POLITECNICO DI TORINO

Corso di Laurea Magistrale in Ingegneria Energetica e Nucleare

Tesi di Laurea Magistrale

CO_2 removal from biogas by adsorption with activated sewage sludges from WWTP

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Sommario

List of figures

List of tables

Abstract

In this study, anaerobically digested sewage sludges, received by a local WWTP, have been used as feedstock in the production of activated carbons through physical activation. The biochar samples produced have been experimentally tested as adsorbent materials to investigate the possibility to separate the carbon dioxide from the biogas. This mixture was simulated to evaluate the capacity to generate biomethane, whose carbon dioxide concentration was fixed following the specifications contained in the Standards EN 16723-1 and EN 16723-2. The effects on the char yield and adsorption capacity of the variation of the main parameters which lead the physical activation (temperature, dwell time, activation agent, heating rate, flow rate and activation methods) have been explored. From the adsorption results the SST6002hN$_2$_Dry_180 has been the sample which exhibited the highest result (102,5 mg_{CO_2} g^{-1}_{sorb}) among the samples activated. A comparison with other materials available in the laboratory have been performed, namely another waste material (ashes) and a commercial activated carbon (Norit RST3). Finally, the materials which have shown the best results, the SST6002hN$_2$_Dry_180 and the commercial activated carbons, have been compared in a preliminary study, whose aims have been to investigate the issues related to the biogas upgrading process passing from a laboratory to a plant scale.

1. Introduction

The quantity of the sludge production resulting from human activities has hugely increased due to the surge of industrialization and urbanization during the past century. In Europe, the progressive implementation of the Urban Waste Water Treatment Directive 91/271/EEC in all Member States has enhanced the quantities of sewage sludge requiring disposal; it is estimated that around 10 million tons of sewage sludges coming from urban wastewater treatment plants have been produced globally in Europe in 2015 (1).

"The unmanageable amount of sludge coming from various sources, the imposition of stringent regulations for the sludge disposal, the high cost and complexity of environmentally-benign sludge disposal/treatment have led to the exploration of reliable and lasting technological solutions" (2): this waste can be considered as an urban burden or as a valuable resource according on the way in which it is handled. Indeed, revoking the waste economy concept, it can be recognised as an input to the economic activity through its material and energy recovery, with economic implications for productivity, government expenditures and the environment.

The disposal of the treated sewage sludges coming from the waste water treatment plants (WWTP) has been traditionally accomplished by the application of this waste mainly for landfilling, soil conditioning, fertilization, production of building materials (e.g. concrete, bituminous mixtures), road construction and energy recovery (3).

Another way to dispose the sewage sludges is following the thermal route; this solution can be performed through processes like incineration/combustion, gasification and pyrolysis moving from a "sewage – to - energy" pathway to "sewage – to - fuel". These options, from the waste management point of view, have all in common the advantage to obtain "the reduction of volume and weight, the destruction of toxic organic compounds and the recovery of energy, but economics need to be carefully evaluated" (3).

In general, the incineration involves the complete burning of the waste, with the production of thermal energy, leaving an inert residue (ash). This is a "sewage – to - energy" process, where the main goal is maximizing the energy production, keeping in mind the minimization of the environmental impact too.

Gasification and pyrolysis methods fall in the "sewage – to - fuel" pathway. The first consists of the production of mainly syngas and ashes by a thermal self-sustaining process in which the organic matter is converted thanks to the presence of a controlled oxygen/steam quantity in the reactive atmosphere. On the other hand, the pyrolysis is an endothermic reaction, performed with an inert environment, which generates three by-products: pyrolysis gas, oil and the char.

Among the pyrolysis products, in this paper particular regards have been showed to the char. Specifically, they may represent a cheap carbon feedstock for the production of activated carbons. Sewage-based adsorbents (SBA) have already been extensively studied for pollutant removal in gaseous and water streams.

The objective of this work is to investigate the behaviour of the biochar obtained from the pyrolysis of sewage sludges as adsorbent for the carbon dioxide contained in a simplified biogas mixture; precisely, the main goal is to investigate the feasibility to re-use the anaerobically digested sewage sludges as activated carbon precursors with the purpose to increase the biogas calorific value converting it into biomethane. The physical activation is the main process that has been kept into account to try to develop the poor structural characteristics, as sorbent, of the starting material.

As far as the author knows, no previous literature dealt with the carbon dioxide adsorption (mixed with methane) using activated carbon obtained from sewage sludges; the most related study found in the literature performed the capture of a pure carbon dioxide stream by activated carbon from thermally dried sewage sludges after chemical activation (4).

1.1. Sewage sludges

In the following paragraphs, a general overview on the sewage sludges will be carried out, starting from a general definition related to their composition and the principal ways in which this product is disposed, taking in consideration the respective European directives. Moreover, a brief description of the origins of the anaerobically digested and dried sewage sludges received will be accomplished, summarizing the steps performed in the WWTP of reference, from the sludge formation and separation from the waste water stream in input, to the final drying processes after the biogas production in the plant. Finally, some sludge traditional valorization routes will be mentioned, introducing the alternative examined in this study, namely the production of sewage sludge-based adsorbents for the carbon dioxide separation from biogas.

1.1.1. Definition and composition

The sludges are originated during the wastewater treatment process. They are a solid or semi-solid residue considered as a toxic waste that is managed by the WWTP. Their composition is a function of both the source materials entering the WWTP and the sludge treatment methods adopted (5). From the provenance point of view, the sludges are distinguished in sewage and industrial; on the other hand, according to the kind of treatments received in the WWTP they are classified in primary and secondary sludges.

“Sewage sludges are identified as a complex heterogeneous mixture of microorganisms, undigested organics such as paper, plant residues, oils, or fecal materials, inorganic materials and moisture. The undigested organics materials contain a highly complex mixture of molecules from peptides, lipids and carbohydrates components present in the wastewater and the inorganic content originated from the soil and man-made synthetic polymers. The sewage sludges are rich in the nitrogenous compounds due to the presence of high protein content in the microorganisms used for the wastewater treatment” (3).

“The industrial sludges are produced from the treatment of industrial wastewater like pulp and paper industry, distillery industry, food industry, steel industry, paint industry, electroplating industry and petrochemical industry etc. Typically, also industrial sludges contain organic compounds rich in nitrogen and phosphorus as well as inorganic materials like heavy metals and other trace elements and pathogens" (6). Once the potentially pathogenic organisms (viruses, bacteria etc.) and the heavy metal concentration are properly treated, the nitrogen and phosphorous content makes the sludges rich in nutrients and the valuable organic matter is useful when soils are depleted or subjected to erosion. "The organic matter and nutrients are the two main elements that make the spreading of this kind of waste on land as a fertilizer or an organic soil improver suitable" (7).

As reported at the beginning of the paragraph, the composition of the sludges changes also according to the treatments received during the wastewater cleaning processes. For this reason, primary and secondary sludges can be distinguished. Primary sludges constitute the material collected from the primary settling tanks employed in WWTP. They are mainly inorganic in nature and produced during operations like sedimentation, filtration, coagulation and floatation processes. Secondary sludges are biological in nature and produced during the secondary wastewater treatment (drained from the settling tanks) like the activated sludge treatment (6) (5).

1.1.2. Background and treatments

The anaerobically digested and dried sludges used in this study during the experimental activity was collected and received by the WWTP located in Castiglione Torinese. This plant is supervised by the SMAT (Società Metropolitana Acque Torino S.p.A.) Group, leader in the field of integrated urban water management operating with one of the most innovative and up-to-date production and management system in the international scenario.

This is the largest WWTP in Italy with a maximum potential of 3.8 million equivalent inhabitants, representing an important technological reference thanks to the high standards of quality achieved. It treats and handles municipal and industrial effluents coming from an area of 450 km^2. Inside the plant, the wastewater is converted into an effluent that is both returned to the water cycle with the minimal environmental impact in the Po river (water reclamation) and reused for industrial purposes.

Figure 1: Castiglione Torinese waste water treatment plant.

The main stream in input is represented by the wastewater coming to the plant; this is treated in the so called "water line". Instead, the solid residue that are filtrated from the water line are moved and treated in the "sludges line". So, the plant is globally subdivided in two main lines working in synchronicity. In the preliminary treatments, coarse solid wastes are sieved and sent to the urban dump. From the primary settlement of the water line, the waste water is purified from sands, oily substances (sent respectively to the degritting and oil/grease removal sections); in this phase, the primary sludges and the ones coming from the denitrification/oxidation treatment section (biological or secondary sludges) are extracted and pumped to the sludges line. Before making the sludges inert, their concentration is increased through thickening. Then, they are pumped to digesters, where the inertisation process takes place: the organic and putrescible substance is eliminated through the anaerobic bacteria activity which develop at temperatures in the range of 37 – 40 °C (for this reason the sludges are pumped inside the digester with a temperature that allows to maintain this range). The sludges remain inside the digesters for nearly 20 days, namely, the time required for the stabilization process. The by-products in output are the raw biogas and the anaerobically digested stabilized sludges, produced thanks to the anaerobic reactions lead by the bacteria with the organic matter. This last is filtered and stored in tanks, ready to be combusted in boilers or motor-generators to generate part of the thermal and electrical load needed by the plant processes. Afterward the stabilized sludges are thickened again, before being sent to dehydration and further drying stages. The dehydration is performed through centrifuges, where the sludges are conditioned by polyecrtrolyte, or, after conditioning the sludges with ferric sulphate or calcium hydroxide, filter presses. In this process the volume of the sludges is decreased due to the elimination of the residual water coming with them. The sludges dehydrated with the centrifuges are stored in silos and they are suitable for a use in agriculture for soil conditioning. Part of the centrifuged sludges during the dehydration step are pumped to the further drying section of the plant; here the sludges are dried for 6 hours. During this stage, the volume of the sludges is further decreased because of the evaporation of the water. The final dried product comes in the form of small granules, powders suitable for a thermal recovery or as a fuel for cement factories due to its good calorific value (around 12 - 20 MJ/kg (3)).

The sludges that have been tested in this work come from the drying section of the plant.

1.1.3. Sewage sludge disposal legislation and valorization

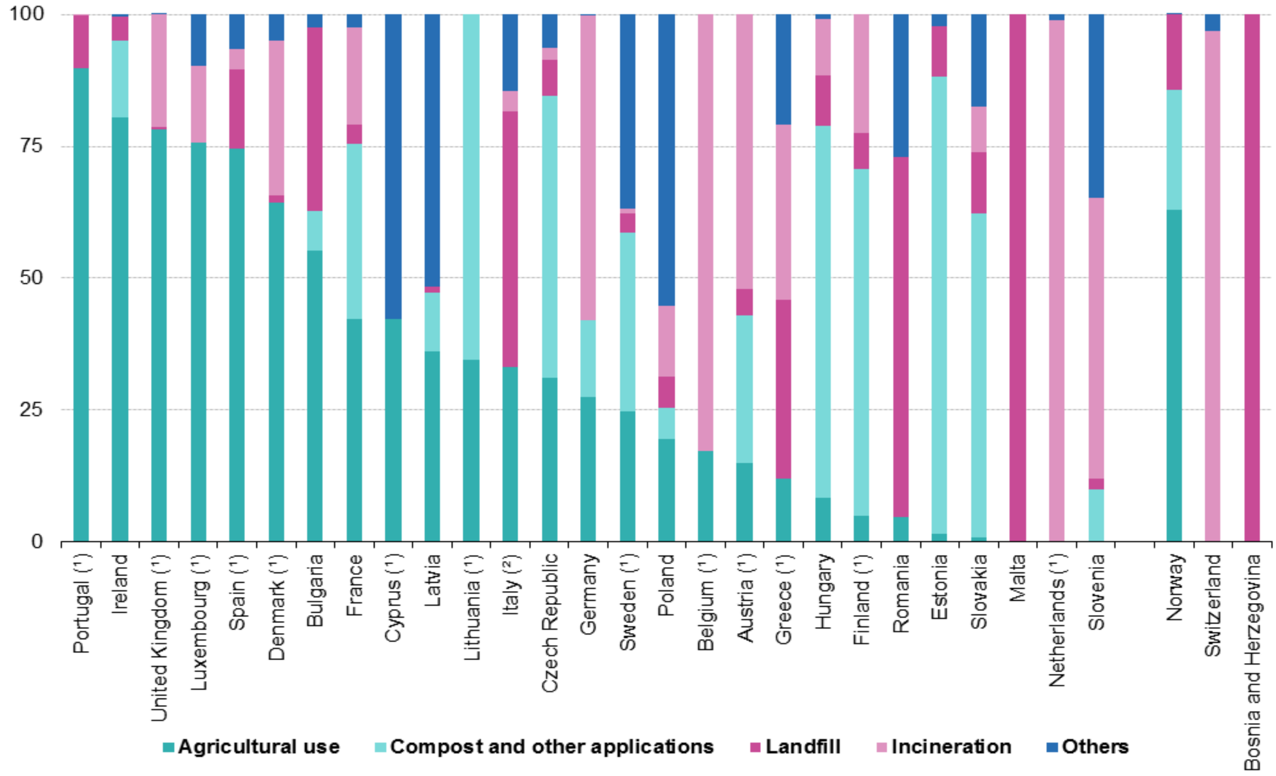
The disposal and the management of the huge quantity of sludges in an environmentally acceptable and economical way represents a big challenge worldwide. The volume of sludges produced does not only depends on the quantity of wastewater in input to the WWTP, but also on the kind of treatments received; once the contaminant present in the wastewater are removed during the treatments, it is important to choose the proper way to dispose the treated sludges. Treated sludges could be considered not only as the final waste of the WWTP process, but they can be regarded as a resource for energy and material recovery. For this reason, a proper disposal legislation is needed to regulate the utilization of this resource, keeping carefully in mind all the issues related to "environmental protection, public health, climate change impacts and socio-economic benefits" (8). Looking at the European background, "the most usual form of EU legislative framework is a Directive which sets the standard conditions and rules for the member States to comply with and to implement in their national legislation according to a defined timetable" (8).

In general, the Directive 2008/98/EC "sets the basic concepts and definitions related to waste management, such as definitions of waste, recycling, recovery. It explains when waste ceases to be waste and becomes a secondary raw material (so called end-of-waste criteria), and how to distinguish between waste and by-products" (9). Concerning the sewage sludges, there are three main disposal routes in the various management schemes: use in agriculture, in landfilling and in thermal processes (e.g. incineration, gasification, pyrolysis). The realization of each of these waste disposal solutions have to keep as a reference the respective Directive.

As illustrated in Figure 2, the **agricultural** disposal is one of the most spread applications implemented in Europe. The basic EU legislation concerning sewage sludge management for the use in farming is the Sewage Sludge Directive 86/278/EEC. It sets rules on how farmers can use sewage sludges as a fertilizer in order to prevent harmful effects on soil, vegetation and man as well as surface and groundwater. To this end, it prohibits the use of untreated sludge on agricultural land unless it is injected or incorporated into the soil. The Directive specifies rules for the sampling and analysis of sludges and soils. "It sets out requirements for the keeping of detailed records of the quantities of sludge produced, the quantities used in agriculture, the composition and properties of the sludge, the type of treatment and the sites where the sludge is used" (7). As for the composition, the Directive includes also the limit values for the concentrations of 7 heavy metals that may be toxic (cadmium, copper, nickel, lead, zinc, mercury and chromium) which are present in the sludges. The specific limits that can be found in the Directive's annexes are:

- Annex IA - heavy metals in the soil;
- Annex IB - heavy metals in sludge;
- Annex IC - maximum annual quantities of heavy metals that may be added to the soil.

Landfilling represents another common method to dispose the treated sewage sludges, as it is showed again from Figure 2. However, "according to the waste management hierarchy, landfilling is the least preferable option and should be limited to the necessary minimum" (10). Indeed, it does not represent an optimal solution both from the sustainable and economical side, due to the increasing disposal costs, constraints in land use and more stringent environmental regulations.



Note: Croatia: not available.
(¹) 2012 data.
(²) 2010 data
Source: Eurostat (online data code: env_ww_spd)

Figure 2: Sewage sludge disposal from urban wastewater treatment by type of treatment 2013 (% of total mass) (EUROSTAT, 2013).

At the European level, the regulation that keeps into consideration the waste landfilling is the Directive 1999/31/EC, whose objective is to prevent and attenuate possible detrimental consequences on the “environment, in particular on surface water, groundwater, soil, air and human health from the landfilling of waste by introducing stringent technical requirements for waste and landfills” (10). The increasingly restrictive targets for the continuous reduction of biodegradable wastes sent to landfills make land application of MSS an unattractive disposal option (8).

Among the thermal disposal options, **incineration** represents another diffused sewage sludge management. In Europe, it is mostly spread in those countries where national restrictions on land application renders this method more interesting economically (8). This is graphically shown from Figure 2, where in nations like Germany, Belgium, the Netherlands, etc, the thermal disposal is preferred to the agricultural sewage sludge management that is often one of the most prevalent options. Among the literature explored, the opinions about the incineration method are controversial. Some authors consider this disposal option as an expansive process that produces “greenhouse gases, toxic compounds like dioxins and furans” (6) and “it gives rise to significant quantities of potentially hazardous ash” (5). In general, incineration and landfilling do not benefit also from a good public image. On the other hand, some authors, without neglecting the environmental issues and limits that are linked with this process, stress more the possible benefits reachable like the "large reduction of the sludge volume, the thermal destruction of pathogens and odor minimization, the recovery of renewable energy" (3) while producing heat that may produce steam that in turn produces power through steam turbines. From the economical point of view, the same authors state that modern fluidized bed incinerators represent a better solution both in terms of capital and operating costs, in comparison to the conventional multiple hearth type (3). The highlighted issues about this technology are the impossibility to have a complete disposal of the sludges due to the ashes left and produced during the process and the harmful emissions. However, new technologies for controlling gaseous emissions can minimize the adverse effects mentioned (3) and the ashes can be further utilized as an ingredient in aggregate products, in bricks, tiles and other building materials as well as a resource from phosphorus recovery (8). The legislative guideline for the incineration process is the Directive 2000/76/EC (Waste Incineration Directive, WID) which has been implemented in the Directive 2010/75/EU (Industrial Emission Directive, IED). The aim is to prevent or decrease as far as possible harmful effects on the environment caused by the incineration and co-incineration of waste, reducing pollution caused by emissions into the air, surface water and groundwater and, then, diminish the risks which these pose to human health. This objective has to be achieved through the application of operational conditions, technical requirements and emissions limit values for incineration and co-incineration plants within the EU. In particular, air pollutants to monitor to check the compliance with the limit values are the dust, NO_x (nitrogen oxides), SO_2 (sulphur dioxide), HCl (hydrogen chloride), HF (hydrogen fluoride), heavy metals, dioxins and furans. The Directive sets controls on releases to water resulting from the treatment of the waste gases (11).

Within the IED, the **pyrolysis** (and gasification) is assimilated under the processes generated in a waste incineration and co-incineration plant (12), despite it is considered less pollutant due to lower operating temperatures and the absence of oxygen, being the primary precursors for the generation of furans and dioxins (3). Pyrolysis represents an interesting way to give value to the abundance of sludges produced worldwide. The valorisation of sludge into some useful product is a sustainable option for the waste management. In this case, the syngas, the oil and the char generated made up valuable outcomes to reuse in several ways. For the first two products mentioned, the energy recovery through their burning is the most interesting; since the technologies that aim to produce pyrolytic oil are only recently reaching the market due to their commercial readiness and reliability, a standardization of this resource is required. For this reason, the European standardization body CEN received a mandate in 2014 to develop European standards and specifications for specific applications.

Lastly, the char produced by the pyrolysis of the sewage sludges, may have an effective application if used as activated carbon to be deployed in adsorption processes; this is the kind of application that have been examined in this study.

1.2. Biogas and Biomethane

In the next introductive sections, general info about biogas production, composition and applications will be given; among them, the biomethane generation will be explored, taking into consideration the European indications related to its composition to be conformed with the limits for the injection in the natural gas grid and for its use in the transport sector. Finally, the main biogas upgrading treatments adopted so far will be illustrated, considering the pros and cons of each technology.

1.2.1. From biogas to biomethane

Biogas is a gaseous mixture generated from the degradation of organic sources in absence of oxygen (anaerobic digestion, AD). Generally, all organic materials like agricultural wastes, municipal wastes, manure, plant materials, food wastes and, as in the case studied, sewage sludges represent valid raw materials for the AD process. Biogas is considered a renewable energy source, whose increasing utilization, instead of fossil fuels, could represent a way for the greenhouse gasses emissions reduction. This because the carbon in biogas comes from the organic matter (feedstock) that is captured from the atmospheric carbon dioxide over relative short timescale. Moreover, biogas production often allows the exploitation of wastes to generate a valuable product. In the reference WWTP of this work, thickened sewage sludges are maintained for about 17 - 20 days at a temperature of 37 - 40 °C in 6 anaerobic digestors (12000 m^3 each) to transform most of their carbon content into biogas. This range of temperatures identifies mesophilic conditions, ideals for anaerobic bacteria. In these circumstances, namely, specific interval of temperatures in absence of a reducing atmosphere (absence of oxygen or other oxidants), these microorganisms find the optimal environment to develop fermentative metabolic processes. The overall process is made up by 4 steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. During the hydrolysis, complex long-chain structures such carbohydrates, proteins or fats are broken down into smaller molecules such as amino acids, sugars and fatty acids. Then, in the following phase, acidogenesis, the intermediate products of the former step are further degraded to form lower fatty acids and other carboxylic acid. Moreover, hydrogen, carbon dioxide and acetic acid are produced, which are the basic elements for the subsequent production of methane. Then, during the acidogenesis, the lower fatty acids are broken down into acetic acid by acetogenic microorganisms. Thus, the starting products are ready for the last step of the process, the methanogenesis, in which acetic archaea bacteria convert acetic acid or hydrogen and carbon into methane.

The result is the production of a blend constituted mostly by methane and carbon dioxide, the so-called biogas. As illustrated in Table 1, these two macro components are mixed with other substances like nitrogen, oxygen, moisture, hydrogen sulphide, other sulphur compounds (e.g., mercaptans, carbonyl sulphide, carbon sulphide), halogens (e.g., hydrogen chloride) and volatile organic compounds (VOC). Nitrogen and oxygen are mainly contained in the biogas mixture due to the incursion of air into the gas collection system; oxygen concentration should be continuously monitored and held to low values for safety reasons. The concentrations of the main and traces compounds are a function on the composition of the feedstock (Table 1).

Composition	**Natural Gas**	**Biogas**			
		Waste water	**Food waste**	**Animal waste**	**Landfill**
Methane [% vol.]	80 - 100	50 – 60	50 - 70	45 - 60	40 - 55
Carbon dioxide [% vol.]	< 3	30 – 40	25 - 45	35 - 50	35 - 50
Nitrogen [% vol.]	< 3	< 4	< 4	< 4	< 20
Oxygen [% vol.]	< 0,2	< 1	< 1	< 1	< 2
H_2S [ppmv]	< 0,1	< 400	< 10000	< 300	< 200
Non H_2S Sulphur [ppmv]	< 10	< 1	< 1000	< 30	< 30
Halogens [ppmv]	< 0,1	< 0,2	< 0,2	< 0,2	< 100
Moisture [%]	< 0,02	~ 3	~ 3	~ 3	~ 3

Table 1: biogas composition from different sources (13).

Beyond these components, biogas may also contain other compounds like ammonia (with concentrations in % in volume), aromatics (e.g., toluene) and siloxanes, namely organic silicon compounds typically used in products such as cosmetics, detergents, pharmaceuticals and lubricant (mostly present in biogas produced from WWTP in ppb – ppm concentrations). The concentration of the main components shows different ranges according to the kind of plants in which the biogas is produced. The presence of all these contaminants within the biogas represents an issue for its utilization. "When biogas is used as a fuel for electricity generation, if the concentrations of the contaminants are beyond the tolerable limits for a combustion engine, maintenance costs for repair may arise and the availability may be reduced due to service interruptions" (14).

Hydrogen sulphide, solved into the water (which could be brought inside the biogas stream), containing sulphur, "is corrosive and can cause damage to the cylinder surfaces, piston rings in the engine" (15). In addition, during the combustion it is responsible for the production of sulphur oxides, which have harmful consequences both on human health (intensification of respiratory diseases) and on the environment (acid rain).

Similarly like for the sulphur compounds, ammonia (NH_3) is responsible for the nitrogen oxides emissions during the biogas combustion, another class of compound deleterious for both human health and the environment.

Siloxanes can thermally decompose into silicates causing the formation of microcrystalline silica which contributes to the abrasion of the inner surfaces of combustion engines, generators and boilers.

Thus, the biogas produced can be used in a variety of ways, as illustrated in Figure 3. Most frequently, it is converted into electricity and heat by a combined heat and power unit (CHP) with the effort towards the maximum use of heat aiming to increase the income and to improve the economics of the biogas plants. However, biogas requires an earlier cleaning process to ensure the removal of the detrimental contaminants briefly listed above.

Carbon dioxide and methane are the principle components of biogas; the quantification of its contents is important to evaluate the calorific value of this renewable fuel. Biogas lower heating value (LHV) range is nearly from 21,300 to 23,400 kJ/m^3, being a function of the methane content in the blend. As higher the carbon dioxide content, as lower is the LHV, since it does not contribute to the energy production (also the water presence is an obstacle for energy production).

