0,31	[106]
Sludge wastewater	0,02	5,0	95,0		35,7	5,2	25,4	3,5	14,8	Experimental study		850	63,5	1,0		5,7	29,6	0,7	1,5	1,4	9,3	43,0	16,0		41,0	44,0	0,27	[106]
Woody biomass		13,2	71,0		51,7	5,3	42,6	0,3	19,6	Experimental study	60	500	202,0	1,3		9,2	85,6	2,8	10,5	1,1	27,6	26,4	24,1		49,5	44,0	0,37	[107]
Woody biomass		21,0	49,1		61,6	4,4	33,0	1,0	21,8	Experimental study	60	500	13,7	2,6		14,3	84,4	2,9	11,7	1,0	27,3	45,9	29,8		24,3	44,0	0,58	[107]
Agricultural waste		7,3	56,4		48,8	6,0	43,3	2,0	19,3	Experimental study	60	500	45,8	2,1		6,5	86,3	3,1	7,4	3,3	28,0	28,0	30,4		41,6	44,0	0,41	[107]
Agricultural waste		11,9	66,8		55,8	5,6	37,7	0,8	21,1	Experimental study	60	500	191,0	0,0		12,3	87,9	2,9	8,1	1,1	28,3	34,0	19,4		46,6	44,0	0,46	[107]
Woody biomass		8,8	80,1		50,5	5,8	43,4	0,2	19,7	Experimental study	60	500	316,0	1,5		12,8	89,3	2,6	7,3	0,8	28,5	24,1	20,0		55,9	44,0	0,35	[107]
Woody biomass		10,0	68,9		53,4	6,1	39,1	1,4	20,8	Experimental study	60	500	13,6	0,4		18,1	84,8	3,1	10,2	1,8	27,6	31,7	20,7		47,6	44,0	0,42	[107]
AD digestate	0,1	7,4	92,6	83,0	52,1	8,2	36,8	2,3	22,1	Experimental study	30	400				76,2	5,2	14,1		26,8	41,1				44,0	0,50	[108]	
AD digestate					52,1	8,2	36,8	2,3	22,1	Experimental study	30	600				84,7	3,8	8,0		28,1	30,3				44,0	0,38	[108]	
AD digestate					52,1	8,2	36,8	2,3	22,1	Experimental study	30	800				88,4	2,9	5,9		28,4	26,0				44,0	0,33	[108]	
Woody biomass		5,6		68,5	48,5	5,9	42,8	2,7	19,2	Experimental study		400		33,9			49,1	6,8	42,0	2,1	20,1	37,6	16,4	7,8	46,0	18,8	0,39	[109]
Woody biomass		5,6		68,5	48,5	5,9	42,8	2,7	19,2	Experimental study		450		39,5			53,8	7,4	35,4	3,3	22,0	32,5	16,8	10,4	50,7	22,5	0,37	[109]
Woody biomass		5,6		68,5	48,5	5,9	42,8	2,7	19,2	Experimental study		500		41,3			54,7	7,0	36,0	2,3	21,9	31,5	7,0	13,6	46,0	22,1	0,36	[109]
Woody biomass		5,6		68,5	48,5	5,9	42,8	2,7	19,2	Experimental study		550		47,0			55,9	6,9	34,4	2,8	22,2	30,6	6,9	14,3	43,1	22,7	0,35	[109]

**Table 4 Comparison table of the Pyrolysis cases studied**

Figure 22 in this section provides an overview of the origin of the feedstock used in the cases analyzed.

