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TESI DI LAUREA MAGISTRALE

**Circularity and decarbonization in steel plants: valorization of  
waste streams for bio-char production**

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## **Statement of originality**

I, Samuele Cherubin, hereby declare that the work presented in this dissertation, titled “Circularity and decarbonization in steel plants: valorization of waste streams for bio-char production”, is entirely my original work. I affirm that it has not been fully or partially submitted previously in any other Italian or foreign university for assessment purposes.

I further confirm that the content of this dissertation is the result of my own intellectual endeavours, and I have appropriately cited all sources used. This work does not infringe upon the intellectual property rights of any third party, and its content do not constitute plagiarism.

I understand the consequences of submitting work that is not my own and affirm the honesty and integrity of this academic contribution.

Samuele Cherubin

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# Abstract

Steel plants are large emitters of greenhouse gases due to their high-power demand and the necessity to include a carbon source in the production process, being steel an alloy of Fe and C; therefore, they fall into the hard-to-abate category.

This thesis explores the feasibility and challenges of the substitution of electrical arc furnace (EAF) steel plants fossil coal by employing a carbonaceous material, man-made and renewable called hydrochar, produced exploiting the waste streams with an innovative industrial process called Hydrothermal Carbonization (HTC).

The findings of the study reveal mixed results: hydrochar obtained by wastewater-grown microalgae is too expensive, even adopting more performing heterotrophic mode, whereas the use of food waste and digestate proved more feasible and competitive. The work contributes valuable insight into advancing eco-friendly and economically sustainable alternatives to fossil source of carbon, paving the way for further investigation on the use of this material in the steel industry and beyond.



# 1. Introduction

Climate change is arguably the most critical issue mankind is facing today, driven mostly by the increase presence of carbon dioxide in the atmosphere, which has reached an absolute concentration of 420 ppm as of 2023 and is rising at a growing pace, by more than 2 ppm/y in the last decade. <sup>(1)</sup> <sup>(2)</sup> Curbing its emission across the many human activities is imperative to avoid or attenuate the worst consequences of the higher planet's temperatures.

The steel industry is one of the most important industrial sectors in the world, as well as one of the largest energy and coal consuming industries and therefore, a significant greenhouse gas emissions source. World steel production amounts to 1885 million tons, with the production concentrated in China (54%), India (6.6%), Japan (4.7%), US (4.3%) and Russia (3.8%), while the European Union has a share of 7.2%.<sup>(3)</sup> Its demand is steadily rising and in the last twenty years the production has more than doubled, from 800 to almost 2000 million tons and it's expected to grow even further. Steel production alone is responsible for 7.2% of global GHGs emissions. <sup>(4)</sup> They are largely associated with the use of fossil fuel-based carbon, employed in several forms in the plants. Given the growing concern over climate change and the necessity to reach the net-zero target by 2050 as stated in the Paris Climate Accords, an effort to reduce or eliminate it is required.

There are three ways to produce steel currently: the first route starts from the scraps and involves the electrical arc furnace technology (EAF), in which an electric current produced by electrodes heats the scrap steel and iron and melts them again; the second uses iron ore, blast furnace and basic oxygen furnace (BF/BOF route), while the third starts again from the ore which is reduced by gas prior to the arc furnace.

This thesis will take into consideration the first route, which uses only scrap metals, as the company Danieli S.p.a. has decided to focus its business strategy on this option.