So, a cleaning step is necessary to burn the biogas, while, a further treatment with the carbon dioxide removal is necessary in order to increase its LHV. With these processes the biogas becomes richer in methane content and turns into **biomethane**, assuming a composition comparable to natural gas. As a consequence, biomethane represents an interesting energy vehicle with several alternative applications; some of them are shown in Figure 3. Thanks to the similarities in terms of compositions with natural gas, biomethane is often injected into the natural gas grid, where it is stored and distributed to the utilities in other locations. Biomethane field of application is currently envisaged like for natural gas, namely for stationary applications to produce both heat and electricity in CHP processes, directly heat for domestic purposes without requiring any customization of end devices (e.g. stoves or gas boilers), or for the transport sector for fuel natural gas vehicles. Biomethane represents so a flexible renewable source and, together with biogas, is a considered to contribute to the mitigation of greenhouse gas emissions.

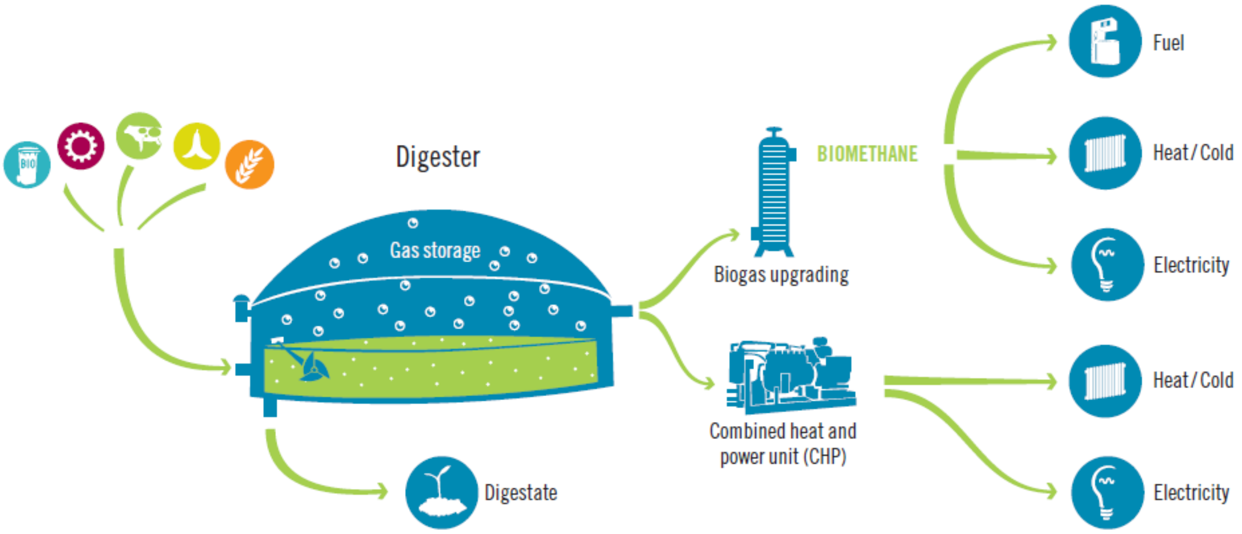


Figure 3: Figure 3: Process description of production and use of biogas and biomethane (16).

1.2.2. Biomethane legislation

In the last decade, in the European Union, the energy and climate policies and the introduction of support schemes for the development of renewable sources have encouraged the development of biogas plants for energy generation. Biogas represents both a central renewable energy source to achieve the goals fixed in Europe by the 20 – 20 - 20 Targets and an advantageous medium to valorize the wastes and residues from agricultural and industry sector, municipal organic wastes, sewage sludge, etc., with consequent benefits for the environment (e.g. decrease in water, soil and air pollution, etc.). Indeed, as it can be observed from Figure 4, the number of biogas plants in Europe has increased with a nearly logarithmical trend, although this amount has been stabilizing since 2015, reaching, taking into account the most up-to-date information available on the biogas markets for the year 2016, around 17662 biogas plants (17). Analyzing the data till 2014, Germany, Italy and the UK have been the main leading countries in terms of the quantity of biogas plants installed so far (see Figure 5).

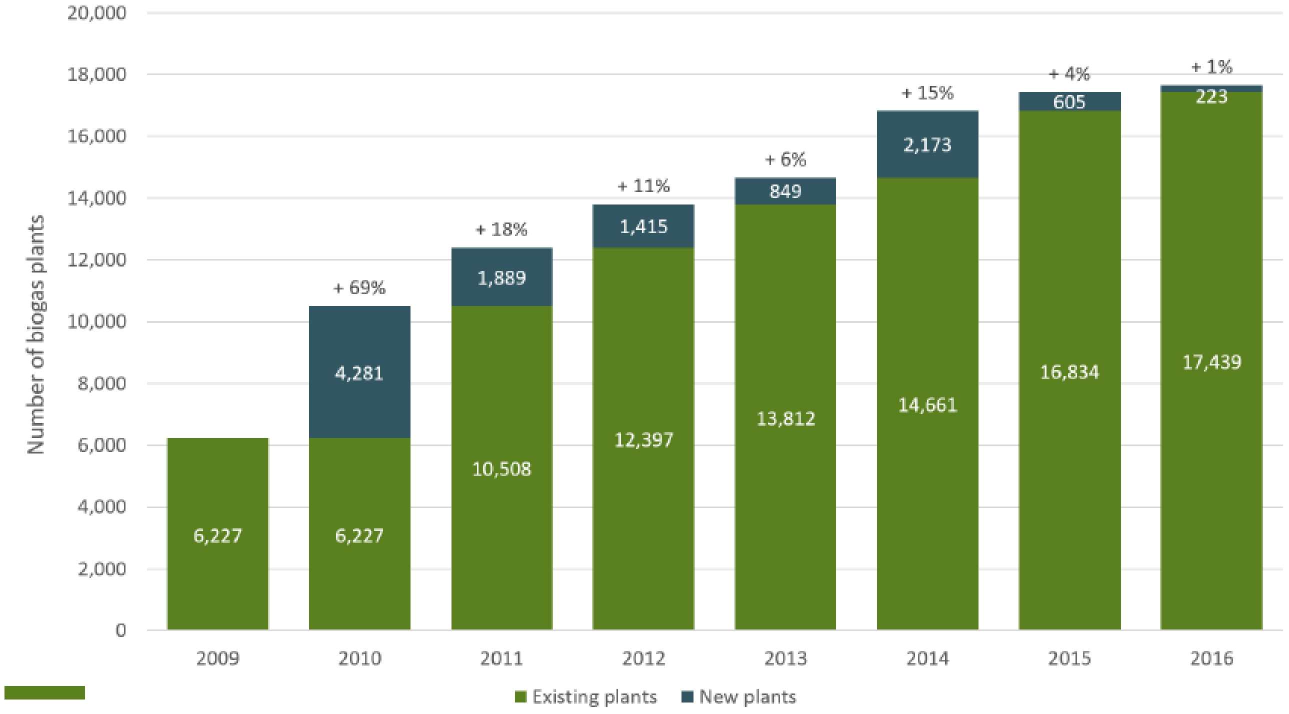


Figure 4: Evolution of number biogas plants in Europe (17).

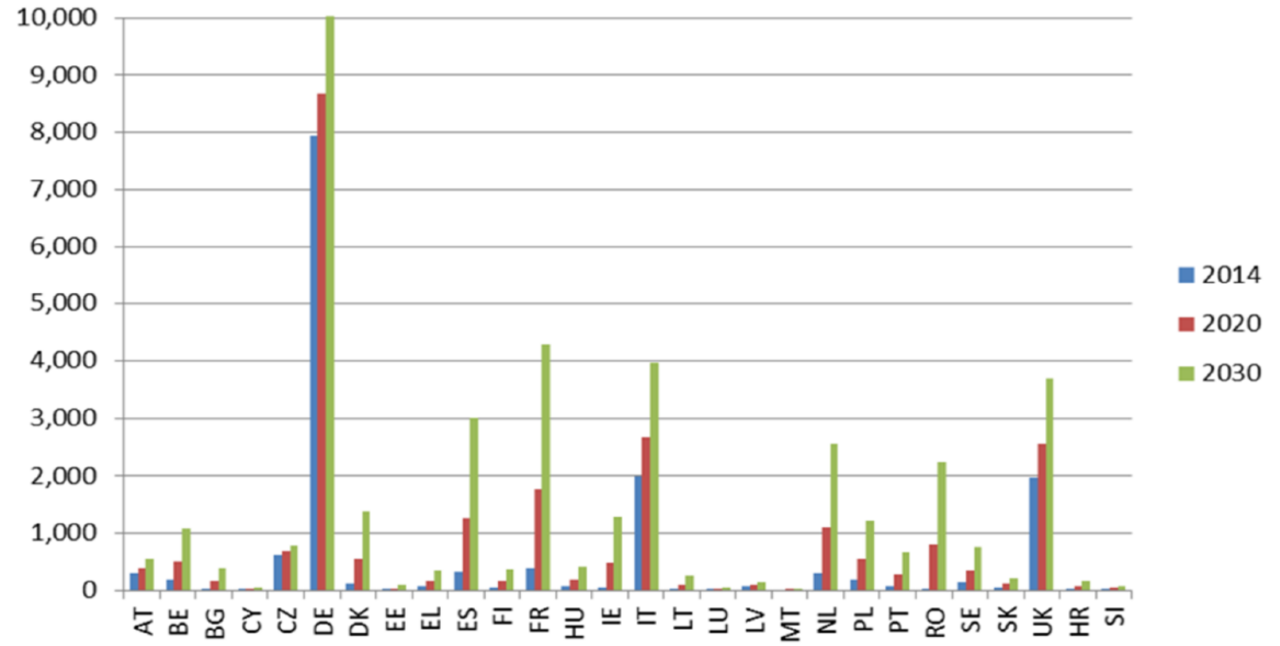


Figure 5: Growth of biogas production per Member State in Scenarios 2 and 4 (accelerated growth) in ktoe (17).

At the same time, the biomethane plants increased with a linear trend from 2011, as illustrated in Figure 6, as a consequence of the increasing of biogas plants installations (around 503 in 2016). The increasing injection of biomethane to the grid is part of the process of reforming the European energy system towards eco-sustainable assets; moreover, this source represents a strategic fuel to reach the 10 % of renewable energies utilized in the transport sector within the 2020.

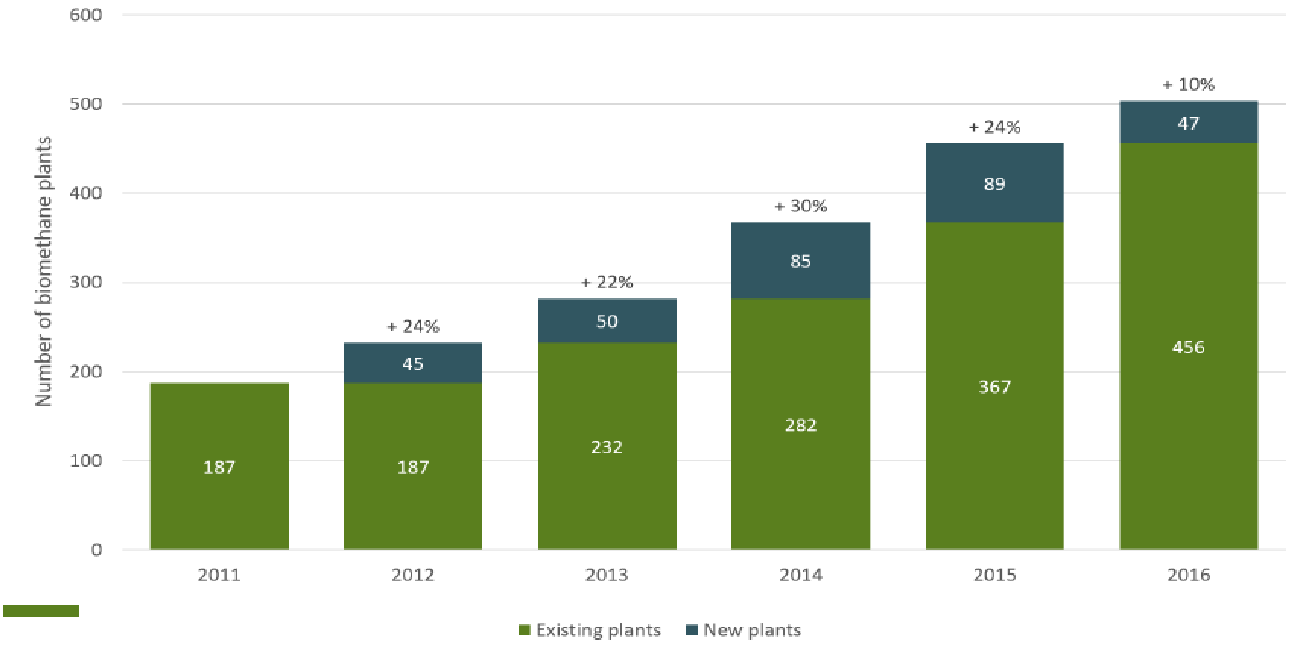


Figure 6: Evolution of the number of biomethane plants in Europe (17).

The injection of biomethane into the pipeline network required a normative activity concerning the specifications of this gaseous fuel, which decreed its suitability for mixing with natural gas. Before 2010, since, in effect, biogas was considered interchangeable with natural gas, the Directive 2009/73/EC, concerning common rules for the internal market in natural gas, was believed it was enough to respect the normal Network Codes, which had to comply with all the gases injected in the pipelines. However, European biomethane producers were used to adopt parameters for feeding and for use as a fuel which could vary largely among the various Member States (for some of the parameters and / or the concentration of different compounds from natural variations may occur even up to a factor of 100) (18); in addition, from searches in the subject, it was realized that the specification of the Network Codes and, in general, the qualitative standards of natural gas, did not include some of the impurities contained in the biogas which do not appear in the natural gas composition. A typical example is represented by the siloxanes. As previously mentioned, they are silica-based products, which can be contained from the biogas produced by municipal solid wastes landfills and in other originated from sewages, due to the presence of detergents in their composition. Siloxanes perform abrasive action on moving parts and are particularly harmful for engines, because they damage especially the sensors, catalysts and spark plugs. Also, other substances that were not normally covered by the Network Codes could have been present in the biomethane; thus, despite the great similarity with natural gas, a specific biomethane standard was needed.

For this reason, the CEN in September 2016 has approved the EN 16723-1 standard ("Specifications for biomethane for injection in the natural gas network"), which defines the European reference concerning the quality specifications for the biomethane to be introduced in the natural gas grid and identifies the requirements and test methods, thus ceasing the standstill period. Moreover, the European guideline for the quality specifications for natural gas and biomethane for use as motor fuels were defined in the EN 16723-2 standard ("Automotive fuels specification"). The standard EN 16723 (Part 1 and Part 2) provides additional requirements to the already existent EN 16726 ("Gas infrastructure – Quality of gas – Group H"), the European standard which specifies the gas quality characteristics, parameters and their limits, for gasses classified as group H that are to be transmitted, injected into and from storages, distributed and utilized (19). In the EN 16723-1, the limits related to components which biomethane contains in common with natural gas have been received from the EN 16726, adding from new only the limits related to the biomethane specifically. The main requirements from the EN 16726 standard which are applied to both natural gas and biomethane are (20):

- Relative density: 0,555 ÷ 0,7;
- Maximum Sulphur content, S: 20 mg m^{-3} (applicable limit for non-odorized natural gas transport networks, in the case of odorized natural gas, a limit of 30 mg/Sm^3 is accepted);
- Maximum oxygen content, O_2: 0,001 % mol (in special cases, where a higher concentration is not harmful, it can rise to 4 % mol);
- Maximum carbon dioxide content, CO_2: 2,5 % mol (in special cases, where a higher concentration is not harmful, it can rise to 4 % mol);
- Maximum hydrocarbon dew point: - 2 °C (between 0.1 and 70 bar);
- Maximum water dew point: - 8 °C (at 70 bar);
- Minimum methane number, MN: 65.

The main new requirements present in the EN 16723-1 standard, introduced to regulate the components present only in the biomethane, therefore, additional regard to the EN 16726 standard, are (20):

- Maximum silicon content, Si: 0,3 ÷ 1.0 mg_{Si} Sm^{-3} (depending on the degree of diluition of the biomethane in the pipeline);
- Maximum carbon monoxide content, CO: 0,1% mol;
- Maximum ammonia content, NH_3: 10 mg Sm^{-3};
- Maximum content of amines: 10 mg Sm^{-3};
- The biomethane must also be free from impurities and the oil and powders contents coming from the compressors must be sufficiently low to not make the biomethane unacceptable for transport and use in all final applications. In this regard, the standard recommends the adoption of filters that manage to retain 99 % of powders larger than 5 μm and 99% of liquids with diameters ≥ 10 μm.

As regards the EN 16723-2, some specifications have been extracted from the EN 16726, making some modifications to adjust the limits to the specific transport sector, even if some contradict the specifications of the network. The main requirements of the EN 16723-2 standard, for the biomethane composition for its use in the transport sector are (21) (20):

- Maximum silicon content, Si: 0,1 ÷ 0,5 $mg_{Si}\ m^{-3}$;
- Maximum sulphur content, S: 30 mg Sm^{-3} including the odorants (as in EN 16726);
- Maximum oxygen content, O_2: 1 % vol (as forseen in some cases in EN 16726);
- Maximum hydrogen content, H_2: 2 % vol;
- Maximum carbon dioxide content, CO_2: 2,5 % vol (as in EN 16726);
- Maximum amine content: 10 mg Sm^{-3};
- The natural gas, the biomethane and their mixtures, at the point of use, must also be free from impurities and the oil and powders content coming from the compressors must be sufficiently low to make these fuels suitable for motor vehicles.

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The regulations for the quality of the biomethane to inject to the grid and the one to be used in the transport sector do not show big differences. The principles ones are the following (21):

- the interval width allowed for the silicon concentration for the biomethane use in the motor vehicles is narrower;
- the carbon monoxide in the EN 16723-2 has not been taken as an issue since it is not considered as a poisonous compound when it is used in a fuel, which is a closed system (the injection in the grid might bring this gas inside indoor environments e.g. while cooking).

In this study, among these limits, a particular attention has been given to the carbon dioxide one, since the main goal is the investigation of its adsorption through activated carbons derived from sewage sludges, which is the principle compound to remove from the biogas during the upgrading process. Both the EN 16723-1 and 16723-2 declare that the permitted carbon dioxide concentration in the biomethane to inject into the gas grid or to use as a vehicle fuel is maximum 2,5 %. For this reason, this is the fixed concentration that has been kept into consideration to calculate the breakthrough time of the filters tested during the experimental session.

1.2.3. Biogas upgrade technologies: a review

As shown in Table 1, raw biogas composition is mainly constituted by methane (45 – 70 %) and carbon dioxide (30 – 55 %), with a series of minor component and pollutants like nitrogen, oxygen, hydrogen sulphide and ammonia, whose quantities are a function of the biogas origin. According to the feedstock used for the biogas production, further pollutants like siloxanes, volatile hydrocarbons or, especially from biogas from landfills, chlorinated and fluorinated hydrocarbons, heavy metal vapours, aromatic compounds and higher hydrocarbons might occur (22). The produced biogas can receive 2 different treatments: cleaning and upgrading. The cleaning step is performed to get rid of the detrimental and/or toxic compounds such as hydrogen sulphide, ammonia, volatile organic compounds, siloxanes, water, oxygen etc., because of the possibility to produce corrosion (e.g., H_2S, H_2O, O_2) or harmful emissions (e.g., NH_3, H_2S). After this treatment, the traditional use of the biogas is to feed CHP engines with electrical efficiencies varying from 33 % (small unites) to 40 % (large units) or, considering the overall electricity and heat generation, a total efficiency between nearly 83 and 88 % (23). On the other hand, with the biogas upgrading, the possibilities to exploit this resource increase. With this further biogas treatment step, the removal of bulk components has been accomplished, with the main advantage to enhance the heating value of the product, the biomethane. Biogas upgrade is generally a multistep process in which the main component that is taken away is the carbon dioxide; generally, the removal of H_2S, siloxanes, water vapour, etc. may be performed prior this step to not damage the biogas upgrading technologies employed in the process. As it has been explained in the previous paragraph, the biomethane composition must follow the national directives, to fit the concentration limits required for its main applications, namely the injection in the natural gas grid and its utilization as a vehicle fuel.

There are several upgrading technologies available on the market that have been utilized and improved for many years. Conventionally, biogas upgrading methods can be grouped as follows:

- Membrane separation;
- Scrubbing technologies/absorption methods (water scrubbing, physical scrubbing, chemical scrubbing);
- Pressure swing adsorption (PSA);
- Cryogenic treatments.

These methods operate following different procedures whose principal aim is to achieve high methane purity and low methane losses with low energy consumption. Methane losses should be avoided both for economic and environmental reasons, since methane global warming potential is 25 times higher than the carbon dioxide one. Figure 7 illustrates how these different technologies were spread in Europe until 2016. Water scrubbing, chemical scrubbing and pressure swing adsorption methods account the greatest proportion of the upgrading systems and are adopted by respectively 123, 77 and 53 facilities in Europe (within 2016). The total biomethane production in Europe was 1,23 billion m^3 in 2015 (16).

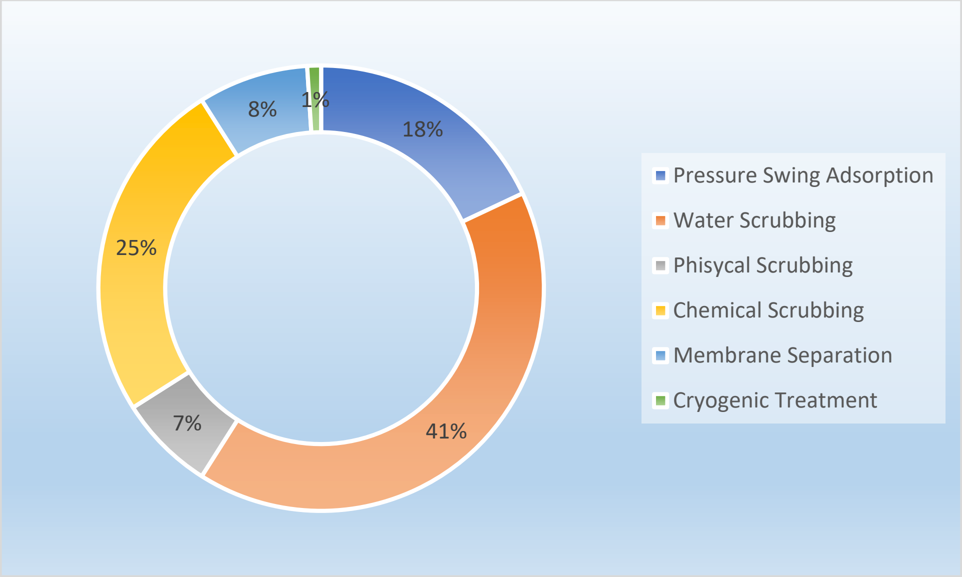

Figure 7: distribution of biogas upgrading technologies in Europe (16).

Each upgrading technology has its own features and its choice is strictly related on local conditions; so, for different utilization purposes, it is necessary to find the best suitable alternative, rather than easily selecting the cheapest one. In fact, a final choice of the upgrading system based only on an economic analysis, may bring damaging consequences, which may end up in higher overall costs or ruin the system (22).

The **scrubbing technologies** takes advantage, with various solvents, the different solubility of the gasses contained in the biogas. With this principle, the great majority of the carbon dioxide is separated through the absorption operated by the solvent, so that biomethane can be extracted separately. In general, the adsorption is promoted by an increase of the pressure and a decrease of the temperature of the system; these two parameters are generally imposed by the optimal thermodynamic equilibrium to enhance the carbon dioxide adsorption. Overall, the different scrubbing technologies follow the same plant scheme, which can be briefly subdivided in three sections: a scrubbing column, flash column and stripping column. In the scrubbing column, the biogas is fed from the lower part of the tank in counter current with the solvent coming from the upper section like in a shower; the biomethane is extracted and collected from the top, while the solvent enriched by carbon dioxide and other minor components (e.g. ammonia, hydrogen sulphide, if not separated in advance) are moved to the flash column. Here, the partial depressurization releases the so-called flash gas, in which also a not negligible amount of methane is contained, that is recirculated to the scrubbing column in order to increase the system efficiency. In the stripping column a deeper regeneration of the solvent has been performed (pumped back to the scrubbing column) and the exhaust gasses are discharged. In the **water scrubbing** method the pressures used are higher, reaching values up to 20 bar (23). In this way, methane solubility in water is approximately 26 times lower than the carbon dioxide one (24). In addition, a proper temperature management of the scrubbing column is fundamental to maintain a higher solubility of the carbon dioxide in water. Therefore, the feeding compressed biogas has to be chilled down to stay inside the 15 - 20 °C interval; this excess of heat may be employed for other processes inside the plant. Depending on the design of the column, the biomethane which comes out from the scrubbing column has a methane content which may vary from 80 to 99 %, depending on the volume of non-condensable gasses such as nitrogen and oxygen (22). The hydrogen sulphide, contained in the biogas, dissolves even better than carbon dioxide in water. However, biogas desulphurization may be necessary prior the upgrading ((16), (22), (24)) since the hydrogen sulphide dissolved in the water could generate corrosion problems and its presence in the exhaust gasses of the stripping column represents an issue because they are generally released to the atmosphere or burnt in an RTO (hydrogen sulphide can be converted in SO_x there so).