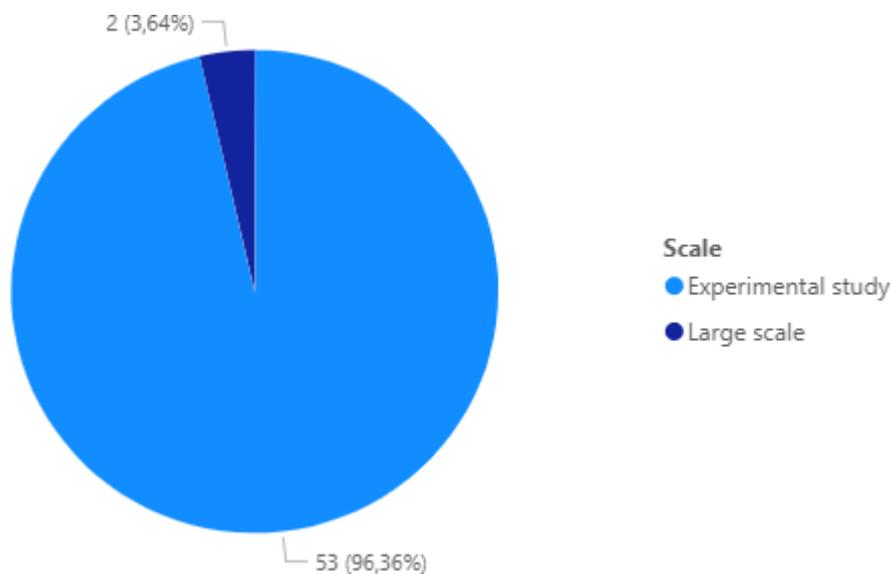


**Figure 22 Distribution of feedstock used in Pyrolysis cases**

The predominant category is agricultural waste, which accounts for approximately 51% of the total (28 cases). This prevalence indicates a high availability of agricultural waste and its suitability for thermochemical conversion

processes. This is followed by woody biomass with 23.64% (13 cases), commonly used for its high carbon content and ease of supply. The AD digestate and sludge wastewater categories are less represented, both at 12.73% (7 cases each), suggesting that the technology is still under development or that these raw materials are less widely available. This demonstrates a certain flexibility in this process in accepting different types of materials, ensuring their use in different contexts.

Almost all of the cases studied (96%) concern small-scale experimental studies carried out in laboratories. Only two cases concern existing large-scale plants (Figure 23).

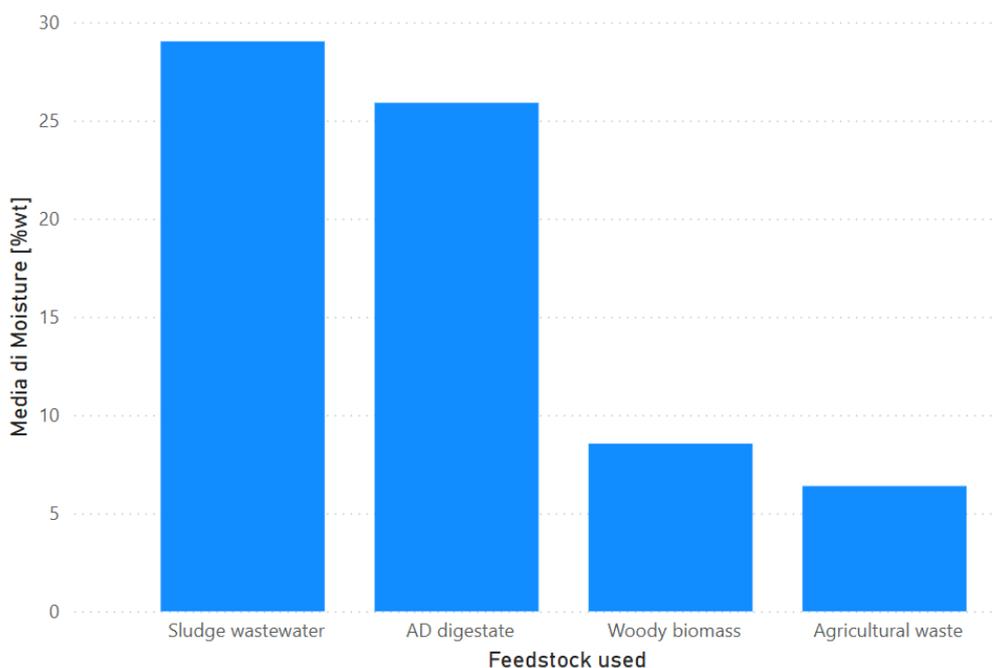


*Figure 23 Scale of Pyrolysis's cases*

Proceeding with the analysis of the pyrolysis process parameters, we will start with the characteristics of the biomass (moisture content, HHV), then move on to process data such as temperature and residence time, and finally to the pyrolysis products and their characteristics.