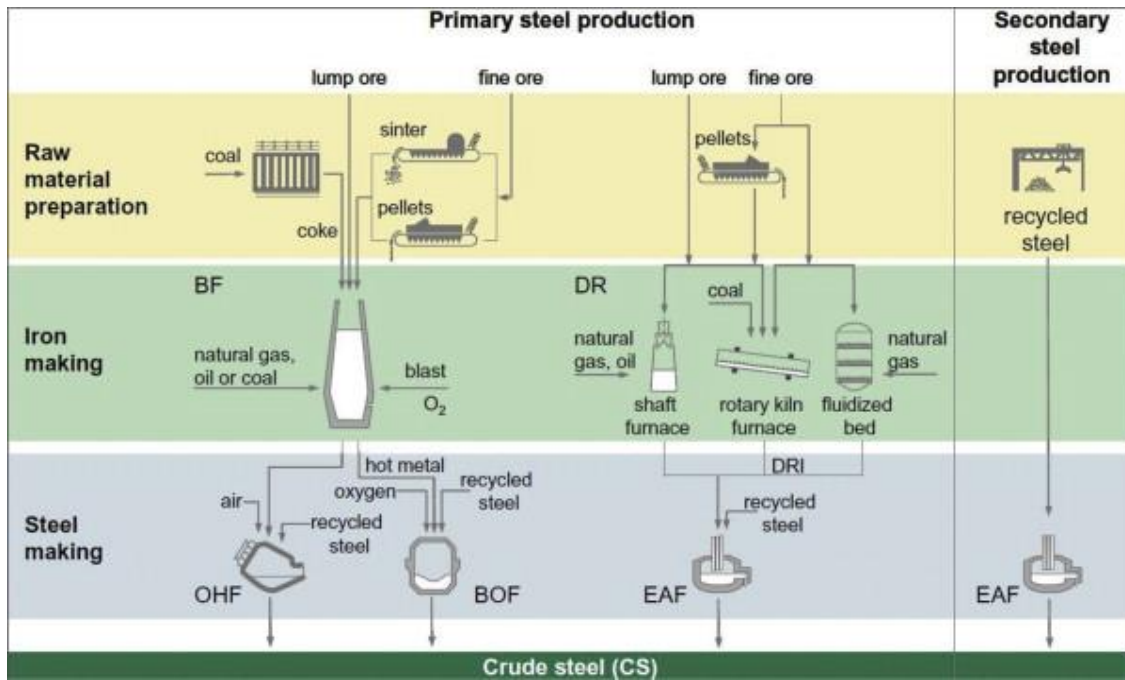


Fig. 1: Main routes for today's steel production.

## 1.1 THE ELECTRIC ARC FURNACE

In 2013, more than 30% of steel produced worldwide comes from the EAF process, <sup>(5)</sup> and projected to grow steadily, although limited by the availability of scrap. The usefulness of this process lies in its capability to manage different types of raw materials, which saves virgin resources and energy. The scrap is melted into liquid steel using energy coming mostly from the electricity through the electrodes and in smaller but significant part from chemical sources like natural gas and coal. Natural gas is simply burned to get heat, whereas coal (anthracite in most cases, a purer and more expensive form of coal) is used for different purposes and at different moments:

- as charge carbon in the EAF
- as pulverized injected carbon in the EAF

In the EAF this carbon sources have the functions of adding chemical energy, controlling the oxidation effect (by avoiding extra loss of iron), facilitating the removal of gases dissolved in steel (like N) by formation of CO in the liquid steel bath, and of

promoting slag formation to minimize the energy losses, according to the main reactions:

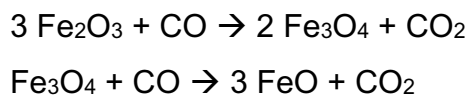
- 1)  $\text{Fe} + \frac{1}{2} \text{O}_2 \rightarrow \text{FeO}$
- 2)  $\text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO}$

Other less frequent reactions involving the reduction of iron are promoted by gases:

- 3)  $\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$
- 4)  $\text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O}$

Most of the oxygen injected in the furnace reacts with the iron of the scrap to form iron oxide. This represents an important loss of iron for the process, so in order to contain these losses carbon is added, and the iron gets reduced back to its elemental form. The latter process is endothermic.

Other forms of ferrous oxides can be present in the scrap: they are reduced by CO or H<sub>2</sub> to arrive in the end in the form of FeO and following thereafter reactions:



These reactions can also take place with pure C instead of CO and producing as byproduct CO instead of CO<sub>2</sub>.

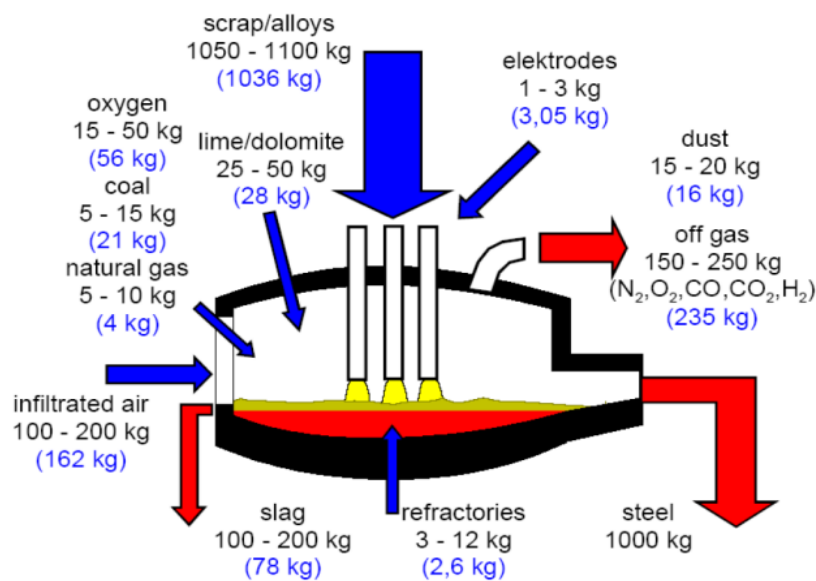


Fig. 2: Mass balance in an EAF. <sup>(6)</sup>

Carbon usage is, ultimately, necessary; and the steel production is therefore classified as a “hard to abate sector” (a category comprising industries where emissions reduction is particularly challenging). This fossil carbon is responsible for approximately 60-70% of the EAF’s direct greenhouse emissions, <sup>(6)</sup> therefore it represents a main target for their reduction from the process.