In the **physical scrubbing,** water is replaced by organic solvents which show a higher selectivity towards carbon dioxide and hydrogen sulphide too. One of the most employed solvents for this purpose is the organic polyethylene glycol dimethyl ether, which is marketed commercially under the names Grenosorbs or Selexol. The consequent advantages brought by a greater selectivity allow the system to work at lower pressures (from 4 to 8 bar), with a littler amount of solvent and with a more compact systems, since the height required for the scrubbing column is smaller than the one necessary with the water scrubbing (16). This may take along energy savings for the compression, but the solvent has to be heated up during the regeneration process at around 40 – 80 °C. With this method, in an optimized full-scale plant, the biomethane generated may contain nearly 96 – 98,5 % of methane and less than 2 % of its losses, with a similar energy consumption of water scrubbing (24).

In the **chemical scrubbing**, differently from the water and physical ones, the solvent reacts chemically with the carbon dioxide (and hydrogen sulphide) present in the biogas blend. Commonly, the detergents used in this process are a mixture of water and additive amines, like monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), etc., which allow to achieve a higher carbon dioxide selectivity with regard to the previous scrubbing methods mentioned. With this method, a further improvement in terms of biomethane quality is achieved, considering the little methane losses (0,1 – 1,2 %) with a methane recovery greater than 99 % (24). The most important drawback of this method is the higher energy demand required for the regeneration of the solvent, since it necessitates temperatures around 110 – 160 °C. Also, in chemical scrubbing, an affinity towards hydrogen sulphide is exhibited; for this reason, for both chemical and physical scrubbing a prior desulphurization step is demanded to prevent the poisoning of the solvent which is followed by the necessity to regenerate at even higher temperatures.

As it is shown in Figure 7, almost one fourth of the biogas upgrading plants within 2016 were adopting **pressure swing adsorption (PSA)**. The core of the process is performed in a series of vertical columns, where the adsorption materials are packed inside. Activated carbons, zeolite are examples of adsorbents adopted, since they are characterized by a large specific surface and a certain pore size. Different gas components like carbon dioxide, nitrogen, oxygen and hydrogen sulphide are adsorbed to specific surfaces or penetrate into the pores of the materials, exploiting their smaller molecular sizes with respect to methane. The biogas feeding the adsorption column should be prior dried and desulfurized, since hydrogen sulphide is adsorbed irreversibly to the molecular sieves, reducing the carbon dioxide adsorption efficiency. The process operated with the gas separation through the following steps (16):

- The purified biogas is compressed up to nearly 2 - 7 bar and channelled into the adsorption column;
- The valve at the top of the reactor is opened to release the biomethane separated from the blend, while the carbon dioxide and the other gases remain attached to the adsorbent surfaces or trapped in the pores;
- Once the valve is closed again, the trapped gases are blown-off as a carbon dioxide-rich exhaust gas;
- The process can restart and the column is filled again with biogas.

Since inevitably a not negligible amount of methane contained in the biogas is adsorbed too, the exhaust gas is burnt in order to avoid methane emission to the atmosphere. With the pressure swing adsorption, the biomethane produced is characterized by a methane content of nearly 96 – 98 %, with consequent 2 – 4 % of methane losses (24).

The second last biogas upgrading technique in terms of spread is the **membrane separation**. This method, which has continuously been improved in the last decade, is based on a molecular separation of the species involved due to a diverse permeability through the membrane. The thinnest molecules like hydrogen sulphide, carbon dioxide, water, oxygen are able to diffuse through the membrane, while methane is separated at the inlet side. Typically, the operating pressures ranges from 5 to 30 bar (23); the smallest molecules pass the membrane reaching the lower pressure side, differently from the methane which is separated at the inlet level (higher pressure side). The membranes are generally made up polymeric materials, combined in a pile of tubes to increase the surface area; moreover, in order to increase the separation efficiency, the tube bundles can be connected in two-stages, three-stage cascades to separate more carbon dioxide still contained in the gaseous mixture separated at the inlet. Also in this case, the membrane's life can be extended removing the sulphur compounds from the blend before it passes through the membrane. Unavoidably, part of the methane contained in the biogas crosses the membrane and it is lost with the exhaust gasses; this decreases the overall separation efficiency, which is however attested to around 98 % (22).

Finally, the last upgrading process to treat in this review is the **cryogenic technique**. In Europe, it represents the least adopted way to separate upgrade the biogas; one of the main reasons may be represented by its high operating costs in terms of energy. This method takes advantage of the different boiling point of the compounds present in the biogas mixture. Indeed, the main substances to separate, methane and carbon dioxide, have respectively boiling points of around – 160 °C and – 78 °C respectively at the pressure of 1 bar. The thermodynamic conditions for the separations depend on the requirement of the plant. During the process, exploiting the same principle, it is possible to separate also the other minor components, even if it would preferable to separate earlier water and hydrogen sulphide to avoid the freezing and other process during the cryogenic process (22). One of the main advantages of this method is that it is possible to extract very pure carbon dioxide, which can be sold or employed for other purposes. Overall, the cryogenic technique allows to achieve very high efficiencies, with reached methane level purities of 99,9 % (16).

In this study, it has been investigated the possibility to employ low cost materials to generate activated carbons to separate carbon dioxide from methane through adsorption mechanisms at ambient pressure. In particular, the carbonaceous source utilized is represented by dried sewage sludges, conveniently activated in order to improve their physical and chemical characteristics to guarantee better adsorption behaviours.

2. Experimental section

The experimental activity has been carried out in the C. Codegone Laboratory, in the Energy Department of the Polytechnic of Turin. It was mainly constituted by the following tasks:

- Sewage sludge pre-treatment;
- Physical activation;
- Biochar samples dehydration;
- Adsorption tests.

The following paragraphs of this section will deal with the explanation of these phases, namely the route of the production of activated carbons starting from the sewage sludges as carbonaceous precursors.

2.1. Materials and equipment

The raw sewage sludges as received from the SMAT WWTP of Castiglione Torinese are illustrated in Figure 8(a). As mentioned in the previous paragraph, the plant takes advantage from this waste, becoming a resource for the biogas production. The anaerobically digested solid output from the digester is, then, dehydrated in various steps with different degrees in order to reduce the volume of the waste and to make it useful for different applications, like for agriculture and for energy recovery through its burn. In this work, the anaerobically digested and dried sludges represent the feedstock for the preparation of activated carbons. The sludges are characterized by an irregular shape and size, ranging from 1 mm to around 2 cm of equivalent diameter. The data referred to the elemental composition has been provided by SMAT; the main components are listed below (see Table 2):

Element	*Concentration (%)*
C	35
H	4.9
N	4.60
S	< 2
P	2.8

Table 2: sewage sludge main elemental components concentration.

Among the main components, from the SMAT analysis it is not present the oxygen percentage concentration; however, looking at the literature dealing with sewage sludges, it can be stated that the oxygen amount may vary approximately between 10 ± 25 % according to the feedstock, a quantity generally higher than the one present in the activated carbons (because of the volatilization during the starting material activation through thermal treatments). The remaining composition part is basically constituted by ashes.

Beyond these main elements, metals and non-metals traces are present in the sludges composition; their quantities, according, again, to the elemental analysis performed by SMAT, are listed below (see Table 3):

Element	*Concentration (%)*
As	0,00057
Cd	0,000157
Cr	0,0222
Hg	0,00009
Ni	0,0149
Pb	0,0079
K	0,18
Cu	0,0386
Se	0,00031
Zn	0,1107

Table 3: sewage sludges traces compounds concentration.

The chemical composition of the sludges is both a function of the treatments received in the WWTP and of the source materials coming in input to the plant (5); for this reason, the sewage sludges chemical composition may be subjected to changes during the year because of the seasonal variation. Anyway, the data showed above, especially the ones referred to the main components (C, N, S, etc.) could be compared with the sludge composition present in studies of other authors (25), (26).

Figure 8: raw and dried sewage sludges as received from the SMAT WWT plant (as received and sieved/milled).

The received sewage sludges have been properly sieved and milled before the thermal treatment (see Figure 8(b)) with a 1 mm size sieve; the reduction in much smaller particles, as will be examined later, has been necessary to match the reactor sizes and to reduce the diffusion paths during the adsorption tests. This has been the main sewage sludge pre-treatment performed at the laboratory. Afterwards, the physical activation of the milled sludges was carried out in a tubular reactor in stainless steel, geometrically characterized by a 57 cm length and 3,4 cm external diameter. The cylindrical electric oven used during the physical activation has a 500 W power and 220 V for the electric connection; so, the heat was provided through Joule effect. The glass wool present in the internal section of the oven guaranteed the thermal insulation necessary to maintain the desired temperature during the activations of the sewage sludges present inside the tubular reactor. The electric power management of the oven has been accomplished by the Horst temperature regulator model HT MC1; the fixed temperature interval ranged from 200 to 600 °C. The operating temperature is communicated through a thermocouple connected to the temperature regulator and placed to the surface of the tubular reactor inside the oven; according to the temperature reported, the oven was able to provide the right amount of power to achieve and maintain the temperature desired. Through the temperature regulator, it was possible to set the desired heating rate and residence time of process. The bench with the electrical oven, tubular reactor and temperature regulator are illustrated in Figure 9(a) and Figure 9(b).

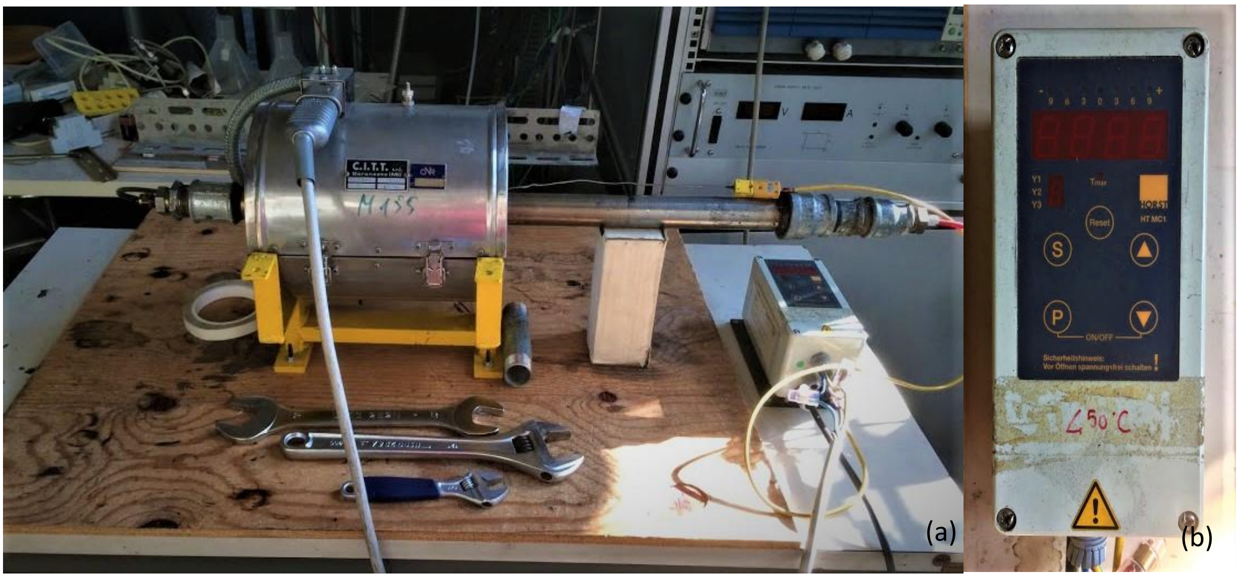

Figure 9: electrical oven, reactor (a) and temperature regulator (b) utilized during the thermal activations.

The width of the electric resistances inside the oven was nearly 21 cm, for this reason, to perform more efficiently the thermal activation, the sludges have been appropriately located in that respective section of the tubular reactor, to reach the best homogeneous temperature distribution; to fulfill this task, the quantity of raw material introduced inside the reactor was around 150 ± 5 g. The gasses employed during the physical activations were nitrogen (to generate the inert atmosphere during the pyrolysis), carbon dioxide and air (as activating agents); on the other end, during the adsorption tests of the activated carbons produced, methane and carbon dioxide were used to simulate the biogas mixture to examine the carbon dioxide adsorption. All the streams were regulated by a specific mass flow controller (MFC), manufactured by Bronkhorst. The flow rates control was actioned electronically through a personal computer making use of the specific software Bronkhorst FlowView or with a manual keyboard present on the MFC itself. The gas streams were circulated through 6 mm diameter tubes made in teflon, both during the activation and the adsorption test activity. As will be examined in the following section, among the outputs of the physical activation, principally from temperatures higher than 300 °C, sewage sludge pyrolysis oil (tar) and a gaseous fraction (mostly syngas) were generated during the process too. These components were released from the output of the reactor to the chimney, where the gasses could be vented outside, while the oily fraction was separated and collected in a container. Once the thermal activations were ended, the activated sewage sludges, namely, the biochar, were collected in small plastic envelopes for the adsorption tests.

In the adsorption phase of the experimental activity, the activated sewage sludges were located filling a glass made reactor (see <u>Figure 10(b)</u>), geometrically described by a 3 cm external diameter and an adsorption bed height of approximately 10 cm. At the base of the reactor, a gauze layer has been located in order to avoid that carbon particles could pass through the filter going to the mass spectrometer. This latter, a Hiden HPR20QIC (see Figure 10(a)), has been utilized to analyse the composition of the mixture in output from the reactor. The software adopted in combination with the spectrometer was the QGA Professional Software for Quantitative Gas Analysis. This program has been necessary to perform the following tasks:

- before the adsorption experiment, the calibration of the mass spectrometer was necessary, to give the information related to the known composition of the mixture in input to the system;
- during the tests of the filter, the program worked collecting the data (concentrations of the selected species and the respective sampling time) necessary to generate the breakthrough curves to understand the actual duration of the filter.

Figure 10: Hiden HPR20QIC mass spectrometer (a) and the reactor for the adsorption tests (b).

2.2. Physical activation

The sewage sludge thermal treatment is a necessary operation to develop the almost non-existent porosity structure in the starting material, to improve their adsorption capacity characteristics. In general, the carbonaceous feedstock to general activated carbons may derive from an abundance of different origins, like from the botanical world (e.g. wood, coconut shells and nut shells), degraded and coalified plant matters (e.g. peat, lignite and all ranks of coals), agricultural by-products, etc. (27). As many other kind of feedstocks, sewage sludges represent an interesting plentiful, low cost material, whose adsorption application is quite interesting as waste recovery solution.

The preparation of the precursors can follow two different routes: physical or chemical. Both the methods have in common a thermal treatment of the starting material. The **physical activation** may include a carbonization and an activation step; the carbonization, namely the pyrolysis of the material, is the first step and generally it is performed in an inert atmosphere (mainly nitrogen) with a temperature often below 800 °C. The pyrolysis generates three different products: a volatile and gaseous fraction, vapours and tar components, solid carbon reach residue (char). For this reason, this technique may also be considered as an interesting way to produce valuable fuels; indeed, the operating conditions may be selected in order to maximize the yield of one of these outputs. Then, in the activation step, oxidizing agents like carbon dioxide, air, steam are adopted, in a range of temperature similar to the pyrolysis one. After the pyrolysis step, the obtained char develops generally a still not very advanced porosity; for this reason, the activation phase is necessary to enhance the char structure, further increasing the pores volumes and the specific areas.

These phases may be performed in a two-stage or one-stage process. In the two-stage process the char obtained from the pyrolysis is removed from the oven and reinserted in a second moment for the activating phase (so, the overall treatment is subdivided in two distinct moments). During the one-stage process, on the other hand, the passage from the carbonization to the activation phase is obtained switching the flowing gasses (from inert to oxidizing atmosphere) maintaining the char inside the furnace for the whole time of the treatment. Making a comparison between the two approaches, one-stage thermal treatment allows to save time, energy and increase the final carbon yield (28).

In this work, the physical activation was performed mainly through pyrolysis only, or direct activation with carbon dioxide and, in a few cases, air; with a direct activation, the oxidizing agent was circulated from the beginning of the thermal treatment. Anyway, also a few samples were activated with the one stage physical activation as explained above.

The **chemical activation** scheme may follow different methodologies too. Some authors performed the treatment making first the pyrolysis of the carbonaceous material only, introducing the activating reagent in a second time, always maintaining an inert atmosphere (4). On the other hand, other authors started the thermal process having generated the mixture in advance (29). Among the most used chemical species adopted in the chemical activation in the literature there are the potassium hydroxide (KOH), sodium hydroxide (NaOH), zinc chloride ($ZnCl_2$), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), etc. (2). One of the main advantages of the chemical scheme with respect to the physical is the possibility to achieve a higher porosity and specific areas in the final product, with the possibility to achieve better performances in terms of adsorption capacity; on the other hand, the introduction of reagent increases the cost of the overall process and makes the management of the exhaust sorbent trickier. Once chosen the physical or the chemical approach, the optimization of the process is performed figuring out the not trivial choice of the several parameters that rule these processes like the pyrolysis temperature, residence time, heating rate, method (one or two-stage), gaseous oxidizing agent, chemical reagent, chemical reagent concentration, etc.

In this study, only the physical activation has been performed and an examination of several parameters has been accomplished to summarize the best activating conditions.

2.2.1. Physical activation: results and discussion

The main parameters explored during the physical activations were the following:

- Pyrolysis temperature;
- Residence time;
- Activation method;
- Heating rate (for one sample);
- Mass flow rate (for one sample).

The influence of these parameters on the char yield and on the adsorption capacity of the activated samples has been analysed. In particular, pyrolysis temperature, residence time and

the activation methods are the factors that have been considered with more attention; on the other hand, the influence of the heating rate and the flow rate value have been only briefly kept into account while making a specific focus on the sample that experimentally has demonstrated to show the best results in terms of carbon dioxide adsorption capacity.
Three main activation methods have been adopted during the first phase of the experimental activity:

- Pyrolysis: physical activation performed using only nitrogen for the whole duration of the process (transitory, stationary and cooling phases);
- Direct activation: the carbonization and activation phases were performed in one stage, utilizing from the beginning of the thermal activity an oxidizing gas, mainly carbon dioxide and for some experiments air (transitory, stationary and cooling phases);
- One-stage pyrolysis + activation (1 - stage): during the transitory phase an inert atmosphere (nitrogen based) was generated, reached the maximum set temperature, the oxidizing gas (carbon dioxide) was maintained for the duration of the stationary phase (2 hours) and, then, for the cooling phase the gas was switched again to nitrogen.

All the samples produced during the experimental activity are summarized in the table below (see Table 4). In addition to the three methods mentioned above, it is present an "Optimization" section which has been dedicated to the activated sample (SST6002hN_2) which was produced the best performances during the adsorption tests. The labels are explained in the following way:

- SS → "sewage sludge";
- Tx → "x" is the maximum temperature reached at the stationary phase;
- yh → "y" is the residence time set once reached the stationary phase;
- N_2/CO_2/Air/N_2-CO_2 → respectively, nitrogen used only, carbon dioxide used only, air used only, nitrogen for the transitory phase and carbon dioxide for the stationary.

Method	Label	Stationary Temperature [°C]	Residence Time [h]	Heating Rate [°C min-1]	Gas	Flow Rate [Nml min-1]	Number of Experiments
Pyrolysis	**SST2001hN_2**	200	1	10	N_2	300	1
	SST3001hN_2	300	1	10	N_2	300	1
	SST4001hN_2	400	1	10	N_2	300	1
	SST2002hN_2	200	2	10	N_2	300	1
	SST3002hN_2	300	2	10	N_2	300	1
	SST4002hN_2	400	2	10	N_2	300	2
	SST5002hN_2	500	2	10	N_2	300	2
	SST6002hN_2	600	2	10	N_2	300	3
Carbonization + Activation	**SST2001hCO_2**	200	1	10	CO_2	300	2
	SST3001hCO_2	300	1	10	CO_2	300	2
	SST4001hCO_2	400	1	10	CO_2	300	3
	SST2002hCO_2	200	2	10	CO_2	300	1
	SST3002hCO_2	300	2	10	CO_2	300	2
	SST4002hCO_2	400	2	10	CO_2	300	4
	SST5002hCO_2	500	2	10	CO_2	300	2
	SST6002hCO_2	600	2	10	CO_2	300	2
	SST2002hAir	200	2	10	Air	300	1
	SST3002hAir	300	2	10	Air	300	1
	SST4002hAir	400	2	10	Air	300	1
1-Stage	**SST4002hN_2-CO_2**	400	2	10	N_2 - CO_2	300	1
	SST5002hN_2-CO_2	500	2	10	N_2 - CO_2	300	1
	SST6002hN_2-CO_2	600	2	10	N_2 - CO_2	300	1
Optimization	**SST6003hN_2**	600	3	20	N_2	300	1
	SST6002hN_2-HR20	600	2	10	N_2	300	2
	SST6002hN_2-400	600	2	10	N_2	400	1
	SST6002hN_2-500	600	2	10	N_2	500	1

Table 4: list of the samples produced during the experimental activity.

In general, for the thermal activations, in average a mass equal to 150 ± 5 g of milled sewage sludge was utilized. At the end of each thermal activation, the system was usually cooled down maintaining the gas flow rate (nitrogen, carbon dioxide, air, according to the case) for still one hour after the residence time imposed and, then, the reactor was left to cool down at environment temperature overnight.

One of the principal quantities of interest during this treatment is the carbon yield, namely, the ratio of masses between the char obtained at the end of the treatment and the original precursor. In formula, the char yield, Y_{char}, is calculated with the following expression:

$$Y_{char}=\frac{m_{char}}{m_{raw}}\cdot 100 \qquad \text{(Eq. 1)}$$

where m_{char} indicates the mass of the solid quantity of the solid residue remained in the reactor at the end of the activation (g) and m_{raw} is the mass of the raw material to activate (g). The yields of the other products of the thermal activations, namely, the tar (see Figure 11) and the gas fraction, have not been analysed in this work. However, during the activations, it was qualitatively observed a different production of these products according to the physical activation conditions. Indeed, various studies have demonstrated that there are specific pyrolysis temperatures and heating rate able to maximize the production and composition of these other two pyrolysis by-products (30), (31).

Figure 11: tarry fraction originated from the thermal activation process.

The oily and gaseous fraction composition depends mainly from the feedstock nature and the values of the main parameters which rule the thermal treatment. The composition of the pyrolytic liquid is mainly made up by "hydrocarbons, organic acids and carbonyl compounds of high molecular weight, phenols, aromatic compounds, aliphatic alcohols, acetic acid and water" (31); on the other hand, the gases principally consists of "hydrogen, carbon monoxide, carbon dioxide, methane and in small concentrations contains low molecular hydrocarbon fractions" (31).

Thus, the right management of the pyrolysis products represents a fundamental issue to keep into account. Inappropriate disposal methods may bring negative environmental impacts, for instance, producing public health risks, possible contamination of the atmosphere, soil and water reserves. This work has focused its attention on the investigation on the possibility to use the char as adsorbent material; the other two by-products, considering their composition, may be exploited as fuels, considering also their appreciable heating values. It is reported that the organic fraction of the pyrolysis liquids may achieve a heating value which ranges between 22400 – 28000 kJ kg^{-1} (31) and the gas fraction around 12000 – 20000 kJ m^{-3} (31).

2.2.1.1. Temperature influence on the char yield

The experimental activity revealed that the operating temperature during the physical activation is the parameter that mostly influenced the char yield value; the figures below (see Figure 12, Figure 13) show the trend of the yield with the variation of the temperature. In these graphs, the fixed parameters are the following:

- Residence time (1 – 2 hour);
- Heating rate (10 °C min^{-1});
- Gas flow rate (300 Nml m^{-3}).

The temperature ranged from 200 to 400 °C for the dwell time fixed to 1 hour and between 200 to 600 °C for the residence time set to two hours. The activations performed with the larger stationary phase received a more in-depth analysis (shown by a greater temperature interval investigated) principally because of better adsorption characteristics obtained by the chars activated with these conditions.