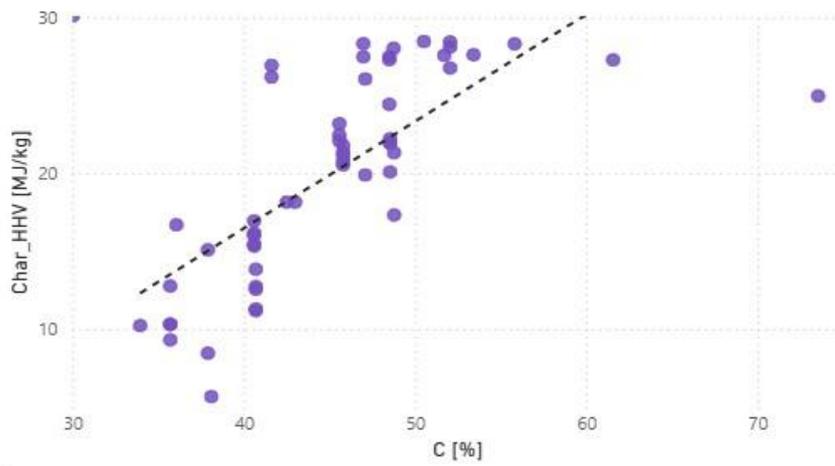
The water content, or moisture, of the biomass used in the cases analyzed (Figure 24) is always within the range of 15%wt to 30%wt on average. In particular, the highest average moisture content is found in sludge wastewater

(29%wt), followed by AD digestate (26%wt). The other biomasses analyzed are drier: woody biomass contain 9.5%wt water and agricultural waste only 6%wt. It should be noted that some of this biomass was previously dried in ovens, resulting in a reduction in biomass moisture content. However, when this pre-treatment is carried out, the moisture content data prior to drying is not always provided, and therefore the biomass moisture content data was collected at the start of the pyrolysis process.

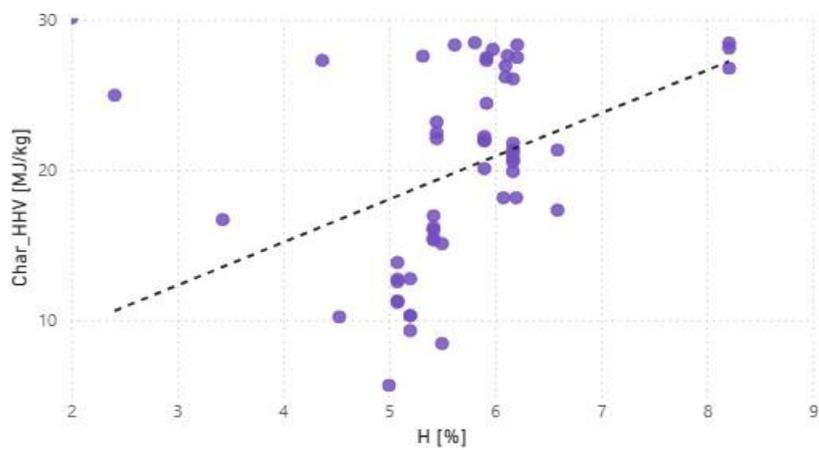


**Figure 24 Moisture in Pyrolysis' feedstock**

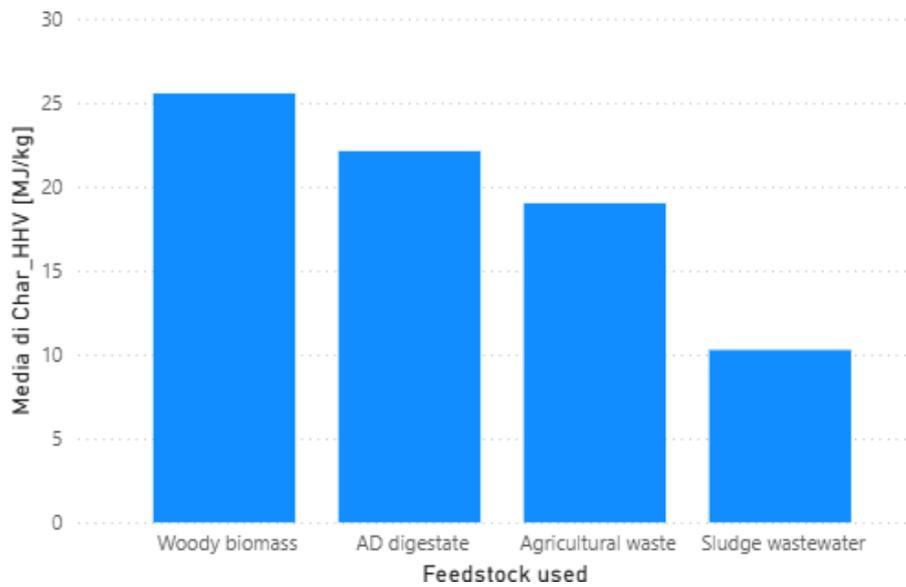
The influence of chemical composition and therefore of the various elements (C, H, O, N) on the HHV value, shown in the following four graphs (Figures 25, 26, 27, 28), highlights how there is a direct proportionality between the percentages of carbon, hydrogen and oxygen and the higher heating value. This trend is inversely proportional in the case of N content, where it is generally observed that as the nitrogen content increases, the HHV value decreases. Wood biomass and digestate from anaerobic digestion, in which the solids content is higher, have the highest carbon concentration.