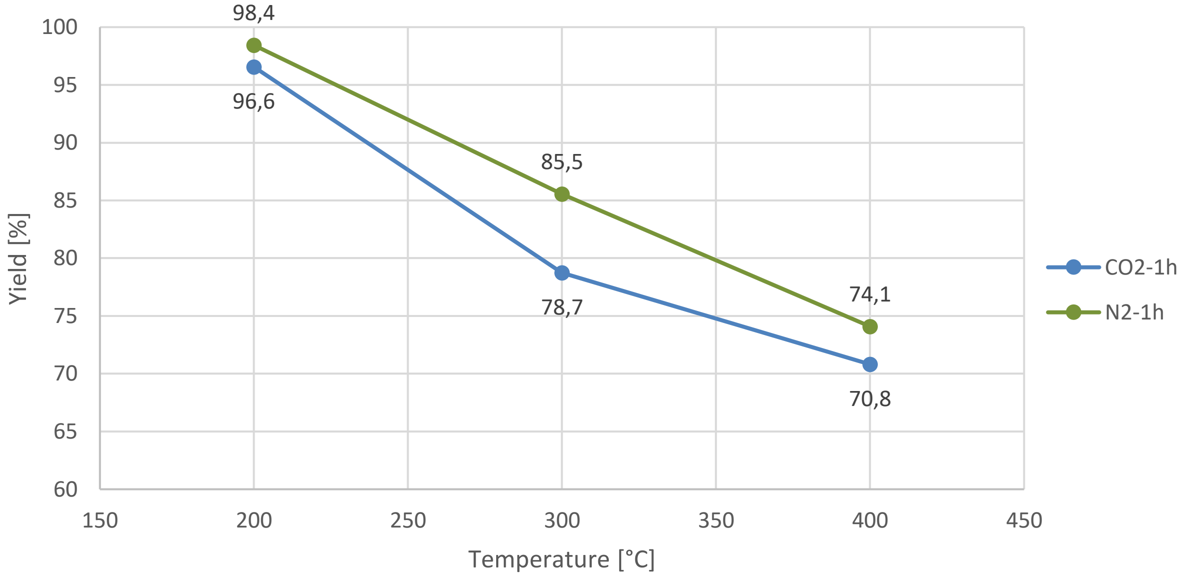

Figure 12: temperature influence on the char yield during the physical activations (dwell time 1 hour).

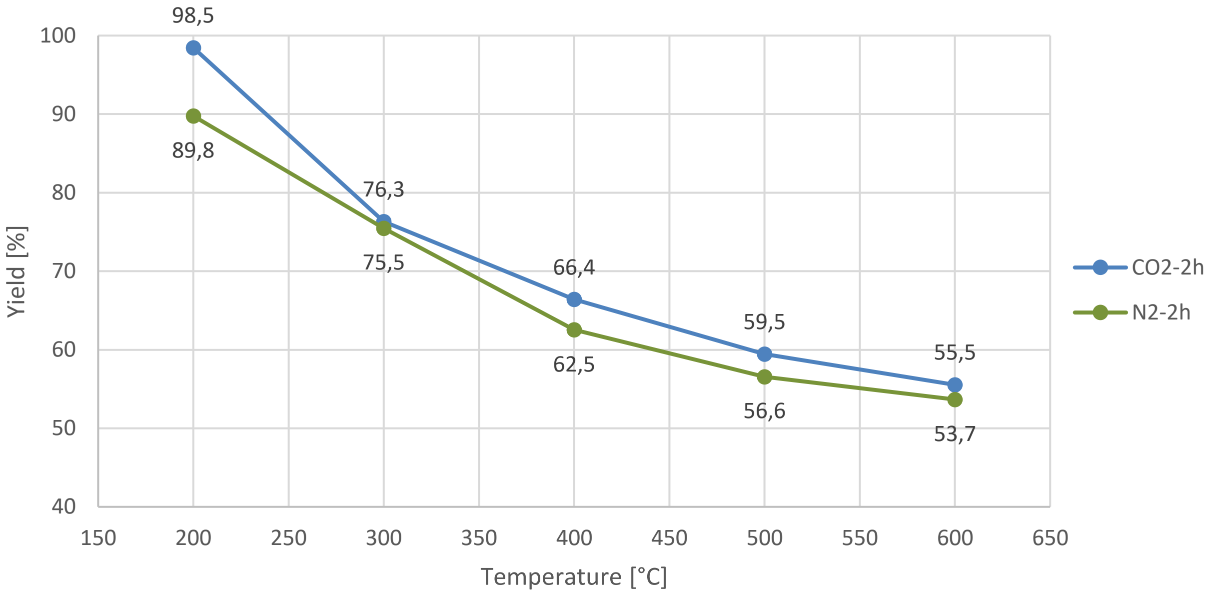

Figure 13: temperature influence on the char yield during the physical activations (dwell time 2 hours).

It is possible to observe that the increase of the pyrolysis temperature produced a decrease of the yield, as an indication of a continuous devolatilization process. In Figure 13, where it is represented the trend of the yield in the wider temperature interval, it can be noted a decrease of the slope with the increase of the temperature; this is explained by a decrease of the devolatilization rate. Indeed, according to the temperature, it is possible to recognize different volatilization stages, characterized by the emission of substances distinguished by a different volatility. In the low temperature region, below 300 °C, the weight loss was mainly caused by the volatilization of moisture and some small organic compounds (32). The considerable difference (around 10 %) in the yield of the samples SST2002hN_2 and SST2002hCO_2 may be explained by a different moisture content of the raw sample treated in those cases. Once exceeded 300 °C, higher molecular organic compounds start to volatilize and decompose, with the formation of the tar oil too (32). The formation of the tar oil from temperatures higher than 300 °C has been confirmed also by the present experimental activity. The slope of the graphs, especially the one related to the curves of the activations with N_2, is almost constant until 400 °C, indicating steady volatilization rate. At this point, the slope of the curves slowly decreases with the increase of the temperature, as an indication that the most prevalent organic content present in the sewage sludges has been already decomposed and that carbonization is taking place. So, in the high-temperature region, nearly from 450 °C onward, the yield decreases with a narrower trend because with the decrease of the organic content, only the inorganic fraction is mostly available to volatilize (33).

2.2.1.2. Residence time influence on the char yield

The residence time (or holding time, or dwell time) identifies the period in which the peak temperature is kept constant during the thermal treatment. In this paper, one and two hours are the values mainly kept into account. A holding time of three hours has been considered only for the optimization case accomplished for the sample SST6002hN$_2$. In the following figures (see Figure 14, Figure 15) is shown the impact of the two different dwell times on the yield value. In this case, the fixed parameters are:

- Temperature (200 – 400 °C);
- Heating rate (10 °C min^{-1});
- Gas flow rate (300 Nml m^{-3}).

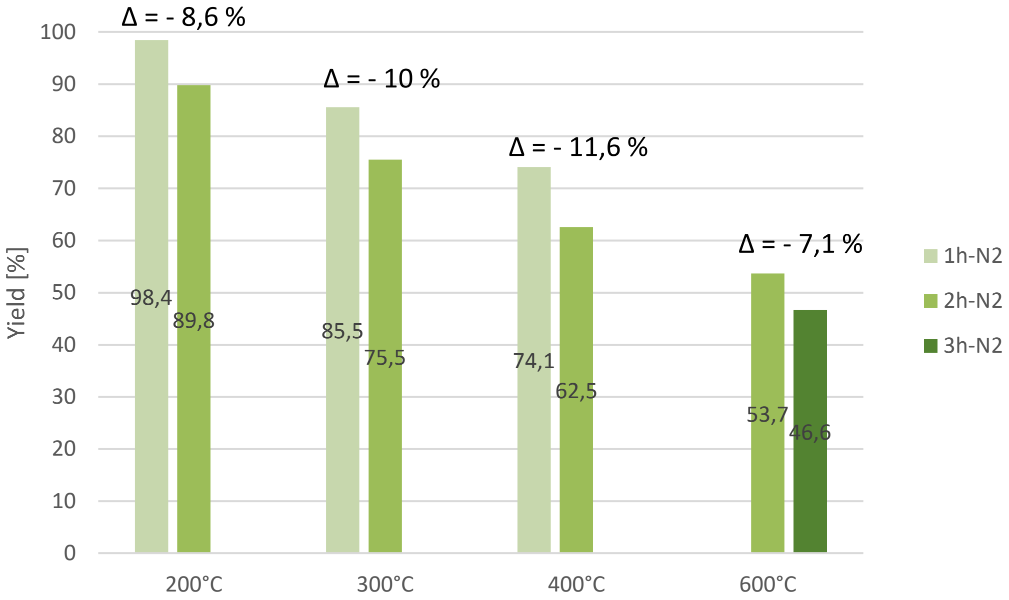

Figure 14: Yield comparison with different residence times with N$_2$.

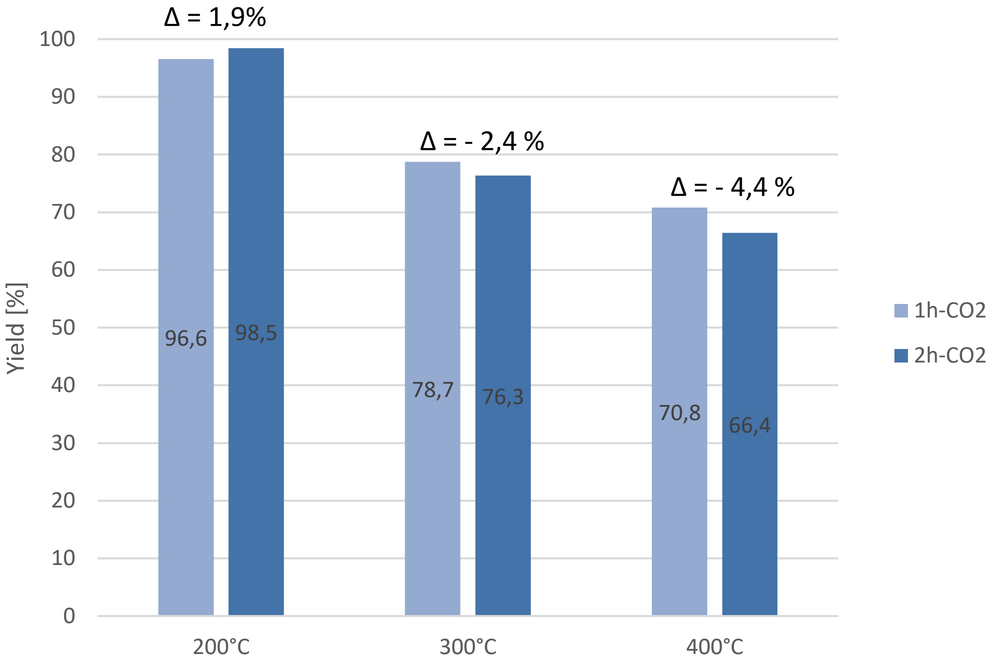

Figure 15: Yield comparison with different residence times with CO_2.

Overall, the char yield has shown a decrease during the change from one to two hours of residence time, in a growing extent with the increase of the temperature. The only exception is represented by the activation at 200 °C with carbon dioxide (+ 1,9 % passing from one to two hours), which may be explained by a smaller amount of precursor employed for the activation in that particular case (Δ ~ 20 g). Moreover, making a comparison of the results summarized in the two figures, it can be observed that the passage from one to two hours have shown a larger impact in the activations realized with nitrogen with respect to the ones with carbon dioxide. Indeed, the maximum variation in the first case is – 11,6 % (at 400 °C) while in the second is – 4,4 % (at 400 °C). Moreover, it can be noted from Figure 14 that, at 600 °C, the yield value decreased with a smaller extent switching the dwell time from two to three hours, differently with all the other cases at lower temperatures in the passage from one to two hours.

2.2.1.3. Activation method and agent influence on the char yield

Three different activation agents have been adopted during the thermal activations: nitrogen, carbon dioxide and air (even if in a much smaller extent). The histogram present in Figure 16 shows the comparison of the char yield value obtained with the different flowing gasses at various temperatures. In these comparisons, the direct activation method has been performed for the thermal treatment of the samples, so, the same gas has been used for the whole duration of the activation (transitory, stationary, cooling phase); as mentioned in the previous section, in the cases with carbon dioxide and air, the carbonization and activation phases have not been separated in different stages during the process. The activations performed with air are limited in the temperature interval 200 – 400 °C for safety reasons, due to the possible exothermic reactions between carbon and the oxygen contained in the air stream that might have been complicated the thermal management during the thermal process (2).

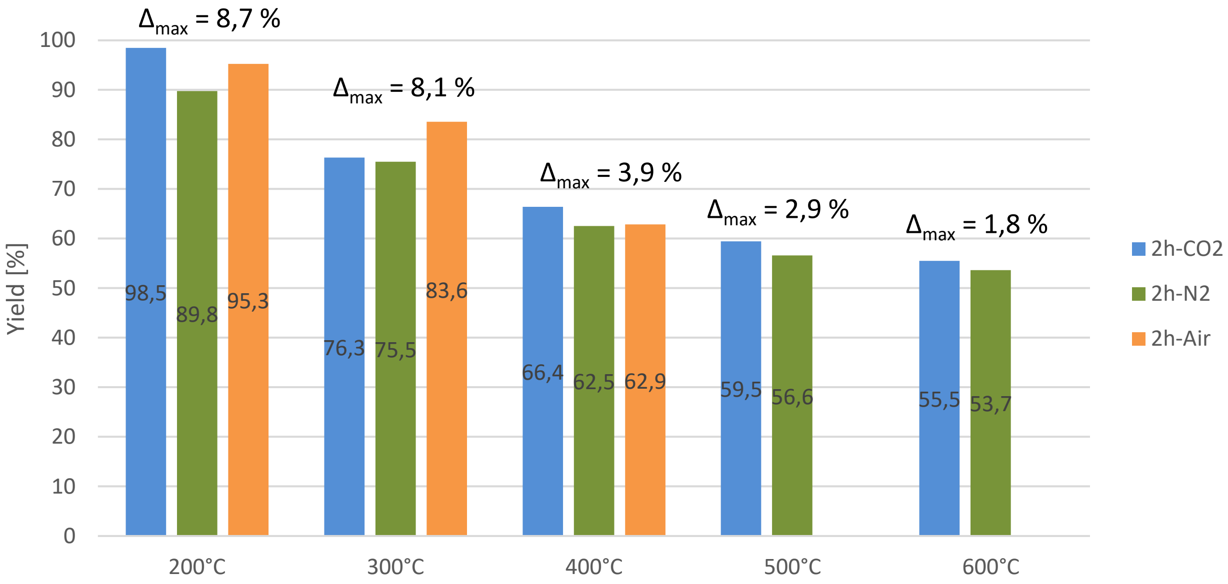

Figure 16: flowing gas influence on the yield value at different temperatures.

The differences which appear in the histogram (Δ_{max}) have been simply computed making the difference between the highest and lowest yield value of the bars group of related to a specific temperature. It is possible to note that the adoption of different gasses it is not influencing the char yield value significantly: the highest differences (8,7 % and 8,1 %) are distinctive for the lowest temperature intervals considered (200 and 300 °C), in which the variable water content in the precursors may have been the reason of such difference. Overall, the yield value seemed to be aligned among the different activations with the increase of the pyrolysis temperature. In Figure 17 it is compared the yield value for different activating methods. The comparison is between the standard pyrolysis process (only flowing nitrogen) with the 1 - stage pyrolysis + activation method, where nitrogen and carbon dioxide were alternated as explained in the previous section. It can be easily observed that the differences of the two processes have not brought relevant dissimilarities in the final amount of char obtained.

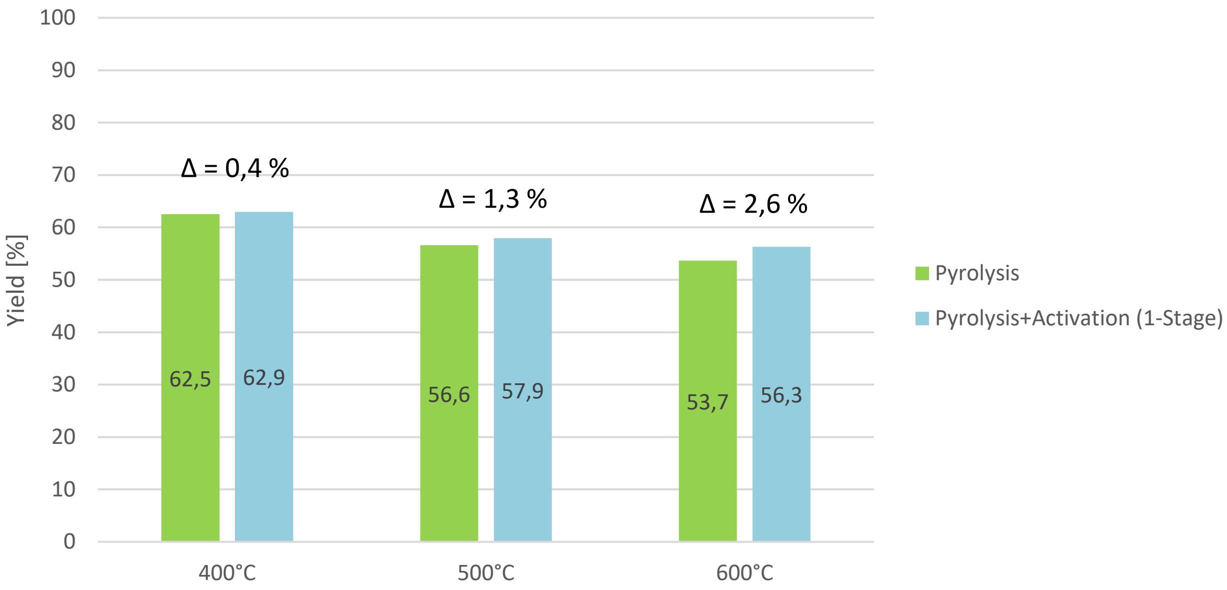

Figure 17: comparison of the influence of the pyrolysis and 1-Stage pyrolysis + activation on the yield value.

2.2.1.4. Heating and flow rate influence on the char yield

The heating and flow rate variation has been explored only for the sample labelled as SST6002hN$_2$, namely for the char obtained with the following conditions:

- Temperature: 600 °C;
- Holding time: 2 hours;
- Heating rate: 10 °C min^{-1};
- Nitrogen flow rate: 300 Nml min^{-1}.

The heating and flow rate values have been varied to investigate the possibility to achieve better adsorption characteristic for the char obtained. The thermal activation performed with a doubled heating rate (around 20 °C min^{-1}) has carried out a negligible variation (- 0,1 %) with respect to the reference case (10 °C min^{-1}), as it is illustrated in Figure 18. In a similar way, increasing the nitrogen flow rate at 400 and 500 Nml min^{-1} caused only a slight decrease of the yield value (see Figure 19); a comparable trend has been observed from other authors (27). Anyway, looking at the data collected from the experimental activity, it could be stated that the main parameters influencing the char yield are the temperature and the residence time, while the others seemed to have given a smaller impact on this quantity.

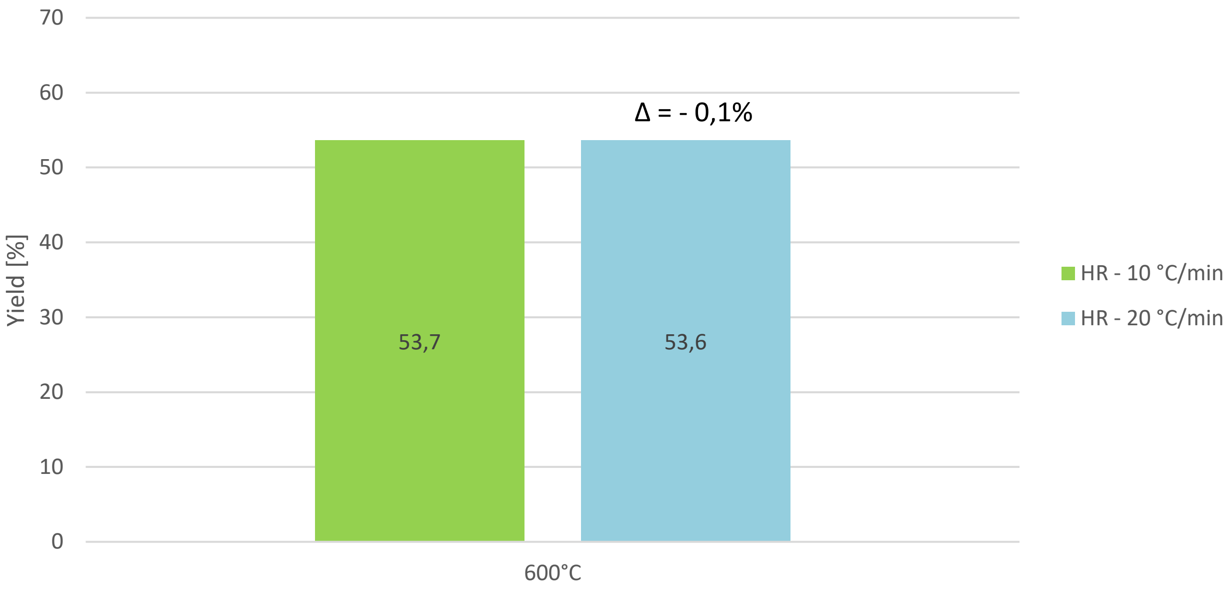

Figure 18: heating rate influence on the yield value observed for the sample SST6002hN$_2$.

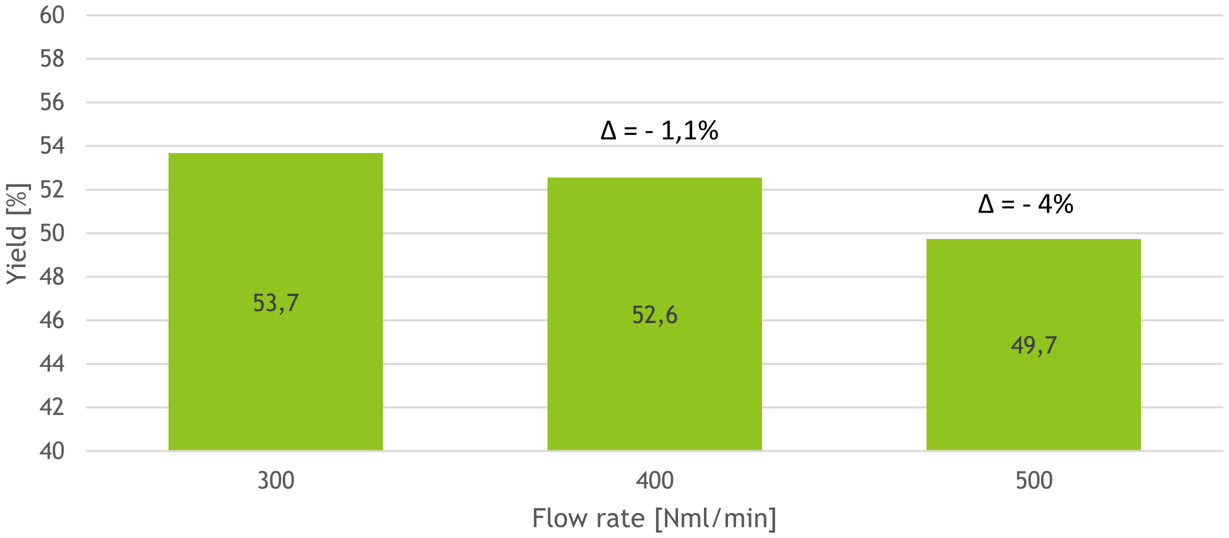

Figure 19: flow rate influence on the yield value observed for the sample SST6002hN$_2$.

2.2.1.5. Textural characteristics variations

Thanks to the collaboration with the Department of Applied Science and Technology (DISAT), it has been possible to study some textural characteristics of the raw sewage sludges and their variations in some samples obtained from the thermal treatment. In the bar graph illustrated in Figure 20, it is shown the percentage concentration variation of some selected elements with respect to the respective quantity present in the initial material (according to the feedstock composition percentages evaluated by the DISAT researchers); overall, the trend depicted by the graph agrees with the results obtained by several other studies dealing with sewage sludge thermal treatments. With the increase of the temperature the most volatile elements tended to reduce their concentration, oppositely to the ash/mineral fraction. Particularly, among the elements detected from the EDS analysis, elements like carbon and oxygen in all the cases considered (temperature range 400 ÷ 600 °C) exhibited a reduction with respect to the starting material. Moreover, especially for the carbon, the extent of the reduction seemed to be influenced from the residence time too, since the samples activated at 400 °C for one hour shown a reduction of –10 ÷ –13 %, differently with the ones activated in the temperature range 400÷600°C for two hours that shown a reduction of –36 ÷ –39 %. The reduction of these elements at considered temperatures could be explained due to the dehydration and decomposition of the organic fraction present in the starting material; indeed, the pyrolysis process is responsible of the formation of volatile substances like carbon monoxide, carbon dioxide and water and hydrocarbon compounds, through which carbon, oxygen, hydrogen are transported (34). In addition to carbon and oxygen, nitrogen and hydrogen are other elements that volatilize as a result of the thermal treatment, decreasing their concentration too (35), (34). On the other hand, it is remarkable the increase of the concentration of all the other elements considered during the analysis (Si, Al, Ca, Fe, Mg, K). This is a consequence of the volatilization of the organic compounds, which let increase the percentage of the inorganic fraction, since their oxides cannot be volatilized (35). Again, the increase of the residence time from one to two hours at the same temperature (400 °C) was followed by an important difference in terms of concentration variation. Moreover, as reported in the literature (35), (34), the conspicuous increased of the mineral fraction, as a consequence of the increase of the pyrolysis temperature, determines an augmentation in the pH level too, modifying the chemical structure of the surface of the obtained sewage sludge-based biochar. It has been demonstrated that the pyrolysis temperature and pH are highly correlated ($r = 0{,}983$, $p < 0{,}01$) (34).

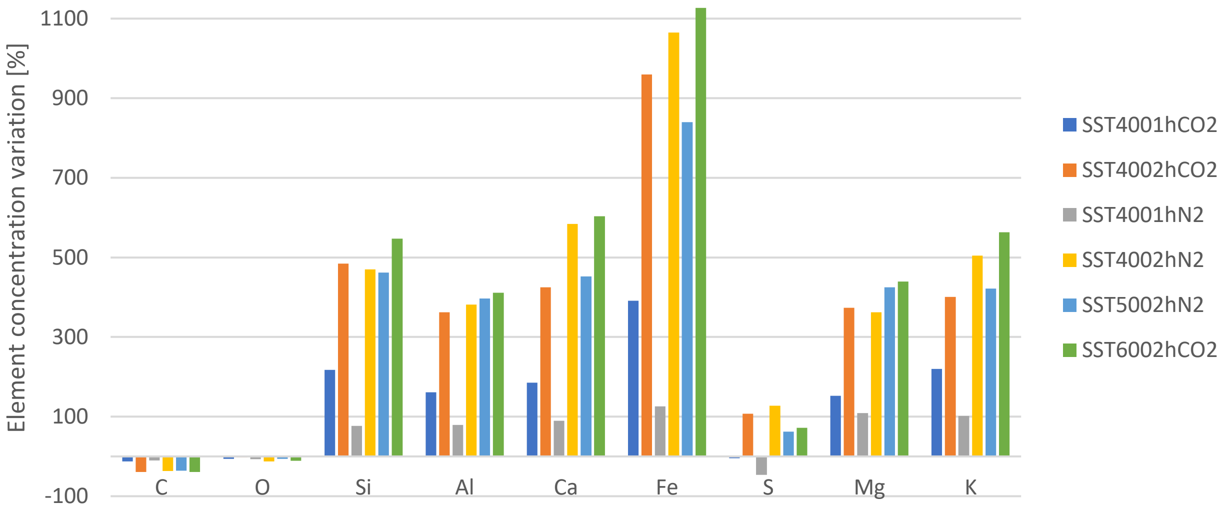

Figure 20: elements concentration variation in comparison with the precursor composition.

The thermal treatments are responsible of the quite enhanced structure characteristics of the sewage sludge-based biochar. As it is summarized in Table 5, the specific surface areas (calculate with the BET and t-Plot methods) and volumes increased of approximately one order of magnitude with respect to the feedstock, which has almost a nonporous structure. In any case, with respect to the specific surface areas that may be achieved from commercial activated carbon (generally higher than 1000 $m^2 g^{-1}$), the values calculated in this study are 2 - 3 order of magnitude smaller. The difficulties to reach a more developed surface area and pore volumes may be caused by different reasons:

- The high inorganic fraction present in the feedstock does not volatilize, limiting severely the development of porosity (36);
- The tar fraction produced during the pyrolysis, may adhere to the surface of the biochar, occluding and blocking the porous gaps (34);
- the adoption of the physical activation scheme which, generally, allows to achieve a less developed porosity structure rather than the chemical activations.

Element Name	S0	SST4001hCO2	SST4002hCO2	SST4002hN2	SST5002hN2
BET Surface Area [m^2/g]	0,323	2,6551	3,2895	2,324	4,3246
t-Plot external surface area [m^2/g]	0,377	3,2701	3,8221	2,7468	4,7013
Volume in Pores (< 1,308 nm) [cm^3/g]	0,00002	0,00038	0,00024	0,00015	0,00074
Total Volume in Pores (≤ 44,883 nm) [cm^3/g]	0,00122	0,01386	0,01913	0,01457	0,02263
Total Area in Pores (≥ 1,308 nm) [m^2/g]	0,111	2,064	3,485	2,399	3,409

Table 5: BET surface area and pore structure for some samples of the treated precursor.

From the data collected in Table 5, the BET surface area and the t-Plot external surface area generally increased with the pyrolysis temperature; in addition, at the same temperature (400 °C), the samples directly activated with carbon dioxide showed larger values increasing the residence time. It has been shown the dwell time enhancement has been followed by a decrease of the char yield and a reduction of the most volatile elemental fractions (see Figure 20), all factors that may have brought to a slightly better porosity development. The same trend has been observed for the value referred to the total volume developed in the biochar structure. On the other hand, the microporous volumes, considering the samples activated at 400 °C with carbon dioxide, have a different trend, decreasing with the increase of the residence time, which is probably responsible of the increase or larger pores (mesoporous and macroporous) due to the formation of sintering processes. In Figure 21, the isothermal adsorption/desorption curves of the activated sample SST5002hN$_2$ are shown. The adsorption isotherm for nitrogen looks like the adsorption curve characteristic of the II Type (according to the IUPAC classification); this category is distinctive of the macroporous or nonporous solid adsorbents.

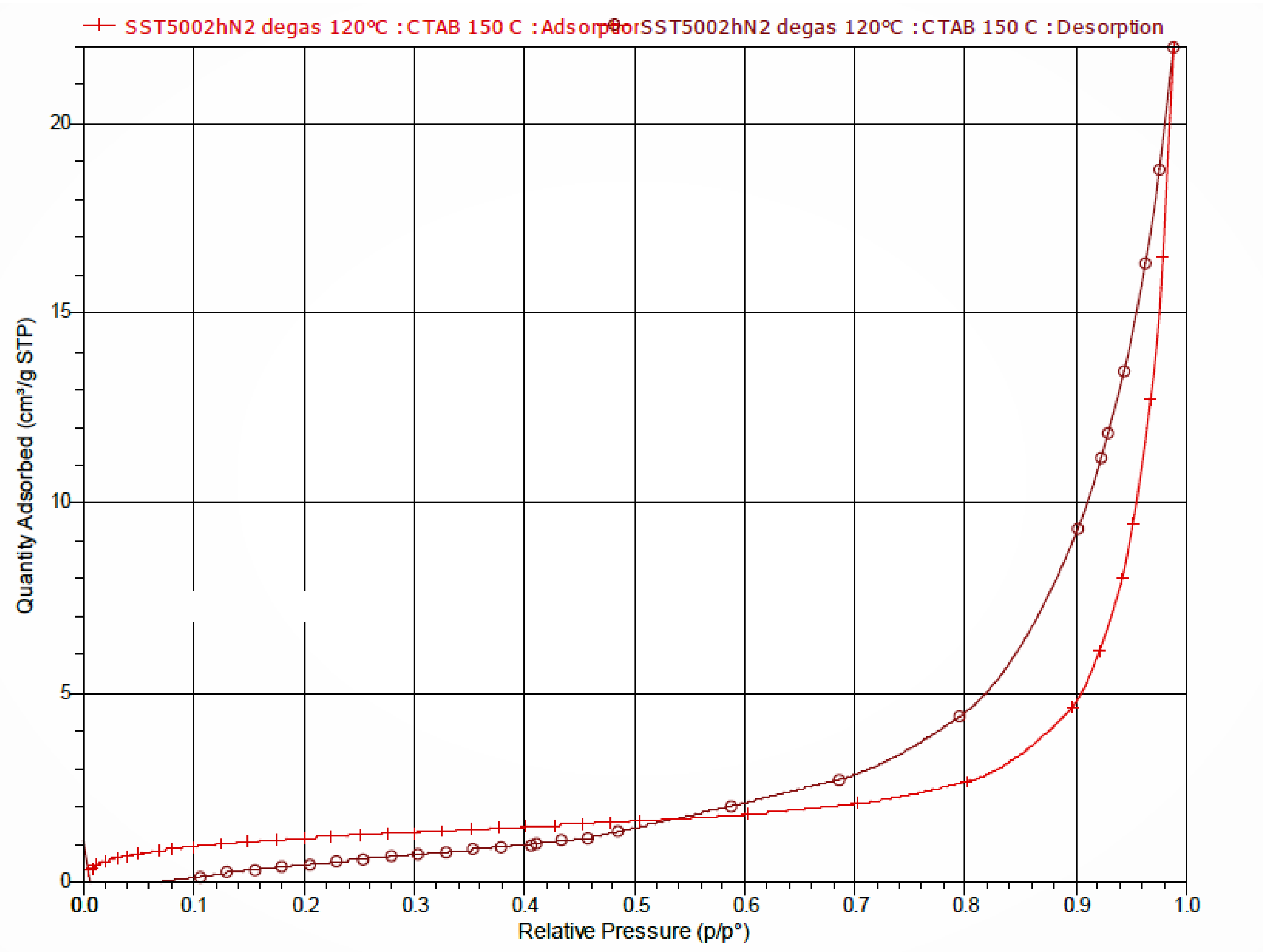

Figure 21: N$_2$ adsorption/desorption isotherms for the obtained biochar SST5002hN$_2$.

2.3. Adsorption tests

In the second part of the experimental activity, the carbon dioxide adsorption behavior of the chars produced with the physical activations have been analyzed. The adsorption dynamics have been accomplished making use of the equipment present in Figure 10. The carbon dioxide capacity was determined studying the response of the fixed-bed column with a simulated biogas blend, analyzing the breakthrough curves generated thanks to the data collected by the mass spectrometer. The simplified biogas mixture was made up by carbon dioxide and methane, with concentration respectively equal to 35 and 65 %. The possible adsorption competition with other acid gasses, like hydrogen sulphide, that are usually contained in the biogas mixture, has not been kept into account in the current study. Other relevant parameters for the adsorption tests are the following:

- Biogas flow rate: 153,8 Nml min^{-1};
- GHSV (gas hourly space velocity): 131 h^{-1};
- C_b: CO_2 breakthrough concentration limit: 2,5 %.

In each test, a biochar mass equal to 49,5 ± 3,5 g was filled inside the reactor, generating a fixed-bed column with a height of approximately 10 cm; this choice has been taken to maximize as much as possible the bed length with the available reactor in order to increase the bed utilization and, consequently, the efficiency of the adsorption process (37). The biogas flow rate and GHSV parameters have not been changed during the experimental activity, for this reason their influence on the adsorption capacity has not been examined in the current work. The carbon dioxide capacity has been computed using the following equation:

$$CO_{2\,cap} = \frac{Q * t_b * CO_{2\,conc} * 44000}{22{,}4 * m_{sorb} * 10^6} \quad \text{(Eq. 2)}$$

Where:

- $CO_{2\,cap}$ $[\frac{mg_{CO_2}}{g_{sorb}}]$ is the carbon dioxide adsorbed in mg per g of sorbent;
- t_b $[s]$ is the breakthrough time;
- Q $[\frac{l}{min}]$ is the simulated biogas flow rate;

- $CO_{2_{conc}}$ [ppm] is the total carbon dioxide concentration in the mixture;
- 44000 $[\frac{mg}{mol}]$ is the carbon dioxide molar weight;
- $22,4$ $[\frac{l}{mol}]$ is the molar volume of ideal gas;
- m_{sorb} $[g]$ is the mass of the sorbent;
- 10^6 is the unit conversion to pass from ppm to molar concentration.

The carbon dioxide breakthrough concentration limit has been set to the value of 2,5 %, according to the limits fixed in the EN 16723-1 and EN 16723-2 received from the EN 16726; this is the value present in the Directive for the carbon dioxide concentration in the biomethane obtained from the biogas upgrading processes, to fit in the best way the already existent natural gas composition, for the injection in the grid and for the use in the transport sector. During the tests, the t_b was identified when the effluent concentration of carbon dioxide was equal to C_b. Giving a look at Figure 22, the time t_b is reached when the mass-transfer zone (MTZ) achieves the end of the cartridge, overcoming the point in where the carbon dioxide concentration at the outlet goes beyond the fixed limit; so, t_b represents the interval of time over which the carbon dioxide concentration (in this case) passes at the outlet from 0 to C_b, namely an estimation of the filter lifetime for this application.

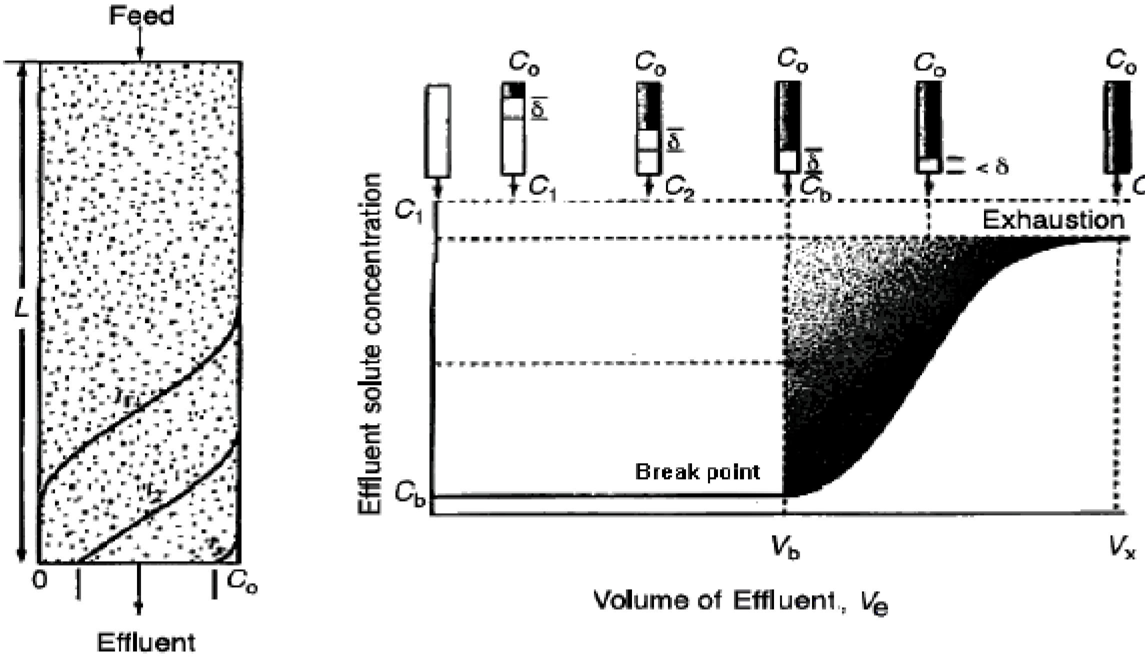

Figure 22: Representation of the movement of primary sorption zone and formation of breakthrough curve (38).

In general, the MTZ represents the length δ over which the concentration of the specie to adsorb in the filter is variable (37). Briefly, the MTZ moves in the direction of the stream, as soon as the equilibrium is reached between the adsorbent surfaces and the solute; the black areas in the cartridge example of Figure 22 represent the zones over which the adsorption occurred and so no mass transfer (so adsorption) happens anymore. Thus, in the figure, the MTZ moves downward, where new adsorption sites not in equilibrium are available; when all the sorbent that constitutes the filter reaches the equilibrium with the adsorbate, it means that the saturation (exhaustion) phase has been reached. The breakthrough curve represents the effluent concentration of interest and it is a tool to understand the efficiency of the fixed-bed column (38). Specifically, the steepness of the curve indicates the actual amount of sorbent that is exploited during its lifetime (degree of column utilization). Indeed, after the breakthrough point, a steeper curve is a good indication in term of adsorption efficiency of the bed, because it means that the MTZ length is narrower as a consequence of a better mass-transfer rate; the ideal breakthrough curve would be identified with a vertical line once having achieved the breakthrough concentration, a situation that would be explained by the formation of a flat front MTZ in the filter (37). In this study, the breakthrough curves have been considered to read the t_b, necessary to compute the carbon dioxide capacity of the several activated samples tested. A focus on the fixed-bed column efficiency, e.g. analyzing the breakthrough curve steepness, has not been performed; indeed, the geometry of the adsorption bed has remained approximately the same throughout the experimental activity.

2.3.1. Adsorption tests: results and discussion

The carbon dioxide adsorption capacity of the sewage sludge-based char was mainly examined keeping into consideration the parameters leading the thermal activations, whose influence have been already accomplished for what concern the yield variation. The raw sludges, before the thermal activation, were sieved, milled and crushed to powder and the biochar samples were sieved again too, so as to fill the reactor for the test trying to reduce as much as possible diffusion paths through the fixed-bed column. Indeed, making adsorption test with the raw sludges as received in terms of size, comparing the milled with the non-treated, the differences in terms of performances were of 1 - 2 orders of magnitude, due to the reduction of diffusion paths and thus higher mass-transfer rates. For this reason, for all the adsorption tests, only powdered biochar was used.

After the physical activation, the samples were chilled down overnight inside the oven at environment temperature and then collected in small plastic sachets, ready to be utilized for the adsorption tests.

2.3.1.1. Temperature influence

The peak temperature of the biochar preparation is one of the most significant parameters in terms of structural modifications of the feedstock. The analysis of the final temperature influence, in relation with the carbon dioxide adsorption capacity, has been performed fixing the following parameters:

- Residence time (1 – 2 hours);
- Flowing agent (nitrogen, carbon dioxide, air);
- Flow rate (300 Nml min^{-1});
- Heating rate (10 °C min^{-1}).

From the results shown in Figure 23 and Figure 24, a positive correlation between temperature and carbon dioxide capacity has been obtained. It is important to specify that the outcomes presented have been obtained with a variable water content; as it will be explained later, a drying treatment prior to the adsorption tests of the biochar samples has shown improvements in terms of capacity.

Anyway, the temperature increase is the main responsible of the textural changes in the biochar samples. The enhancement of the specific surface areas and the total volume of the pores makes more sites available for the carbon dioxide to adsorb. In addition, the increase of the metal concentration changes the surface chemistry, which may play an important role. Indeed, the positive correlation between temperature and pH makes the biochar structure more neutral/alkaline in the highest range of temperatures, increasing the number of the “base sites where the carbon dioxide may react like a Lewis acid” (4).

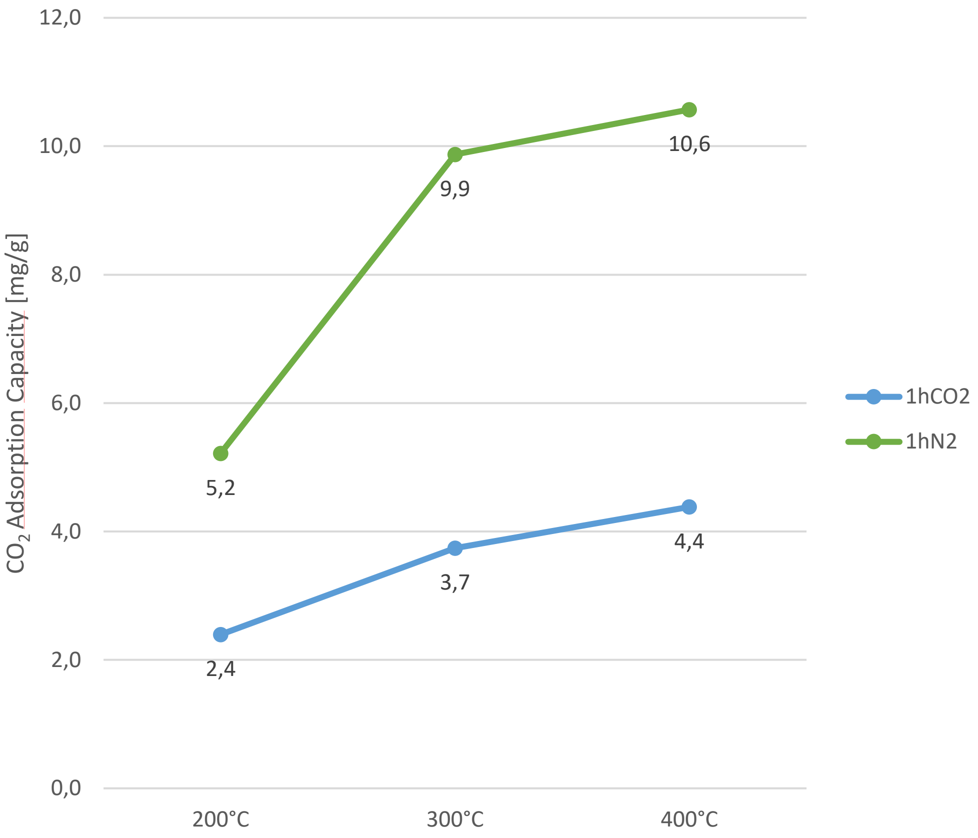

Figure 23: CO_2 adsorption capacity at different temperatures (1 hour holding time fixed, variable water content).

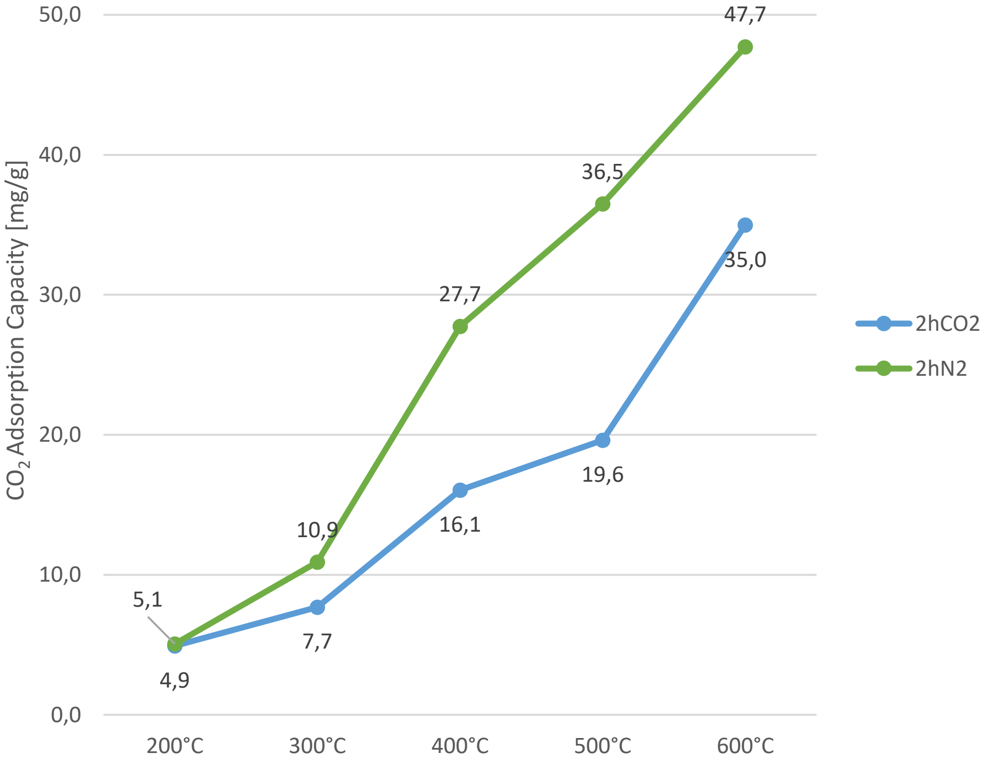

Figure 24: CO_2 adsorption capacity at different temperatures (2 hour holding time fixed, variable water content).

2.3.1.2. Dwell time influence

The dwell time is another parameter whose value has strongly determined the biochar characteristics, influencing the filtering performances. In order to study the impact of this factor, the following quantities have been fixed:

- Temperature (200 – 400 °C);
- Flowing gas (nitrogen, carbon dioxide);
- Flow rate (300 Nml min^{-1});
- Heating rate (10 °C min^{-1}).

Again, the water management has not been kept into account yet in this section, so, the biochar samples considered did not receive any dehydration process post activation.

Figure 25 and Figure 26 summarize the influence of the residence time passing from 1 to 2 hours at the final temperature during the thermal process (stationary phase). It can be observed that for both the physical activation methods adopted, pyrolysis and direct activation with carbon dioxide, switching from one to two hours has, in the great majority of the cases, brought improvements in terms of adsorption capacity; moreover, this betterment increased with the increase of the peak temperature too.

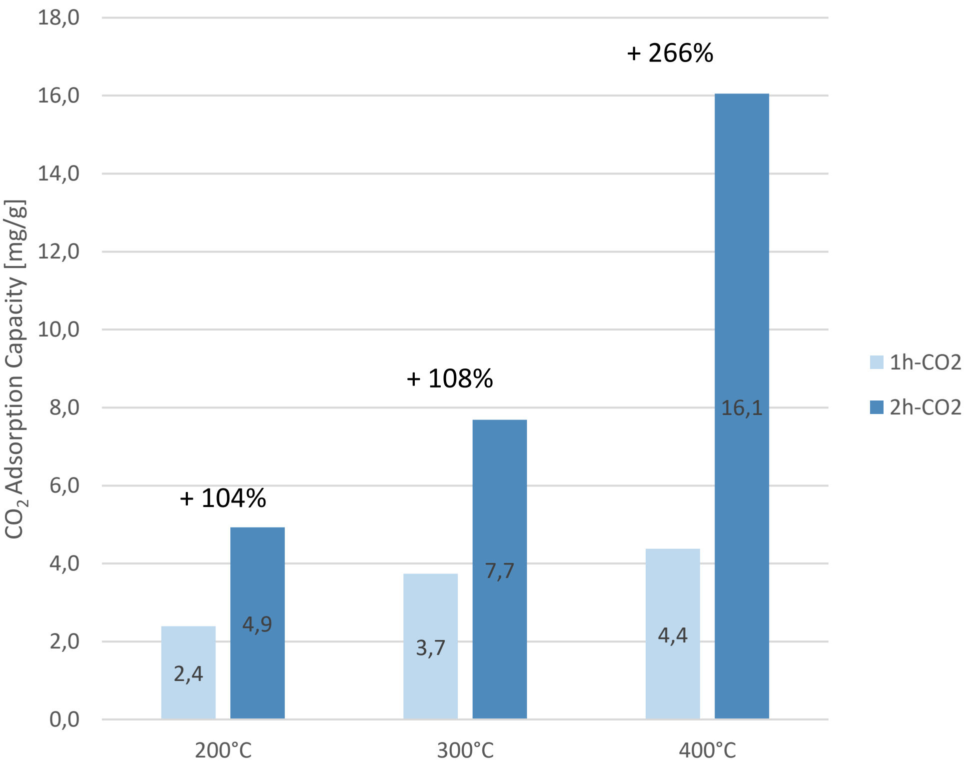

Figure 25: dwell time comparison between 1 and 2 hours for direct activation with CO_2 (variable water content).