*Figure 25 Bio Char's Higher Heating Value and its Carbon content*

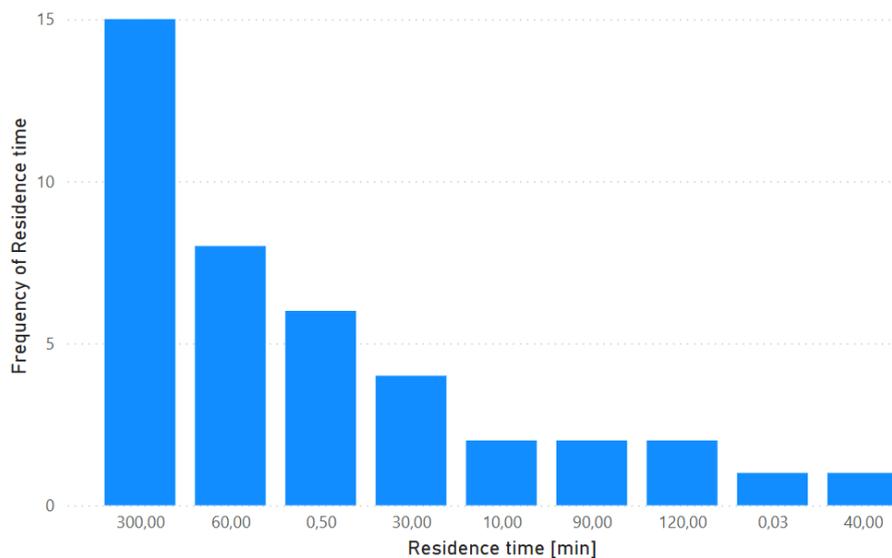






*Figure 29 Bio Char's HHV [MJ/kg] produced for different feedstock*

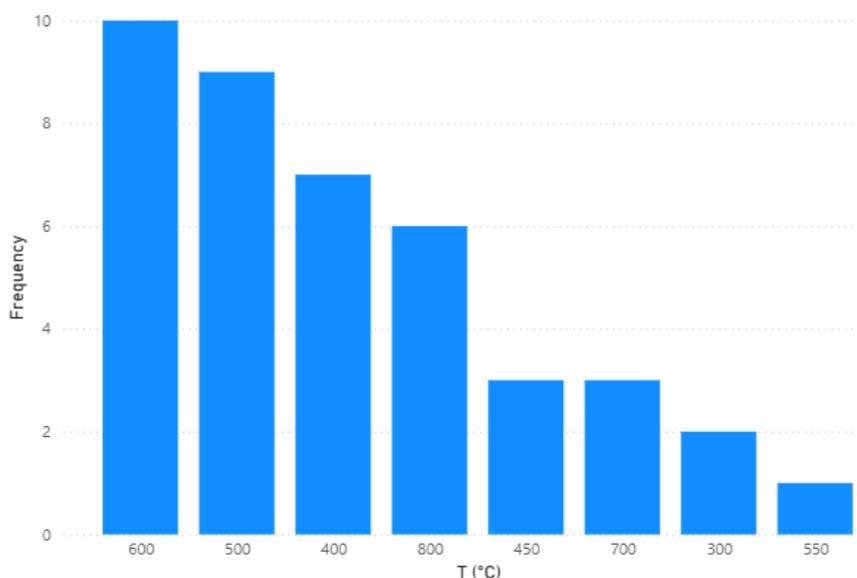
As regards the time required for the various pyrolysis processes, summarized in the figure 30, it can be said that these are mostly slow pyrolysis processes in which high quantities of pyrolysis gas are expected to be obtained. However, there is also one case of fast pyrolysis (2 seconds) and several cases of intermediate pyrolysis, in which the residence time in the reactor is several tens of minutes.