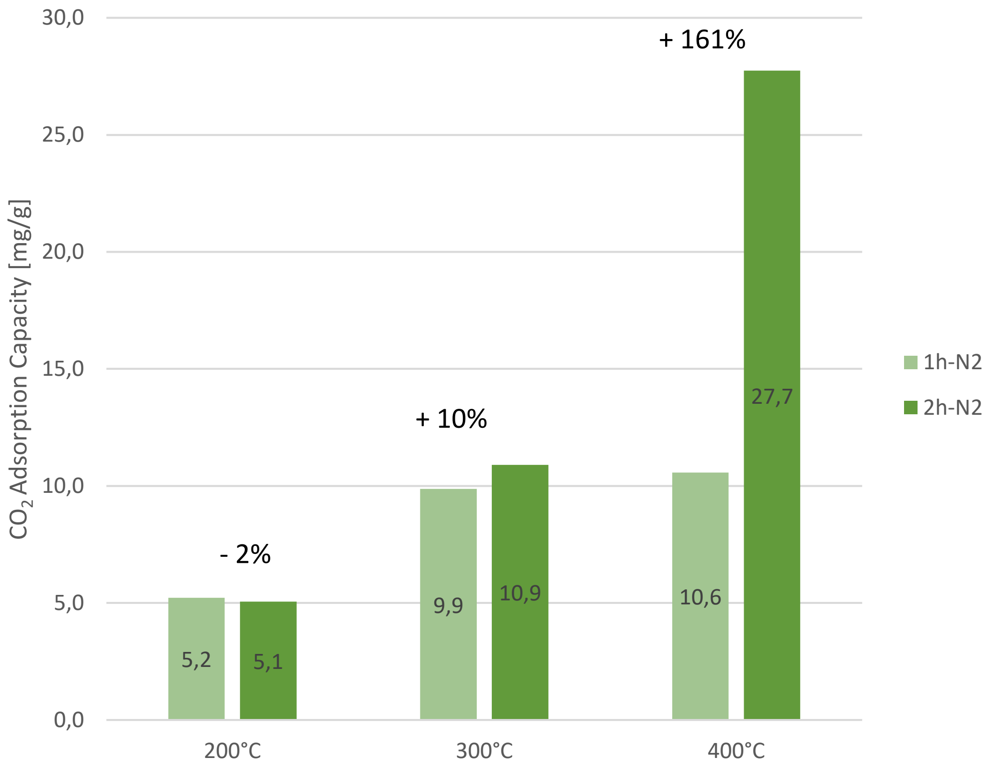

Figure 26: dwell time comparison between 1 and 2 hours for pyrolysis (variable water content).

One of the possible reasons of the adsorption capacity improvement with the holding time increase (in the temperature interval considered) may be the higher release of volatiles matter, which is confirmed by the decrease of the yield value too. Looking at Table 3, the only available case analysed which could be considered to examine the textural variations increasing the holding time is the sample obtained with direct carbon dioxide activation at 400 °C (SST4001hCO$_2$ and SST4002hCO$_2$). It can be noted that the BET surface area, the t-plot external surface area, the total volume and area in pores shown an improvement, while the only parameter which slightly decrease is the volume in pores with sizes smaller than 1,308 nm. Some authors (5) have stated that at elevated temperatures (above 900 °C) the increase of dwell time may generate deleterious effects, testified by the solidification and shrinkage of the carbonaceous matrix, narrowing or closing the pore entrances. Anyway, in this paper the maximum temperature achieved is 600 °C, but for the biochar samples activated in the range 500 – 600 °C basically only 2 hours as residence time has been fixed, having considered 2 hours as the best residence time value to choose according to the results obtained at the lower temperature intervals (200 – 400 °C).

2.3.1.3. Water content influence

The samples activated through pyrolysis and direct carbon dioxide activation process have also received a post drying treatment, before being tested for the adsorption capacity analysis, with the purpose to make an investigation on the moisture influence on the adsorption capacity. Once having noted the beneficial outcomes of the drying, the samples activated directly with air and with the 1-Stage method received this treatment, without re-considering the cases with variable water content.

The drying process was performed making use of the heat available coming from the surface of another oven used in the lab to perform other experiments (see Figure 27). The samples were set inside metal container, in order to guarantee have a good thermal conductivity from the surface of the oven to the biochar samples. The temperature was measured utilizing an Omega HH12B Digital Thermometer; the values ranged in an interval 100 – 110 °C and the thermocouple was placed near the layer closest to the metal container. The samples were dried overnight and approximately 60 g of samples were introduced in each container. This procedure, in the legend of the sample labels, contained in the following graphs, will be named as "Dry_100".

During the dehydration process around 1 – 10 g were lost; the highest weight lost values were generally addressed to the raw sludges and to the biochar samples that were collected after the physical activation since a longer amount of time.

Figure 27: drying treatment of the biochar before the adsorption test.

Keeping into consideration the biochar samples produced with pyrolysis and direct carbon dioxide activation, it was obtained that all the samples which received the drying process have exhibited an improvement in their carbon dioxide filtering capacity. These results have been summarized in the bar graphs contained in Figure 28, Figure 29, Figure 30, Figure 31; all the samples (included the feedstock) have shown improvements with regards to their respective "water variable reference", heedless of the activation method and residence time selected. Considering these outcomes, it seems that the lowest temperature to consider for the biochar production is 400 °C; the samples activated at lower temperatures have shown results similar or, in certain cases, even smaller than the feedstock tested dried or as received, as a probable indication that 400 °C is the minimum temperature to fix to perform the carbonization process and start to develop a certain porosity on the starting material.

Anyway, considering the results summarized in Figure 28 – 31, the moisture amount accumulated to the activated samples seemed to have negatively influenced the adsorption behaviour of the biochar obtained. Indeed, the water presence in the sorbent structure may have been responsible of the reduction of available surfaces that might have been dedicated to the carbon dioxide adsorption.

Among all the biochar samples produced, the SST6002hN$_2$_Dry_100 was the one that exhibited the highest adsorption capacity value, namely equal to 68,5 mg g^{-1}. For this reason, this sample has been selected to try to perform an optimization for all the parameters ruling the thermal activation (residence time, dehydration level, heating rate, flow rate, etc).

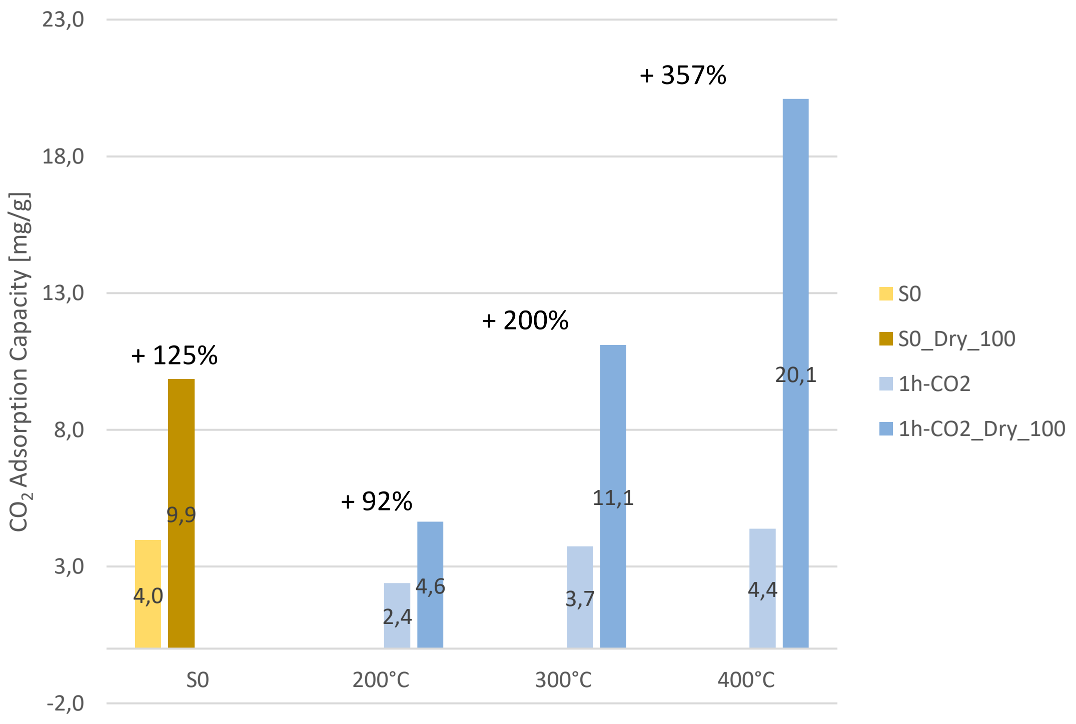

Figure 28: drying treatment effect on the biochar samples activated with CO$_2$ for 1 hour.

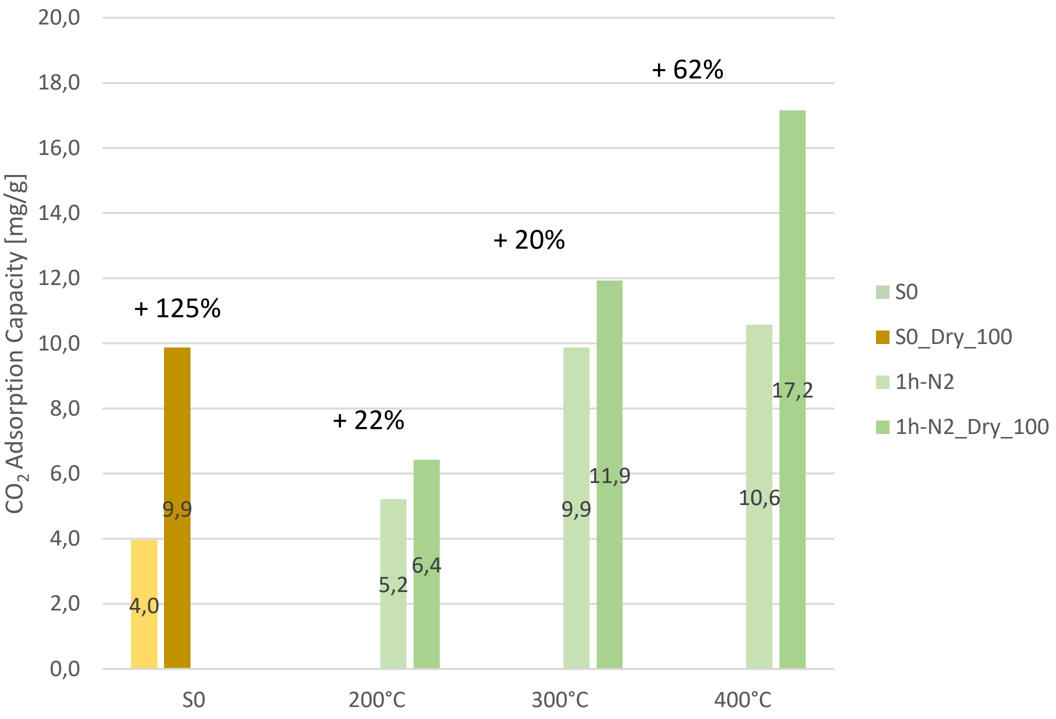

Figure 29 drying treatment effect on the biochar samples activated with N_2 for 1 hour.

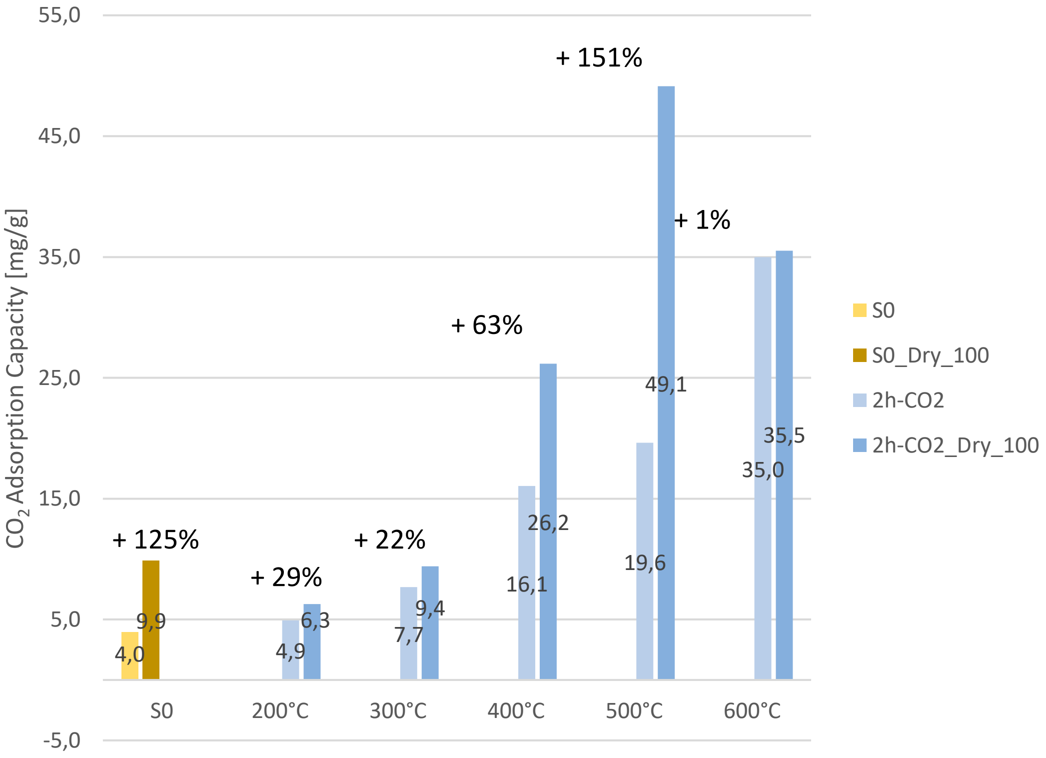

Figure 30: drying treatment effect on the biochar samples activated with CO_2 for 2 hours.

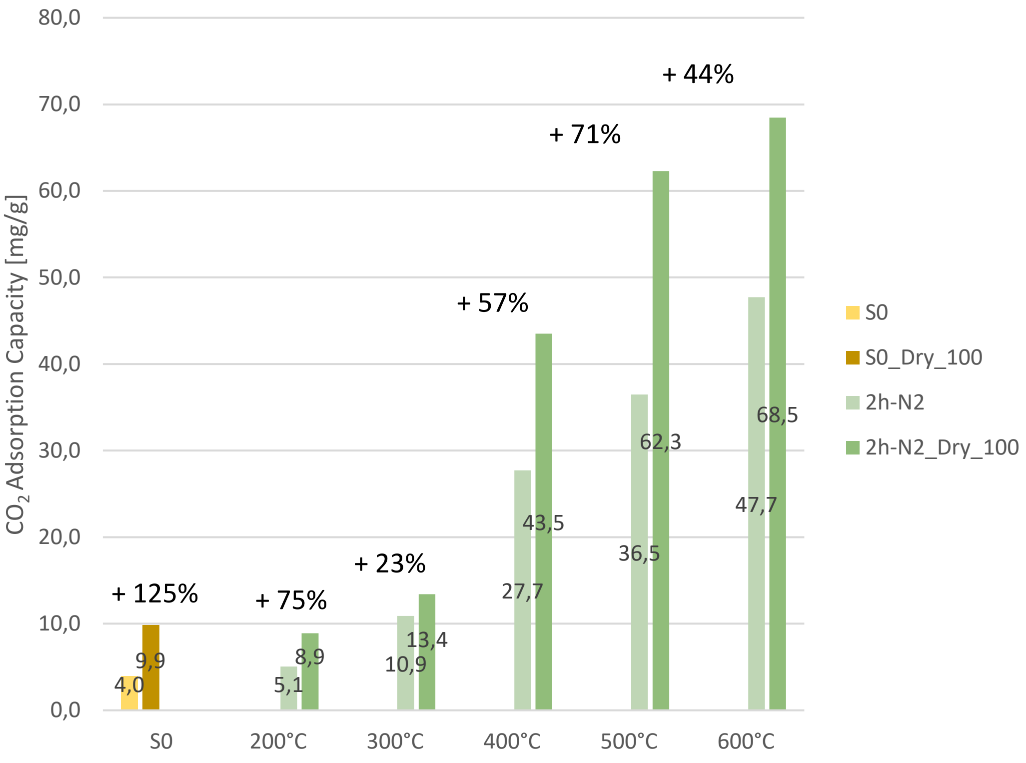

Figure 31: drying treatment effect on the biochar samples activated with N_2 for 2 hours.

In the graph present in Figure 32, the adsorption capacity results obtained from the dried sewage sludge-based biochar produced by pyrolysis (green curve) have been compared with the ones obtained by direct activation with carbon dioxide and air (respectively blue and orange curve). All these samples were activated with a holding time equal to two hours and received approximately the same drying treatment. It stands out that from temperatures above 400 °C, the biochar samples activated in inert atmosphere have generally showed greater results with respect to the ones activated with carbon dioxide and air.

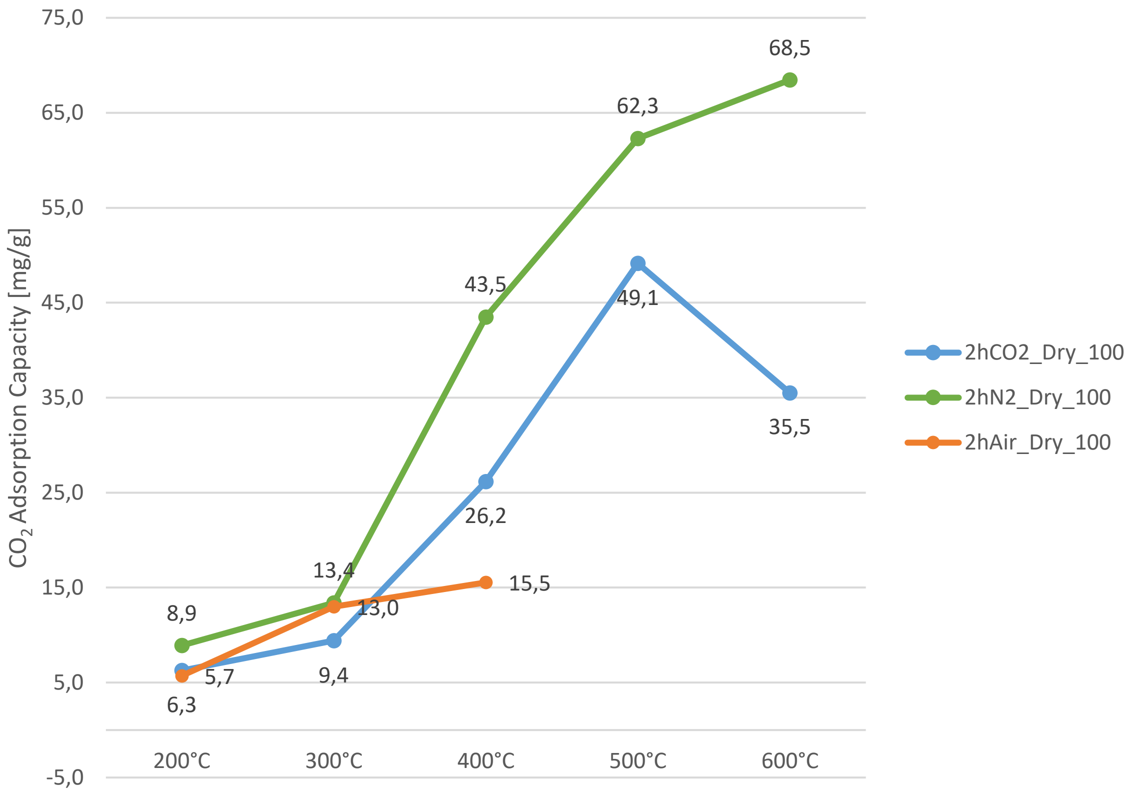

Figure 32: drying treatment effect on the biochar samples activated with N_2, CO_2 and Air for 2 hours.

2.3.1.4. Activation method influence

In the bar graph illustrated in Figure 33, the adsorption capacity results obtained from the samples generated by the different activation methods adopted have been summarized. These treatments have shared the following conditions:

- Temperature range: 400 – 600 °C;
- Residence time: 2 hours;
- Gas flow rate: 300 Nml min^{-1};
- Drying process performed following the same procedure.

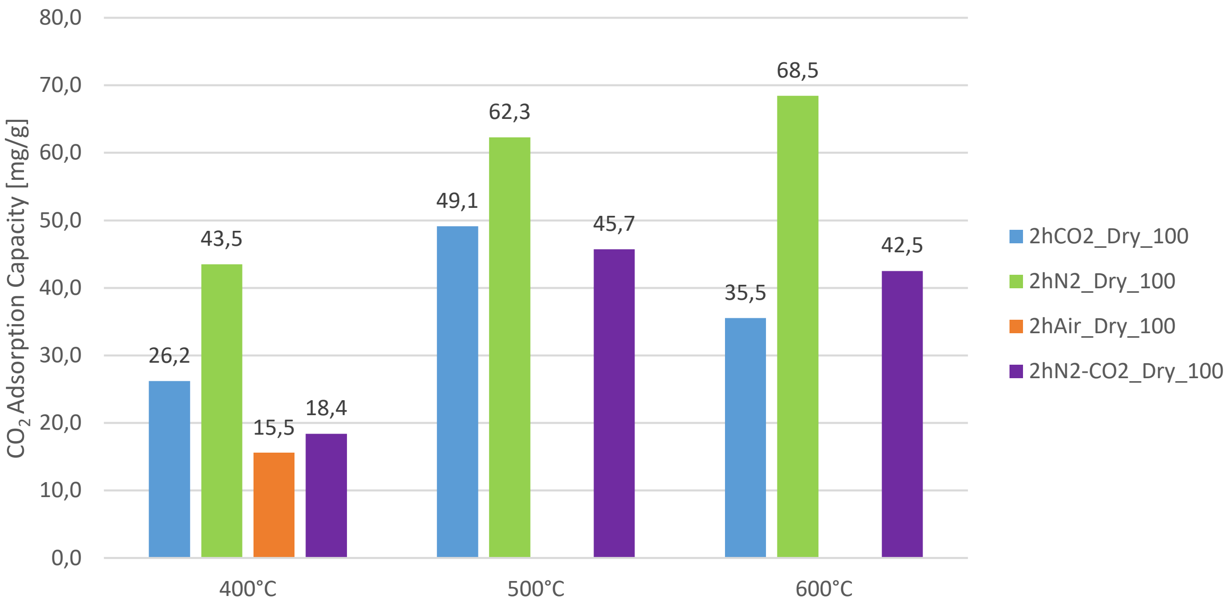

Figure 33: CO_2 adsorption capacity comparison with the different methods adopted.

From this experimental campaign, the pyrolysis method has been more effective regard to the others for the carbon dioxide separation in a biogas simulated stream. The biochar obtained from the 1-Stage (violet bar) and direct carbon dioxide activation (light blue bar) methods have not shown considerable differences in this temperature range. As explained previously, the direct activations with air have been considered only in a low temperature range (200 – 400 °C) as a precaution. The air would represent an interesting agent for the physical activations due to its cheaper cost with respect to the others; in addition, even if it was not investigated in this study, other authors have obtained similar BET surface areas and micropore volumes values, in the low range of temperatures (200 – 400 °C) with regard to samples activated at much higher temperatures (700 – 800 °C) using carbon dioxide as activating agent (36). It is important to say that, for the direct air activation and 1-Stage method, only one sample for each temperature has been produced.

Anyway, the adsorption results obtained with the different methods in this experimental activity, summarized in Figure 33, have underlined how the sewage sludge carbonization performed with nitrogen only has represented the most effective treatment; for this reason, a further analysis on the activation parameters related to the best sample obtained with this method has been performed.

2.3.1.5. Parameters optimization

So far, the biochar sample SST6002hN$_2$_Dry_100 has produced the best result in terms of carbon dioxide adsorption with respect to all the other samples (68 mg g^{-1}); for this reason, it has been selected as biochar reference to explore the effects produced by the variation of some parameters on the filtering performances. The temperature was the only fixed parameters, while some variations for the other parameters have been investigated to find the optimum activation condition according to the feedback given by the adsorption tests.