*Figure 30 Distribution of time of pyrolysis processes*

Figure 31 shows the frequency of temperatures used in the pyrolysis studies analyzed. The most frequently used temperature is 600 °C, with 10 cases, followed by 500 °C (9 cases) and 400 °C (7 cases). High temperatures such as 800 °C (6 cases) are less common, while intermediate values (450 °C and 700 °C) have a low frequency (3 cases each). Lower temperatures, such as 300 °C, are poorly represented (2 cases), and 550 °C appears only once.

This distribution reflects a prevalence of studies conducted in the 500 – 600 °C range, typical of slow pyrolysis, which is used to maximize biochar yield through increased solid carbon formation. Higher temperatures (700 – 800 °C) are generally associated with fast pyrolysis or partial gasification, geared towards the production of pyrolysis gas and bio-oil rather than biochar. Lower temperatures (<400 °C) are linked to low-temperature roasting or carbonization processes, which produce biochar with higher mass yield but lower carbon stability.

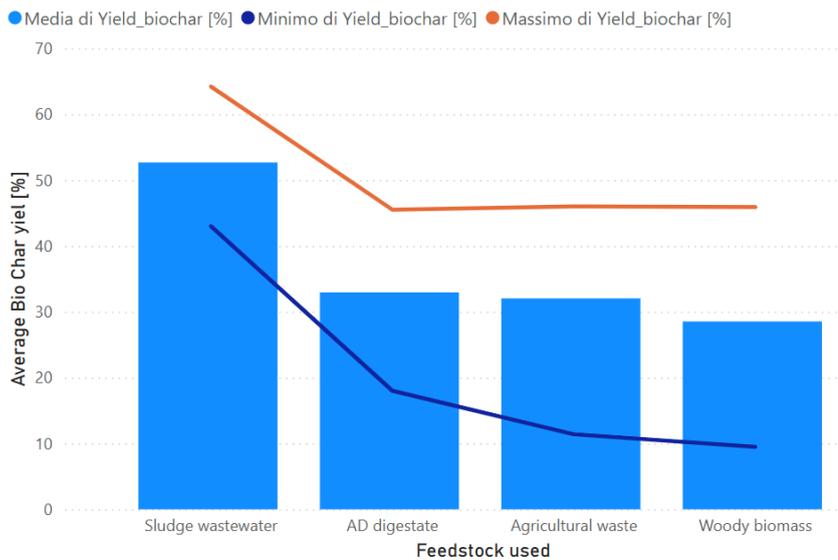


***Figure 31 Distribution of Temperature in Pyrolysis processes***

Figure 32 shows the biochar yield (expressed as weight percentage of products in dry conditions) obtained from different types of biomasses used in pyrolysis processes, reporting the average, minimum and maximum values for each kind of

feedstock. The highest average yield is observed for sewage sludge, with average values above 50 % and a range that can reach approximately 65 %.

This is followed by anaerobic digestion digestate (AD digestate), with an average yield of around 30 %, while agricultural waste and woody biomass show similar and lower yields, around 25–30 %. It should also be noted that the difference between the maximum and minimum values is more pronounced for sewage sludge, indicating greater variability in yield depending on operating conditions and composition. Lignocellulosic biomass (woody biomass and agricultural waste) shows lower and more stable yields, consistent with its higher structural carbon content and lower volatile fraction compared to sludge. In general, the graph highlights how the type of biomass significantly influences biochar production, with wetter feedstocks rich in labile organic substances tending to generate higher yields.



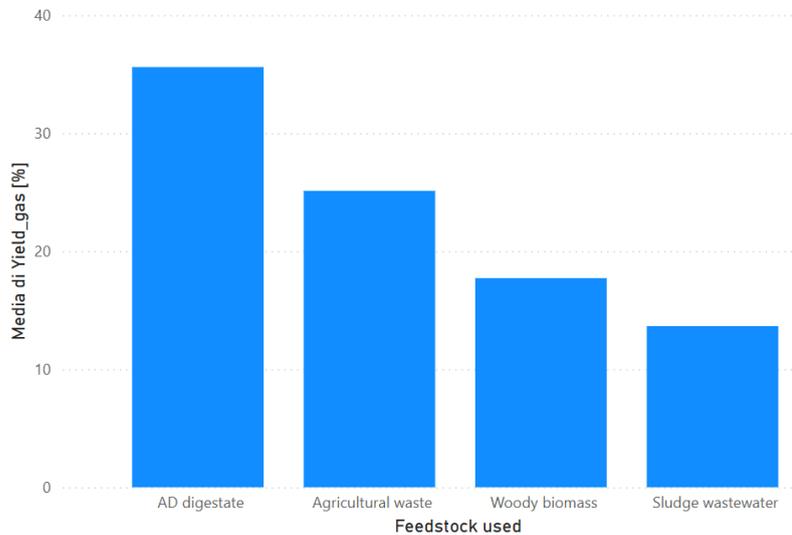
**Figure 32 Yield of Bio Char [%] produced for different feedstock**

Besides the production of biochar, the pyrolysis process also generates pyrolysis gas and bio-oil, whose production data, expressed as a percentage by weight of total products in relation to the biomass used, are shown in Figures 33

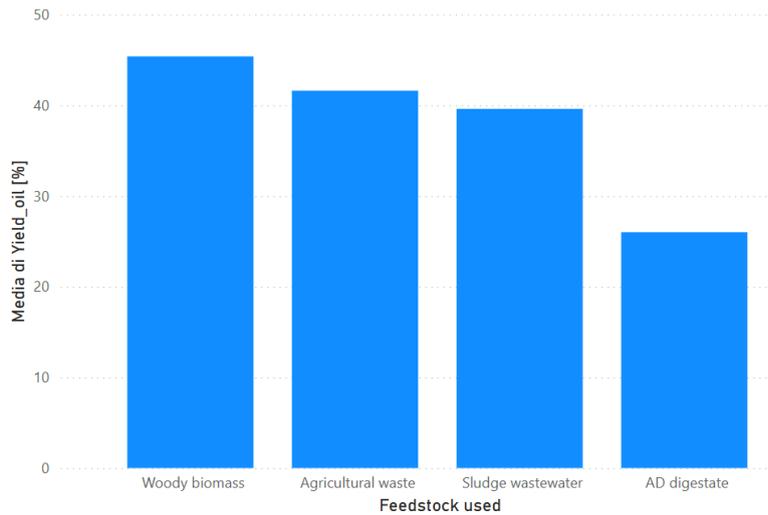
and 34 respectively. Based on the product considered, it can be seen how different materials generate higher yields and therefore how it is necessary to carefully choose the best mix of feedstock based on whether biochar, bio-oil, or pyrolysis gas is desired.

In order to maximize the production of syngas, and therefore also that of bio- $\text{CH}_4$  or  $\text{H}_2$ , the best material is digestate from AD, with yields by weight compared to products of around 35%, followed by agricultural waste (25%). Woody biomass and wastewater sludge appear to be less efficient in this respect, with percentages between 15% and 20% of the weight of pyrolysis products.

On the other hand, when aiming for high bio-oil production, there appears to be little variation in production between the different materials used. In particular, woody biomass, agricultural waste, and wastewater sludge show a percentage of bio-oil production compared to pyrolysis products that varies between 39% and 45%. On the other hand, the percentage of bio-oil production from anaerobic digestion digestate is lower (25%) (Figure 34).