The **dwell time** is the first parameter analyzed for the optimization process. The reference biochar sample (SST6002hN$_2$_Dry_100) was compared with the SST6003hN$_2$_Dry_100, whose physical activation was characterized by a residence time increased to the value 3 hours. The drying post activation treatment followed the same procedure of the compared case. The histogram present in Figure 34 illustrates that, switching from 2 to 3 hours, the holding time value has produced almost no changes in the carbon dioxide adsorption process. The increase of the residence time to values higher than two hours seems to not generate significant changes in the sewage sludges derived biochar structure, as reported by other authors (36).
With this result, the optimal residence time selected is two hours; this choice is advantageous for at least 2 reasons:

- Higher amount of solid fraction produced during the physical activation due to a greater char yield value obtained (53,7 vs 46,6%);
- Lower energy cost expenditure during the thermal treatment for the biochar production.

Figure 34: dwell time optimization, comparison between 2 and 3 hours.

A further investigation on the **drying process** has been carried out too. In particular, a temperature of approximately 180 °C has been applied to the biochar sample SST6002hN_2 and SST6001hN_2 during the drying treatment. This latter has not been considered during the residence time optimization section previously debated because of the different drying conditions. Indeed, in Figure 35 it has shown a further improvement in the adsorption characteristics passing from 100 – 110 °C to 170 – 180 °C, which may be explained by a more completed dehydration of the samples during the post activation treatment at higher temperatures. It can be observed that the samples SST6002hN_2_Dry_180 and SST6001hN_2_Dry_180 have generated better results than the SST6002hN_2_Dry_100 and so, the SST6002hN_2_Dry_180 has become the new best biochar sample produced.

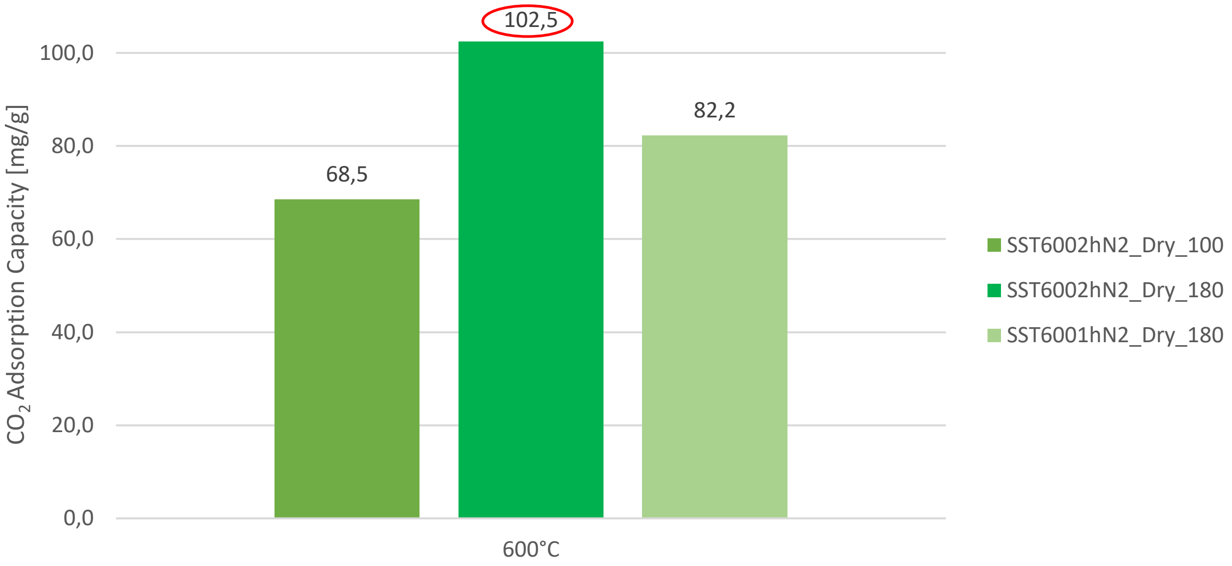

Figure 35: drying temperature optimization, comparison between 100 and 180°C.

The second last parameter that has been explored is the **flow rate** of the nitrogen stream utilized during the thermal activations, which have been always fixed at the value 300 Nml min^{-1}. In Figure 36, the reference sample adsorption capacity is compared with the sample activated at the same conditions but with a flow rate equal to 500 Nml min^{-1}. The results show a sharp decrease of the biochar performances in these new conditions. Some authors (27) have reported the trend of the BET surface area and micropores volume with the flow rate variation during the physical activation process; despite some differences with the current study (activations agent, feedstock), it has been displayed that at low (below 200 Nml min^{-1}) and high (above 400 Nml min^{-1}) flow rates, the BET surface area and the micropores volume showed a sudden decrease, identifying a plateau of optimal values approximately in the flow rate range values 200 – 400 Nml min^{-1}. A similar trend may be hypothesized for the current study too, determining the possible reason of the drop in carbon dioxide adsorption capacity. Therefore, the 300 Nml min^{-1} value has been considered as the optimal flow rate, which is in addition more favorable considering the fewer amount of nitrogen utilized during the thermal process.

Figure 36: flow rate optimization, comparison between 300 and 500 Nml min^{-1}.

Finally, the last factor considered during the optimization process is the **heating rate**. Looking at Figure 37 it can be observed that doubling the eating rate value, switching from 10 to 20 °C min^{-1}, the adsorption capacity is more than halved in a similar magnitude to what happened for the flow rate increase. The reason may be explained considering, in general, the phenomena which rule the carbonization happening during the thermal treatment. Indeed, the transitory phase of the carbonization process is made up by two phases, a softening and shrinkage stage. In the course of the first one, a lower heating rate is able to favour a better formation of the pores, because the gases can be released slowly without the collapse of deformation of the char (39). In addition, the increase of the heating rate value from 10 to 20 °C min^{-1} has been demonstrated to reduce the BET surface area of the sewage sludge-based biochar obtained (39); thus, a different porosity development of the two samples may justify the collapse of performances occurred.

Figure 37: heating rate optimization, comparison between 10 and 20 °C min^{-1}.

At the end of the optimization process, in this study, the most efficient sewage sludge-based sorbent for the carbon dioxide separation, in a simulated biogas stream, has been produced with the following conditions:

- Temperature: 600 °C;
- Dwell time: 2 hours;
- Drying temperature: 170 – 180 °C;
- Flow rate: 300 Nml min^{-1};
- Heating rate: 10 °C min^{-1}.

2.4. Comparison with other feedstocks

The sewage sludge-based adsorbent sample obtained with the optimal conditions found (SST6002hN$_2$_Dry_180) has been compared with other feedstocks: a waste material and a commercial sorbent, both available in the laboratory. The waste material is represented by ashes, while the commercial is the activated carbon Norit RST3. The adsorption tests were accomplished with the same conditions of the ones performed with the sewage sludge derived sorbents. The only difference is represented by the length of the bed, reduced to around 6 cm, which corresponded to a utilized mass equal to 10 ± 0,5 g. Before being deployed for the tests, these materials have been milled (only the activated carbon pellets, the ashes were already into a dust size) and sieved too, with the same procedure used for the raw sewage sludges.

2.4.1. Sorbent characterization

The **ashes** came from a forestry wood-chips boiler (3,3 MW, Viessman, Allendorf Germany) and, likewise the sewage sludges, they represent a low-cost feedstock, whose reuse as adsorbent may represent a valuable waste recovery and management. On the other hand, the **Norit RST3** is a commercial activated carbon, "steam activated with catalytic properties, impregnated with calcium hydroxide and potassium hydroxide" (40). Their elemental composition and structural available info are summarized in the following tables (see Table 6, Table 7):

Element (Atomic %)	*Ashes*	*Norit RST3*
C	7,73	91,15
O	39,99	5,3
Mg	2,74	0,2
Al	4,07	
Si	9,09	
S		0,57
Ca	10,87	0,76
Na	0,68	
K	10,82	0,78
Fe	11,68	
Mn	0,73	
Ti	0,85	
Zn		1,15

Table 6: elements identified with SEM-EDS analysis in the ash sample (41), (40).

Sample	*SSA ($m^2\ g^{-1}$)*	*V_{tot} ($cm^3\ g^{-1}$)*	*V_{micro} ($cm^3\ g^{-1}$)*
Norit RST3	1117 (Langmuir)	0,447	0,300

Table 7: Norit RST3 surface and volume analysis (40).

The two materials present an antithetical composition, as it is summarized in Table 6: the ashes, being the residues of a combustion, are basically made up inorganic elements, rich in metals, while the Norit is mainly constituted by a carbonaceous structure. Making the comparison between Table 5 and Table 7, it is remarkable to observe the large structural differences between the activated carbon and the best sewage sludge-based biochar whose textural properties have been available (SST5002hN_2); indeed, the Norit specific surface area, total pores volume and total micro pores volume are respectively three, one and three orders of magnitudes larger. This comparison stresses also the predominance of meso and macropores in the sewage sludge-based biochar samples with respect to a commercial activated carbon, justified by a different initial material and different activation treatments.

2.4.2. Water influence

Considering the significant effects on the sewage sludge-based biochar samples, the influence of the water content has been analyzed also for these materials. For the drying temperature, it has been chosen the same optimal range found for the biochar samples, namely the temperature interval 170 – 180 °C, following the same dehydrating procedure. In Figure 38 and Figure 39, the comparison of the adsorption carbon dioxide tests between the as received and dried conditions for both materials has been illustrated.

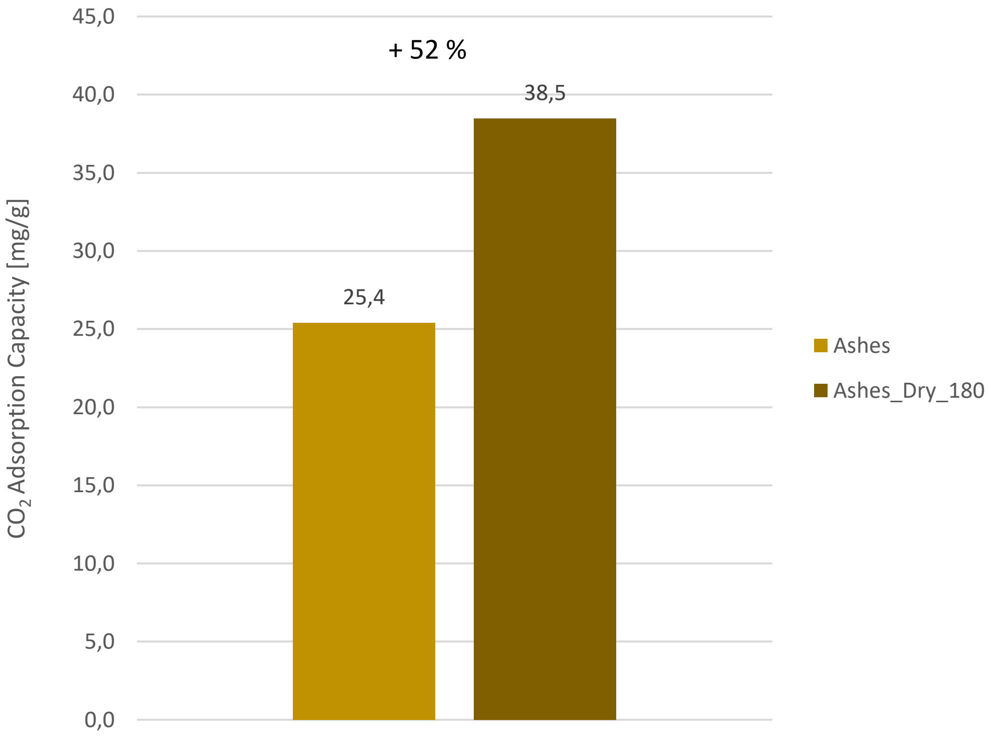

Figure 38: water content influence on the ashes adsorption capacity.

Also in these cases, it has been demonstrated the negative influence of the water presence for the carbon dioxide adsorption; in fact, both the ashes and the Norit RST3 displayed substantial improvements in terms of capacity after the drying treatment.

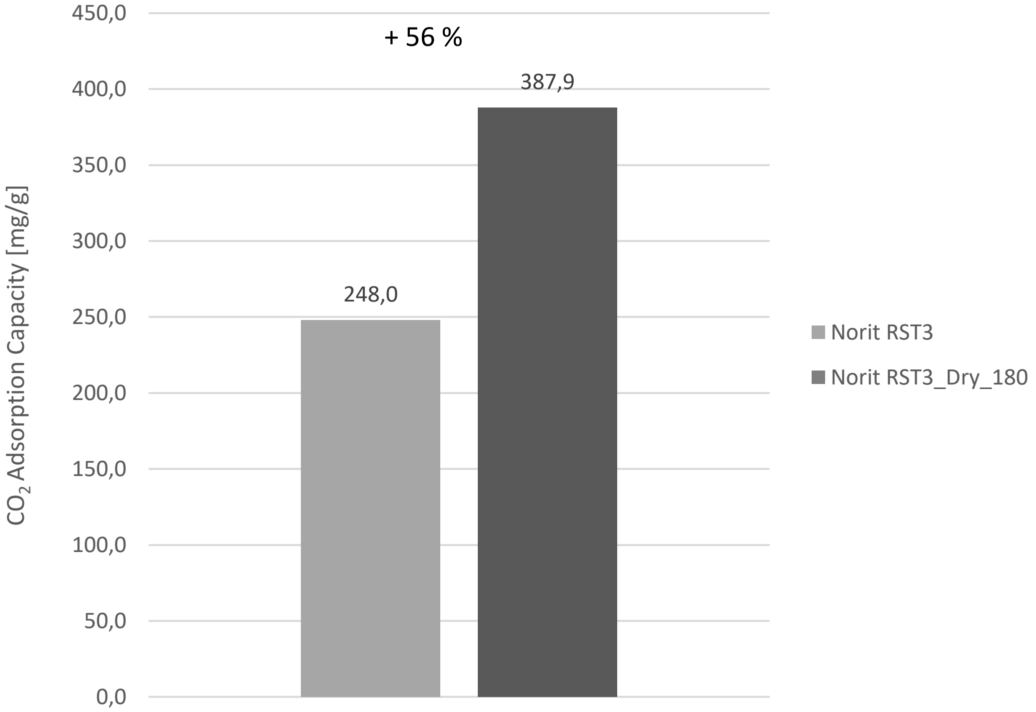

Figure 39: water content influence on the ashes adsorption capacity.

2.4.3. Overall comparison

In Figure 40 is shown the overall comparison of the carbon dioxide adsorption capacity of all the materials examined in this study. As it was expected, considering their almost non-existent porosity in their structure, the bottom of the chart is taken by the raw dried sewage sludge, which have an adsorption capacity almost 10 times lower than its derived biochar activated at 600 °C with N_2. The second last result has been achieved with the dried ashes. With respect to the dried raw sewage sludges, better performances have been achieved, justified by the high metal concentration in their structure. Moreover, it is interesting to note that its carbon dioxide adsorption capacity, around 38,5 $mg_{CO_2}\ g^{-1}_{sorb}$, is generally higher than all the sewage sludge samples activated at temperatures equal or below 400 °C, both through pyrolysis and direct activation with carbon dioxide and air. Considering the activations at 400 °C, this result is comparable with the performances obtained with the sample SST4002hN$_2$_Dry_180 (43,5 mg$_{CO_2}$ g$^{-1}_{sorb}$), while, at the higher temperature, it is greater than the sample SST6002hN$_2$-CO$_2$_Dry_180 (35,5 mg$_{CO_2}$ g$^{-1}_{sorb}$). In general, this may highlight the fact that, to develop effectively relevant adsorption characteristics with the activated sewage sludges, it may be necessary to increase the operating temperature at minimum 500 °C. Finally, among all the materials tested, the commercial activated carbon Norit RST3 has shown the best performances in terms of carbon dioxide adsorption, which resulted to be approximately 4 times greater than the best biochar sample obtained from the sewage sludges activation. The difference may be explained considering the noteworthy difference in terms of specific surface area and total pores volume; in addition, the biochar sample may not have sufficiently developed suitable chemical surface characteristics, which would have allowed to achieve similar or better performances regard the commercial activated carbon, despite the structural differences, like it has been obtained from other authors (4).

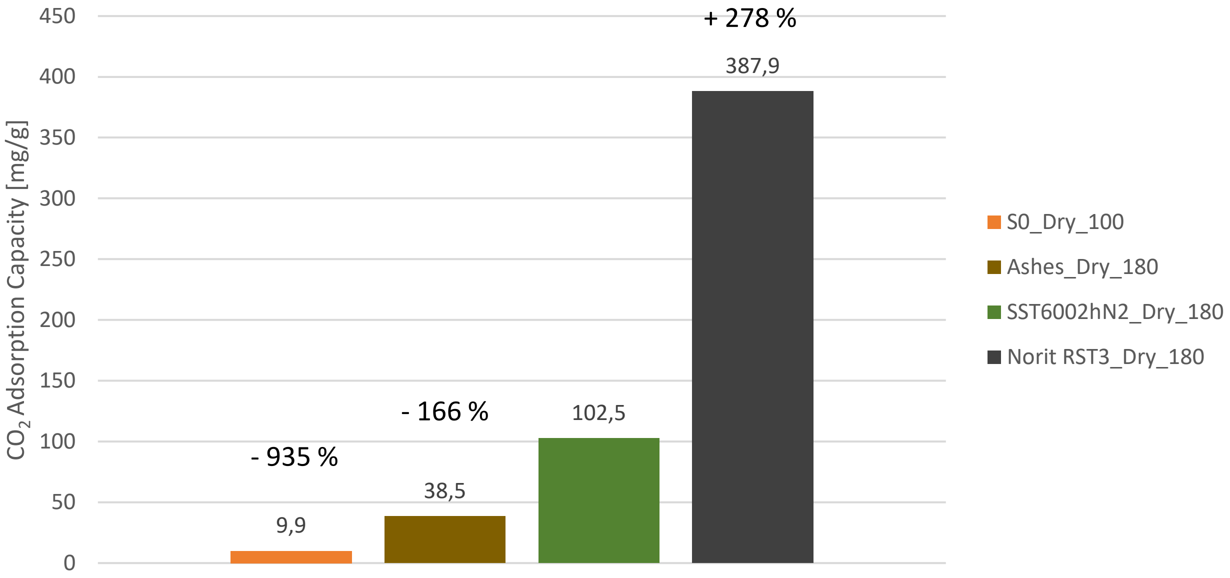

Figure 40: CO2 adsorption capacity comparison of all the materials considered.

2.4.5. Efficiency

The adsorption capacity expresses the attitude of the solute to collect on the surface of a solid, namely the sorbent; this affinity between the two is a function of several parameters, e.g. "molecular characteristics such as size, shape, polarity, partial pressure or concentration in the fluid, and the system temperature" (37). Generally, the adsorption occurs under the form of physisorption, namely weaker forces than chemical bonds are prevalent, as the van der Waals forces. The adsorption capacity value is an important parameter for the design of a filter: simply, as higher will be the affinity between the solute and sorbent, as lower will be the amount of this last necessary for the cleaning applications. Anyway, for the purpose of this work, namely the analysis of the adsorption as biogas upgrading technique, the value of the adsorption capacity for the carbon dioxide is not enough to have the overall background to define the efficiency of this method. Indeed, other important features, characterizing a biogas upgrade method, to be considered are the purity of the methane produced, the amount of methane losses and the energy required to perform the process.

During the adsorption tests performed in this study, the biomethane quality has been considered acceptable whenever the carbon dioxide concentration was below the 2,5% (the removal of the other traces compounds has not been taken in consideration). This limit is necessary to estimate the breakthrough time and, in turn, to evaluate the adsorption capacity of the adsorbent materials. The graphical tool to understand this information is represented by the breakthrough curves; Figure 41 and Figure 42 illustrate the partial breakthrough curves of the best sorbents discovered during the experimentally activity, namely the biochar in lab activated, SST6002hN_2_Dry_180 and the commercial activated carbon Norit RST3.

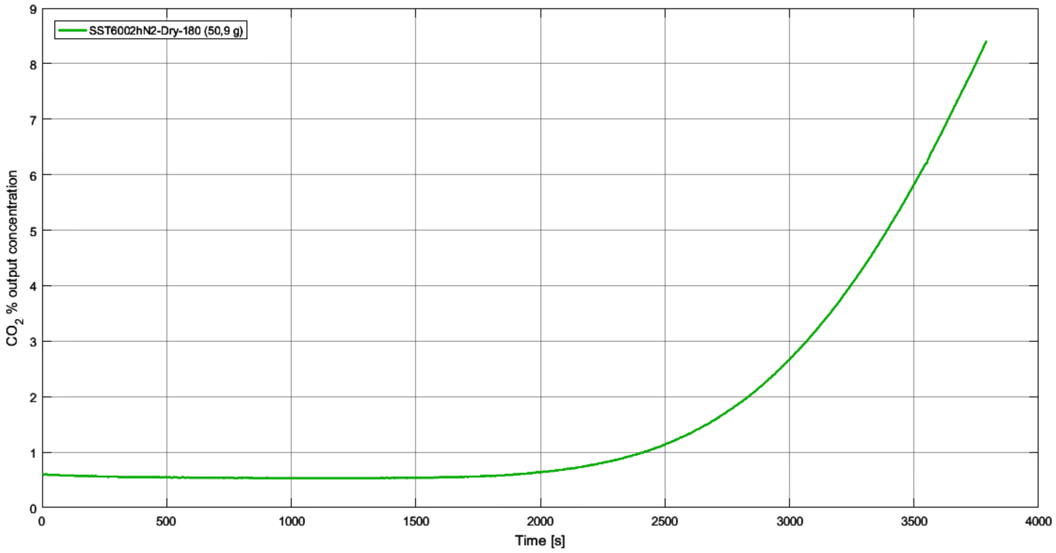

Figure 41: breakthrough curve of the biochar sample SST6002hN2.

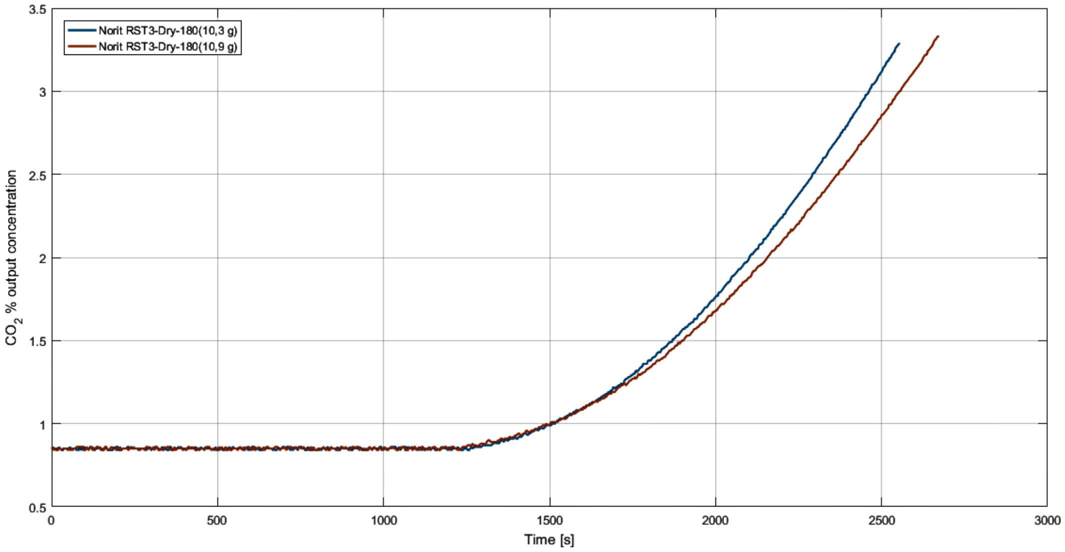

Figure 42: breakthrough curves of two activated carbon samples of Norit RST3.

They are produced by the mass spectrometer which measures the carbon dioxide concentration outgoing from the filter. In these cases, the curves are "interrupted" before reaching the saturation point, because the interests of this study were focused on the capacity evaluated at the breakthrough concentration; for other samples tested until the saturation, the breakthrough curve was depicted by the common "S" shape, reaching the horizontal asymptote around the concentration value of 35 %.

The carbon dioxide concentration data acquired from the breakthrough curve have been examined to make an estimation of the possible methane losses to charge to this process too.

Indeed, looking at the concentration present in Figure 41 and Figure 42, the carbon dioxide never reaches the “0” value. There may be a twofold explanation for this phenomenon:

- a fraction of the blend has been inevitably adsorbed by the sorbent;
- slight errors in the measures may be attributed to the mass spectrometer.

Anyway, supposing negligible the measuring error to allocate to the mass spectrometer, the methane adsorption by the filter might be estimated looking at the breakthrough curves. In particular, it may be quantified making an average of the concentration values related to the part of the curve that still has not experienced any increasing trend. Making a comparison of the two materials, following this procedure, the estimated methane losses counted to the sewage sludge-based biochar SST6002hN_2_Dry_180 and the Norit RST3 are respectively 0,55 % and 0,85 %, which highlight a good adsorption selectivity towards the carbon dioxide for both the materials.