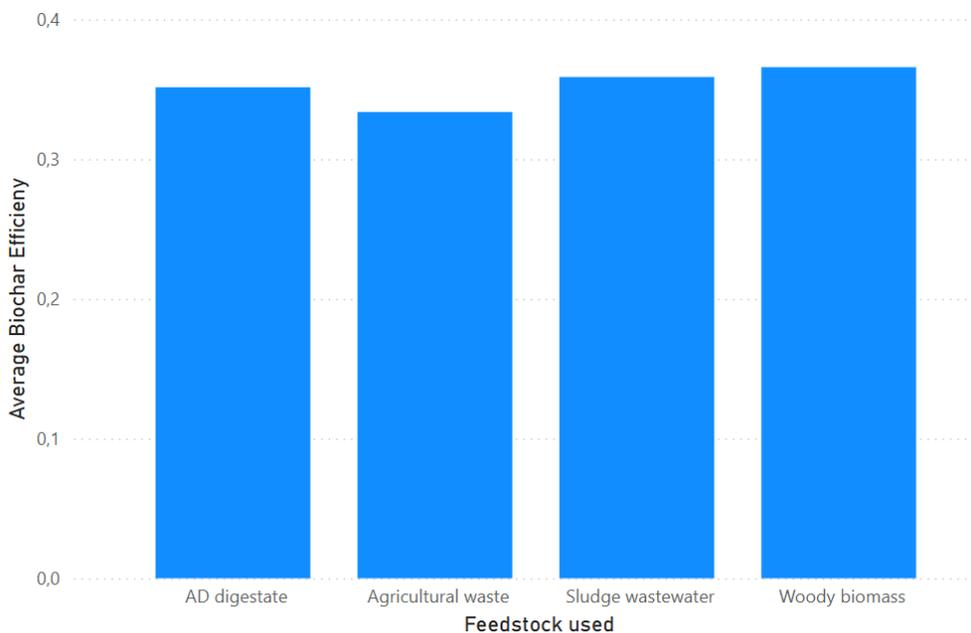


**Figure 33 Yield of Gas [%] produced for different feedstock**



**Figure 34 Yield of Bio Oil [%] produced for different feedstock**

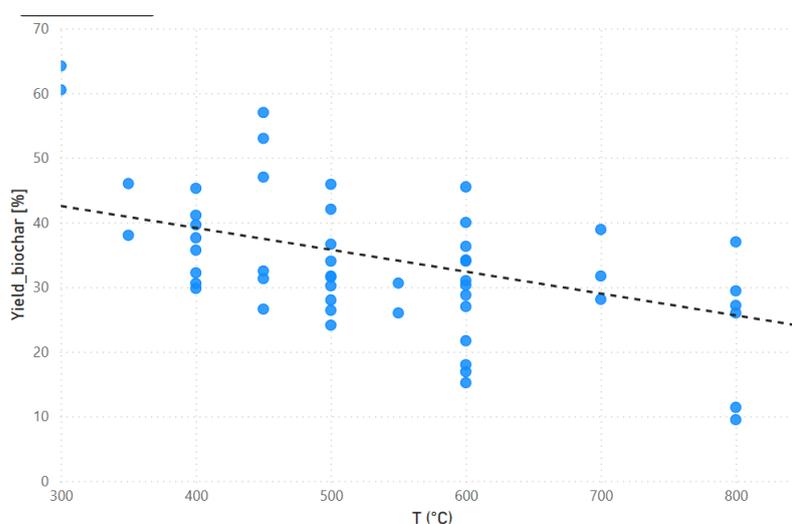
The efficiency of biochar production shown in Figure 35, assessed as the ratio between the energy potential of the biochar produced in the different types of pyrolysis and the energy content of the biomass entering the process, shows a value that is close to being equal for each of the four types of biomasses studied.



**Figure 35 Efficiency of Bio Char production for different feedstocks**

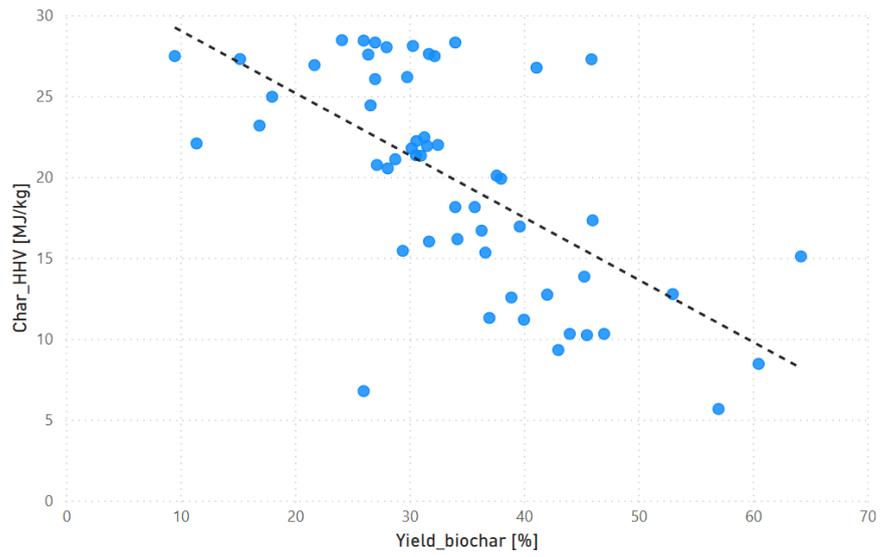
The water content within the feedstock is directly proportional to biochar production and inversely proportional to bio-oil production.

In order to better characterize biochar production, it should also be noted that its production is inversely proportional to the temperature of the pyrolysis process. Therefore, a pyrolysis process conducted at high temperatures, between 700 °C and 800 °C, results in a lower amount of biochar produced, ranging from 10 kg/kgDM to 30 kg/kgDM. This is presented in Figure 36.



**Figure 36 Yield of Bio Char [%] produced for different Temperature of Pyrolysis**

The qualities of the biochar obtained depend on the amount of biochar produced itself. More precisely, HHVs, between 25 and 30 MJ/kg, can be obtained when less biochar is produced, with yields between 10 and 30 % (Figure 37).



**Figure 37 Bio Char's HHV [MJ/kg] and yield of Bio Char produced [%]**

# Chapter 6 Conclusion

The aim of this master's thesis was to analyze two biomass conversion processes that play a very important role in ecological transition, namely AD and pyrolysis. In particular, the aim was to analyze the articles in literature for both processes to compare the biomass feedstocks used, the operating parameters, and the yields of the products generated. This was done in order to generate a database of information on AD and pyrolysis. This information on processes would then be used to formulate policy guidelines on the use of these biomass enhancement technologies.

The work consisted of reading several papers dealing with experiments or actual anaerobic digestion and pyrolysis plants. At this stage, a selection was made of papers useful for the purpose of the thesis, with particular attention paid to those containing information on the feedstocks used and their properties, on the operating parameters of the processes, and on the products obtained in the two technologies as the feedstocks and operating parameters varied.

Following the selection process described above, the data collected was organized and compared to draw conclusions and make recommendations about the processes themselves.

For anaerobic digestion, the following conclusions were reached as a result of this analysis:

- Approximately 54% of the studies analyzed use waste materials from agricultural activities as feedstock for the AD process.
- All the materials used, such as agricultural waste, animal waste, municipal solid waste, wastepaper, and woody biomass, represent waste from various sectors.

- Three-quarters of the cases considered are experimental studies, indicating a lack of information on large-scale operational plants.
- Many studies predict a residence time in the digester of approximately 30-35 days, with some cases exceeding 100 days.
- Approximately 88% of the studies analyzed focus on mesophilic processes, with temperatures between 35 °C and 37 °C.
- Biomass of animal origin generates the highest methane production (350 L<sub>bioCH<sub>4</sub></sub>/kg<sub>DM</sub>), while woody biomass produces only about 29 L<sub>bioCH<sub>4</sub></sub>/kg<sub>DM</sub>.
- Large commercial plants show higher average yields (240 L<sub>bioCH<sub>4</sub></sub>/kg<sub>DM</sub>) than laboratory studies (177 L<sub>bioCH<sub>4</sub></sub>/kg<sub>DM</sub>). In general, there is a difference in behavior between plants of different scales, probably due to different mixing dynamics and biomass entry into the reactor.
- It can be seen that the highest bio CH<sub>4</sub> production occurs at average values of 260 L<sub>bioCH<sub>4</sub></sub>/kg<sub>DM</sub> at 35 °C, under mesophilic conditions.

Regarding pyrolysis, based on the data collected, the following conclusions can be drawn:

- Feedstock origin: 51% of the cases analyzed use agricultural waste, followed by woody biomass, AD digestate, and sewage sludge. This indicates high availability and good adaptability to thermochemical conversion processes.
- The moisture content of the feedstocks at the start of the pyrolysis process varies between 15 % and 30 % by weight; sludge wastewater has the highest moisture content (29 %), followed by digestate (26 %), while woody biomass (9.5 %) and agricultural waste (6 %) are drier but have higher HHV values due to a higher C content. Some of this

biomass was previously dried, resulting in a reduction in biomass moisture content.

- The most frequent process temperatures are 500–600 °C (typical of slow pyrolysis), with peaks at 600 °C (10 cases). Higher (700–800 °C) or lower (<400 °C) temperatures are less frequent.
- Average Biochar yield is highest in sewage sludge (53 %), followed by AD digestate (33 %); it is lower for agricultural waste/woody biomass (25–30 %) Where biochar yields are lower, they have a higher HHV, between 25 and 30 MJ/kg.
- The best pyrolysis gas production is found with AD digestate (35 %), followed by agricultural waste (25 %); woody biomass and sludge generate only 15–20 %.
- Bio-oil production is similar for woody biomass, agricultural waste, and sludge (39–45 %), and lower for AD digestate (25 %).

In conclusion, AD and pyrolysis are two biomass conversion processes that play a fundamental role in the energy transition in many sectors able to give waste materials a second use.

AD is an optimal technology for biomethane production, particularly when using animal feedstocks and agricultural waste. Pyrolysis of AD digestate, in particular, has shown a double advantage: maximizing the production of gases, which can be used for further usable for further energy processes, and produce a solid biochar with carbon sequestration potential. This highlights a promising combined approach (AD and Pyrolysis) for the complete valorization of biomass.



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