Finally, regard to the energy required from the adsorption process, the filters have been tested working at environmental temperature and pressure; so, the main energy expenditure, during the operation, might be represented from the feeding of the pumping system required to win the pressure drops that may be generated by the filter. Out of the operating phase, the main energy expenditure for both the materials is the one necessary for the activation of the feedstock which constitutes the carbonaceous starting material.

3. Scale up section

Regarding the carbon dioxide adsorption results illustrated in the previous sections, in the following paragraphs, general scale up considerations will be performed, comparing the two sorbents which exhibited the best results: the sewage sludge-based biochar SST6002hN$_2$_Dry_180 and the tested commercial activated carbon Norit RST3. The choice of these two materials has been accomplished to briefly investigate also the differences in terms of sorbents masses employed and related costs during the application of a recovered waste in contrast to a commercial material.

Keeping in mind some SMAT WWTP, for example, in the ones present in Collegno (TO) and Castiglione Torinese (TO), the biogas produced from the anaerobically digested sewage sludges is stored and used to satisfy a fraction of the electric and thermal energy demand, while the treated and dried sludges are mainly disposed as fertilizers and as incineration feedstock (42).

In the following sections, a preliminary investigation on the possibility to recover part of the dried and treated sewage sludges through the production of biochar adsorbents will be explored, so as to involve these materials in the upgrading of a fraction of the biogas generated, making the comparison with a parallel scenario in which a commercial activated carbon is utilized.

3.1. Preliminary yearly oprational estimations

The SST6002hN$_2$_Dry_180 and activated carbon yearly masses will be evaluated considering the following hypothesis and simplifications:

- The adsorption capacities obtained for both the materials are constant;
- The biogas composition is the same of the one simulated and adopted in the lab tests. This simplification presumes that siloxanes, sulphur compounds, water vapour, etc. are separated from a prior cleaning treatments unit (which is indeed suggested to increase the biogas upgrading efficiency).

Considering the following values for the carbon dioxide concentration in the biogas mixture and density:

- $CO_{2_{conc}}$ = 35 %;
- ρ_{CO_2}= 1,976 kg m^{-3} (at normal conditions).

In this scale up estimations for the preliminary study, the design of the reactors containing the sorbent materials has maintained a similar geometry of the reactor utilized in the laboratory for the carbon dioxide adsorption tests (see Figure 10(b)); thus the same L/d (length of the column bed over the reactor diameter) will be kept constant. Considering the sizes of the tests reactor:

- $L_{lab} = \ 10\ cm$;
- $d_{lab} = 3\ cm$;

The ratio obtained is:

$$\frac{L_{lab}}{d_{lab}} = \frac{10}{3} = 3{,}33$$

and the related volume V_{lab} occupied by the char during the test is around 70,7 cm^3.
The carbon dioxide removal unit will be constituted by 8 cylindrical reactors, having the following sizes:

Geometrical data	Size	Unit of measure
Height (l)	1,93	m
Diameter (d)	0,58	m
Volume	0,51	m^3
L/d	3,33	-

Table 8: geometrical sizes of the reactors adopted in the scale up section.

with a resulting total volume obtained equal to approximately 4 m^3. The reactors are supposed to work in couples in a “lead & lag” configuration; the number of operational loadings will be counted considering replacements performed when 6 out of 8 reactors do not allow to produce biomethane respecting the target composition.

The preliminary study realized in the next paragraphs will contemplate two possible scenarios according to the amount of biogas stream to deal with by both the materials tested:

- Case 1: the biogas flow rate upgraded is a spillage of the whole plant production;
- Case 2: the biogas flow rate upgraded is computed according to the GHSV present during the lab test on a scale plant size.

In the first scenario, the set biogas flow rate value is 0,5 m^3 h^{-1}, while the whole biogas remaining fraction is considered to be utilized to keep on satisfying part of the electrical and thermal energy requirements of the plant. In these conditions, the consequent GHSV is pretty smaller than the one adopted during the laboratory experiments; despite the adsorption capacity would be characterized by a higher value with a lower GHSV, in the following calculations the number obtained during the experimental activity will be maintained for both the materials.

On the other hand, in the second case the biogas flow rate has been set regard to the GHSV specific of the adsorption tests in the laboratory (131 h^{-1}) and the reactors volume employed during the scale up estimations (0,51 m^3), giving a result equal to approximately 67 m^3 h^{-1} of biogas treated during the upgrading process.

In both the cases, operational estimations will be evaluated, highlighting the differences caused by the different flow rates values in the two scenarios and by the adoption of a waste recovered or commercial material for the same purpose.

3.1.1. Char, pyrolytic oil and gas

The **char** SST6002hN_2_Dry_180 characteristics evaluated during the experimental activity to keep into consideration for the estimations performed during the preliminary study are:

- carbon dioxide capacity: 102,5 mg_{CO2} $g^{-1}{}_{char}$;
- apparent density: 702,7 kg m^{-3};

in which the apparent density is an approximation obtained keeping into consideration the char mass placed inside the volume of the reactor used for the adsorption tests in the laboratory. With this value, the amount of char loaded to each reactor considered for the scale up is around 358 kg.

Being aware of the char capacity and the maximum amount loadable in each reactor, it has been estimated a carbon dioxide adsorbed mass by a single vessel equal to approximately 36,7 kg. Once the volume of the reactors has been fixed, the main driving force establishing the breakthrough time for each vessel is the biogas flow rate, whose value determines the amount of carbon dioxide passing through the sorbent materials.

In a one year of working operation, the results obtained in the two scenarios are schematized in the following table:

Quantity	Case 1 (0.5 m^3 h^{-1} of biogas)	Case 2 (67 m^3 h^{-1} of biogas)
Charge time [h]	106	0,8
Yearly CO_2 separated [kg]	3029	404114
Yearly Biomethane production [Sm^3]	2847	379806
Yearly char used [kg]	29553	3942574
# Reactors yearly replaced	83	11019
# Operational loadings	14	1836

Table 9: comparison of the estimated results related to the char replacements for Case 1 and Case 2.

where the quantity "operational loadings" considers the number of times during the year in which the assigned workers are supposed to deal with the sorbent replacements.

Giving a look to the estimated results of Table 9, it seems obvious that only Case 1 could represent a possible practical scenario. Indeed, because of the huge amount of carbon dioxide foreseen to be treated in the Case 2, with a higher biogas flow rate, it makes impossible to achieve a realistic amount of times in which the plant should replace the exhausted sorbents. On the other hand, considering only a spillage of the biogas flow rate generated, the replacement operations seem more practical (nearly once every month) and allows the plant to keep on satisfying almost the same fraction of the energy needs.

An important concern is the estimation of the **activation energy** for the sewage sludge feedstock pyrolysis. The thermal activation energy required for the process has been approximated consulting the specific thermal energies required from the literature; indeed, according to this research (43), considering the pyrolysis of wet sewage sludges (so, with a probable higher energetic cost regard the feedstock of this study, which has been received almost completely dry), the evaporation energy cost has been estimated to 2,47 MJ kg^{-1} and the carbonization to 0,62 MJ kg^{-1}. So that, it has been estimated an overall thermal energy need of neary 44,11 MWh_{th}, keeping into account a staring feedstock mass equal to 51396 kg, necessary to produce around 29553 kg of biochar. Therefore, this is the estimated thermal energy that the feedstock would require to be activated for the biochar production. Moreover, considering the nature of the feedstock, a specific oven, suitable to perform pyrolysis, might have to be thought; the state of art in this field might be represented by the Thermo-Catalytic Reformer recently projected by the Fraunhofer Institute for Environmental, Safety, and Energy Technology (44).

Indeed, another issue to consider is the supplementary management of the other products generated by the physical activations, this time on a larger scale. As explained in the Physical activation section, beyond the solid carbonaceous residues, the pyrolysis process generates also a **liquid and gaseous** fraction. Contrary to the char yield trend, the oil and gas yields increase with the temperature in specific intervals, reaching a maximum value and then decreasing. In another study (30), the optimal temperature to maximize the oil and gas yields have been experimentally found at respectively 575 and 625 °C; after those temperatures, the yields decrease has been observed. More in depth, the yields of the pyrolysis by-products are also influenced from the factors which lead the thermal process; so that, for example, the maximum operating temperature, the residence time represent some crucial parameters in this sense. Indeed, as stated from other authors (31), "low temperatures and high residence times lead to carbonization" (maximization of the char yield), "high temperatures and high residence time lead to increased gas yield" and "in average temperatures and very fast process" the liquid yield is maximized. During the experimental activity of this work, considering the different goals to pursue, a detailed analysis on the oil and gas yield variations, like the one that has been carried out for the char, has not been performed. However, from the weighing of the pyrolytic oil produced from the activation of a few samples, some information expressed above by the other searches consulted may be confirmed. Specifically, for two samples, SST6003hN_2 and SST6002hCO_2, both the char and oily fractions have been weighted; thus, the estimations of the three yields are reported below:

- SST6003hN_2 → char yield: 46,6 %, oil yield: 32,2 %, gas yield: 21,2 %;
- SST6002hCO_2 → char yield: 57,5 %, oil yield: 31,3 %, gas yield: 11,2 %.

Comparing the different yields of samples activated at the same temperature, even if with different activation agents, it could be noted that the increase of the residence time seems to have enhanced the gas yield for the SST6003hN_2 biochar sample.

For the preliminary study of this section, the biochar activated sample SST6002hN_2 is considered and, since its oil and gas yields are not known (only the char yield has been calculated), they may be approximated with the ones obtained for the sample SST6002hCO_2, whose char yields are anyway similar (53,3 and 57,5 % respectively). Keep on considering the evaluations obtained for the Case 1, looking at Table 9, it can be noted that the yearly estimated char used for the biogas upgrade is around 29553 kg. Thus, considering the following yields values:

- Char yield: 57,5%;

- Oil yield: 31,3%;
- Gas yield: 11,2%;

the mass of the initial raw sludges to be pyrolyzed can be calculated applying the yield formula and considering the yearly char produced (giving a yearly feedstock pyrolyzed equal to around 51396 kg). The yearly amount of feedstock treated is necessary to calculate the oil and gas masses yearly generated utilizing the yield formula with the oil and gas yields, giving the following results:

- Yearly oil mass: 16087 kg;
- Yearly gas mass: 5756 kg.

Since the gaseous composition has not been analysed in the current study, the average molecular mass of the blend has been considered from the literature. Other authors (30), considering the gas fraction produced by the sewage sludges pyrolysis in a temperature range between 475 – 600 °C, have found that the molecular mass assumed values from 26 to 32 g mol^{-1}. For this reason, it will be estimated an average value of 32 g mol^{-1} for the gas fraction considered in this preliminary study (since the reference biochar sample has been activated at 600 °C). Therefore, the yearly volume of the gas fraction generated from the pyrolysis process, considering the:

- Yearly gas mass: 5756 kg;
- Average molecular mass: 32 g mol^{-1};
- Molar volume at normal conditions: 0.022414 Nm^3 mol^{-1};

is estimated to around 4032 Nm^3. In the following table (see Table) the yearly pyrolysis by-products quantities produced considering the Case 1 scenario have been summarized:

Pyrolysis product	Value	Unit of measure
Char	29553	kg
Oil	16087	kg
Gas	4032	Nm^3

Table 10: pyrolysis products amounts generated in the Case 1.

Considering the estimated oil and gas quantities generated through the pyrolysis process, it may be interesting to investigate their **energy content**. For the heating values the following ranges may be consulted (31):

- 22400 – 28000 kJ kg^{-1} (oil);
- 12000 – 20000 kJ m^{-3} (gas).

Keeping into account the averages of the calorific values (respectively 25200 kJ kg^{-1} for the oil and 16000 kJ m^{-3} for the gas), regarding the oil mass and gas volume present in Table 10, the potential thermal energy content offered by these sources has been estimated to respectively 112,61 MWh and 17,92 MWh, making these products interesting bio-fuels.

However, in this work, particular attentions have been dedicated to the **biomethane** production. Looking at Table 9, it can be read that the yearly biomethane production, in the Case 1, dealing with a very small fraction of the biogas produced, is around 2847 Sm^3. The selling of this amount would represent the main income for the plant from the biogas upgrading process. So as to investigate this possibility, it has been considered the Italian Decreto Ministeriale 2 Marzo, which is the official document to refer to what concern the regulations of the "operating procedures for the issue of the qualification and for the determination and recognition of incentives to biomethane producers and other advanced biofuels other than biomethane" (45). The estimation of the earnings from the biomethane selling is the summation of two parts:

- in the first part, the produced biomethane monthly volume produced multiplied by the average monthly natural gas price (decreased by 5 %). For the purposes of this study, it is assumed a constant monthly production and a constant gas price, referring to June 2018 one, whose value is 22,84 € MWh^{-1} (21,69 MWh^{-1} if decreased by the 5 %). So that, considering the estimated biomethane yearly volume produce in the Case 1 (2847 Sm^3) and its low heating value (37,7 MJ/ Sm^3), the first part of the incentives E_{iy}:

$$E_{iy} = \frac{V_{biom_y} \cdot LHV}{3600} \cdot 21{,}69 \quad \textit{(Eq. 3)}$$

  resulting 646.7 €;

- for the second part, the number of CIC ("Certificati di immissione in consumo") has to be calculated according to the following formula:

$$\# \, CIC = \frac{V_{biom_y} \cdot 0.008111}{5} \quad \textit{(Eq. 4)}$$

and for every CIC (around 5 in this case) the plant is supposed to receive 375 € (in this case 1732 €).

So that, considering these two amounts, the plants would earn around 2379 € every year for the duration of the incentives campaign.

The really limited incomes generated by the biomethane selling are a direct consequence of the extremely small yearly production, which is confined from the restricted biogas treated performed in the Case 1. However, the choice of a small production has been forced in order to maintain a realistic number of sorbent replacements during the year and reasonable reactors design and numbers. Therefore, in these conditions, despite the cost of the feedstock would be practically null, the plant would not be able to repay in a reasonable amount of years all the operating (e.g. sorbent replacements, energy for the activations, general maintenance) and fixed costs to keep in mind (e.g. reactors, oven suitable for the pyrolysis) for the conversion or extension of part of its building area for the biogas upgrading.

3.1.2. Activated carbon

For the Norit RST3 activated carbon, the adsorption capacity was fixed selecting the value which resulted from the experimental activity, while the apparent density has been set according to the producer's specifications. Thus, for this preliminary study, the following values have been adopted:

- carbon dioxide capacity: 387,9 $mg_{CO2}\ g^{-1}{}_{char}$;
- apparent density: 325 $kg\ m^{-3}$.

Because of the lower density value characterizing the chosen activated carbon, the amount of mass loadable in each reactor (whose dimensions and number are the same of the biochar case) will be smaller than the char's one, specifically around 165 kg. On the other hand, the greater carbon dioxide adsorption capacity allows the activated carbon to separate a higher amount of carbon dioxide per reactor, namely approximately 64,2 kg.

Both the scenarios, the one that adopts biochar and the one with activate carbons, deal with the same amount of biogas streams, so the same amount of carbon dioxide to separate: this has been useful to compare the number of yearly replacements the plant should keep in mind with the two different sorbent materials.

During one year of working operation, the results estimated for the two scenarios are summarized in the following table:

Quantity	Case 1 (0.5 m^3 h^{-1} of biogas)	Case 2 (67 m^3 h^{-1} of biogas)
Charge time [h]	185,6	1,4
Yearly CO_2 separated [kg]	3029	404114
Yearly Biomethane production [Nm^3]	2847	379806
Yearly Norit RST3 used [kg]	7809	1041799
# REACTORS YEARLY REPLACED	47	6295
# OPERATIONAL LOADINGS	8	1049

Table 11: comparison of the estimated results related to the Norit RST3 replacements for Case 1 and Case 2.

In the same manner to what has been assessed for the upgrading scenario with the biochar, despite better carbon dioxide adsorption performances exhibited by the Norit RST3, the biogas flow rate selected for the Case 2 has again produced an unrealistic number of filter replacements that the plant would have to carry out. Again, the enormous amount of carbon dioxide to deal with, as a consequence of the high biogas flow rate generated, seems to not be practically managed through the adoption of an even more effecting material represented by a commercial activated carbon. Anyway, making the comparison between the Case 1 results (see Figure 41) obtained with the two materials, having considered the same quantity of carbon dioxide yearly separated from the biogas stream, the higher adsorption capacity of the commercial activated carbon has brought a nearly halved number of operating loadings regard to the use of the sewage sludges-based sorbent (see Figure 41).

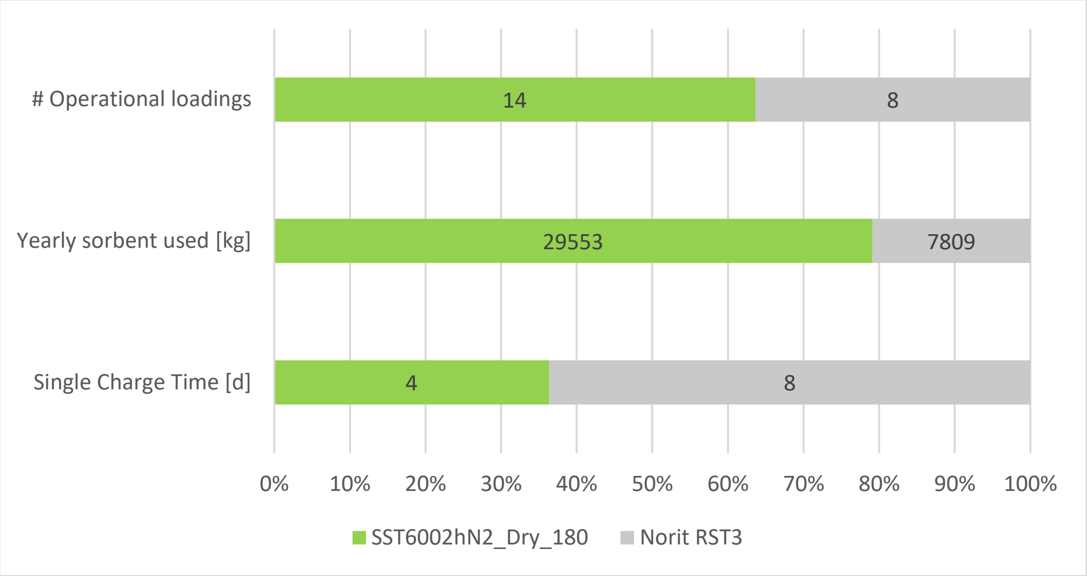

Figure 43: comparison of the operating quantities related to the different materials employed for the Case 1.

Anyway, also in this scenario, having fixed the same biogas flow rate, the issue of the small biomethane production subsists. The earnings that the plant would gain from the biomethane selling would be the same of the ones computed in the previous paragraph. Moreover, the adoption of activated carbons brings some additional expenditure that were not accounted in the biochar cases, like the costs related to the feedstock, to the exhausts disposal etc. Making very brief economic considerations on these fixed costs, considering:

- Activated carbon cost: 6,50 € kg^{-1};
- Activated carbon transportation: 150 € for each one;
- Activated carbon disposal: 0,710 € kg^{-1};

and considering the yearly activated carbon mass employed and operational loadings (see Table 10), the fixed costs estimations would be:

- Yearly activated carbon cost: 50.758 €;
- Yearly activated carbon transportation: 1.200 € (assuming a number of transportations equal to the number of yearly operational loadings);
- Yearly activated carbon disposal: 5.544 €.

Summing only these yearly fixed expenditure estimations, the resulting cost would be around 57.502 €, much higher than the possible incomes obtainable from the biomethane selling.

4. Conclusions

This study has highlighted the potential offered utilizing sewage sludges as precursor material for the adsorbents production; indeed, promising results have been obtained making use of the sewage sludge-based adsorbents for the carbon dioxide adsorption in a simulated biogas stream. It has been demonstrated how the pyrolysis process represents an effective way to valorize a waste into a feedstock in the production of activated carbons. Thus, during the experimental activity, considerable efforts have been dedicated to the optimization of the parameters which rules this thermal process, so as to discover the most suitable conditions to generate the best biochar adsorbent material.

The physical activation is the route followed to develop the textural characteristics of the starting material, analyzing the effects produced by the variation of the temperature (200 ÷ 600 °C), residence time (1 ÷ 2 h), activating agent (nitrogen, carbon dioxide, air), heating rate (10 ÷ 20 °C min^{-1}), flow rate (300 – 500 Nml min^{-1}) and activation method (pyrolysis, direct carbonization and activation) on the char yield and carbon dioxide adsorption capacity.

Among these parameters, the temperature is the prevalent factor influencing the weight loss during the thermal process; it has been confirmed that, with different extents, the temperature increase is followed by a char yield decrease (with a variable slope). Switching the dwell time from one to two hours has also produced the same effect, even if in smaller degree regard to the temperature variation.

The structural characteristics development of the raw material during the thermal activations has been confirmed by the enhancement of the porosity structure, witnessed, for example, by the increase of the total volume of the pores and BET surface area. Anyway, the values obtained are far from the ones characterizing commercial activated carbons. Indeed, the adsorption isotherm curve for nitrogen evaluated for one of the best samples is of II Type, which, according to the IUPAC classification, is distinctive of the macroporous or nonporous solid adsorbents. An important factor which may have positively influenced the carbon dioxide adsorption is the increase of the metal concentration during the physical activations, changing the biochar to a basic nature, especially at temperatures higher than 500 °C.

The water presence is another aspect which has been discovered to determine the adsorption capacity of the biochar samples produced; it has been highlighted how the water content removal has been favorable to obtain better filtering performances.

At the end of the experimental campaign, the sample SST6002hN$_2$_Dry_180 has demonstrated the best carbon dioxide adsorption capacity (102,5 mg$_{CO_2}$ g$^{-1}_{sorb}$), showing that the best activation conditions tested have been the following:

- Temperature: 600 °C;
- Residence time: 2 hours;
- Heating rate: 10 °C min-^{1};
- Flow rate: 300 Nml min^{-1};
- Activation method: pyrolysis (only nitrogen used);
- Drying temperature: 170 – 180 °C.

The carbon dioxide removal attitude of the sample SST6002hN$_2$_Dry_180 has been compared with other materials: ashes (another waste material) and the activated carbon Norit RST3 (a commercial material). The commercial activated carbon has shown an adsorption capacity almost four times higher than the best biochar activated during the experimental activity (the SST6002hN$_2$_Dry_180), which anyway performed better than the ashes.

The results obtained in a laboratory scale, related to the best biochar obtained and the commercial activated carbon, have been scaled up while performing a preliminary study, analyzing the application of the biogas upgrading through adsorption at plant scale. From the estimations obtained, both the materials resulted to not be suitable for this purpose. Indeed, in order to have a realistic number of yearly replacements of the reactors containing the sorbents, only a small quantity of biogas stream produced by the plant could be effectively treated. However, the main consequence was the production of a tiny amount of biomethane, not sufficient to justify economically the investments necessary to convert part of the plant for the biogas upgrading. Therefore, the enormous amount of carbon dioxide to yearly manage at plant scale makes, in general, the adsorption an inappropriate method for the biogas upgrading, since the same issues occurred also for a commercial material.

Anyway, the promising results obtained during the experimental activity suggest how the sewage sludges may represent an interesting and valuable cheap feedstock to fabricate activated carbons; indeed, further studies could be performed to investigate for example:

- the adoption of these materials in applications where the carbon dioxide is present in smaller concentrations, so as to find more suitable contexts which allow to exploit in a more effective way the potentialities of this material;

- the possibility to produce higher quality sewage sludge-based sorbents through chemical activations, analyzing if the supplementary cost of the chemical agents is worthing on the buying of commercial activated carbons.

The pyrolysis could be considered an encouraging alternative to deal with the urgent issue represented by the sewage sludge disposal; among the various advantages which this treatment could bring, the possibility to recover the other by-products as bio-fuels is another interesting topic to dedicate further searches. Indeed, as demonstrated by the estimations performed in the scale up section, the potential energy content of these sources is not negligible. The necessary treatments and upgrading to carry out to these products would allow their utilization for CHP applications (oil and gas), for duty truck engine in the transport sector (oil) (44), etc.

Finally, another important issue to consider, scarcely taken into account in the literature, is the management of the exhausted adsorbents. It has been shown by other authors (46) that the chars produced from the pyrolysis could be successfully employed as fertilizers; further investigations may be accomplished to illustrate if the carbon dioxide contained in the exhausted biochar may be stored underground without generating detrimental effects to the soil.

Acknowledgements

Firstly, I would like to thank the Professor Massimo Santarelli for the possibility given to me to work on an experimental project, making use of the available resources present in the laboratories of the DENERG.

I would like the express also my gratitude to my supervisor, the Doctor Davide Papurello, for being my main reference in the experimental world through his important help and advices, throughout all the thesis period; moreover, I would like to thank the kind laboratory technician Maurizio Bressan for his precious help in the construction and maintenance of the reactors which have made possible to perform the experimental activity.

Other thanks go to the DISAT for the collaboration which has allowed to analyze the textural characteristics of various samples and to SMAT which has provided the feedstock examined in this work.

Finally, a special gratitude is dedicated to all the dearest people who have truly sustained me during all these years, giving me the essential strength to reach this important goal.

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