Biomass-based carbon-enriched material (biocoals or biochars) have the potential to replace fossil carbon, and the use of bio-based material coming from renewable resources enable to reduce the emissions, also avoiding the purchase of CO<sub>2</sub> certificates, which price is only destined to grow. <sup>(7)</sup>

## 1.2 AIM OF THE THESIS

This study has the goal to assess the feasibility of substituting with biochar half of the fossil anthracite used in a medium-sized EAF steel plant, with a yearly output of one million tons of steel. As a reference it was considered the steel plant operated by “ABS – Acciaierie Bertoli Safau S.p.a”, a steelmaking division of Danieli Group, (46°00’33.6” N 13°15’21.4” E), located in the municipality of Pozzuolo del Friuli (UD).

After analyzing and comparing the desirable characteristics of various biomass waste feedstock, the two most promising options have been selected for further study: microalgae grown on wastewater and food waste plus digestate. From their treatment it’s possible to obtain different products, rich in carbon, that may be suited for the employment in this industry.

## 1.3 BIO-BASED COALS

Biocoals or biochars are a broad term used to define any solid carbonaceous fuel obtained by thermochemical treatment of a carbon-rich source, usually wood and other biomass (but also polymers). Based on the treatment used the solid obtained has different characteristics and takes different names, although in the literature many are used interchangeably. These treatments are used to improve the heating values and other properties of raw biomass for various end-uses. Generally, harsher conditions

will lead to more carbon rich solid with superior HHV but at the expense of mass yield in favor of liquid and gas products. <sup>(15)</sup> <sup>(16)</sup>

Possible bio-based coals are presented below.

### *Torrefied*

This char is obtained by heating the wood or other source of biomass at a temperature between 200 and 300 °C in an ambient with little or no oxygen and a residence time generally of 1-3 hours. Also known as mild pyrolysis process, it yields about 70 % of a solid product with the rest being gas. It has good grindability, low moisture, high density and the process requires a dried feedstock as input. Many chemical reactions happen simultaneously or sequentially and most are shared among the thermal treatments: hydrolysis (where molecules are broken down into smaller fragments through the addition of water), decarboxylation (the removal of carboxyl groups – COOH – typically in the form of carbon dioxide), dehydration (removal of a molecule of water from for example an alcohols groups to get alkenes), decarbonylation (the removal of carbonyl groups – C=O – from the organic compounds in the form of CO and a smaller hydrocarbon), demethoxylation (the removal of methoxy groups – OCH<sub>3</sub> – which produces phenolic molecules and methanol), dehydrogenation (the removal of hydrogen atoms with formation of high energy double bonds), cyclization (the formation of valuable aromatic ring from aliphatic compounds), condensation, and many more.

### *Biochar*

Biochar is obtained after a pyrolysis process. It's the thermal decomposition in complete absence of an oxidizing agent (or in such a limited supply that combustion or gasification do not occur significantly). During pyrolysis reaction, conditions are harsher, leading to a more complete carbonization process with loss of additional volatile compounds. Biomass is heated at more elevated temperatures (400 – 700 °C) and produces three kinds of products of which their proportion is strongly dependent on process conditions: biochar (25 – 35 %), tar oil, a liquid fuel rich in organic carbon (20 – 30 %), and a gas phase composed of a mixture of CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub> (25 – 35 %). Cellulose, hemicellulose, and the lignin fraction first undergo dehydration, then, at

higher temperatures, depolymerization and further decomposition into the vapor phase, where also cracking and water-gas shift happen. Depending on reaction temperature, heating rate, reaction time, the process can be further subdivided into slow, fast, flash, and intermediate pyrolysis, but to produce biochar slow pyrolysis is preferred because of higher solid yield, by heating the biomass with longer residence time (hours) at slower heating rate (10 - 30 °C/min). The feedstock used must also have low moisture content (less than 10 %).

### *Hydrochar*

To get this particular biochar the feedstock is treated in a temperature range of 180 – 250 °C immersed in subcritical water and under autogenous pressure (2 – 6 MPa) for a time ranging from 30 minutes to some hours. This process takes the name of hydrothermal carbonization (HTC) and was discovered by F. Bergius in 1913 to describe the natural coalification process. At the beginning of the process, hydrolysis, depolymerization and decarbonylation reactions prevail, and the bond-breaking of the organic matter produce many kinds of acids which further promote the process. For example, the peptide bond linking amino acids contained in the protein hydrolyze at moderate temperature, producing organic acids. At a later stage monomers polymerize and deoxygenize, and through condensation reactions aromatic and complex compounds form. Products obtained are mainly a solid fuel called hydrochar (50 – 70 %), a liquid phase rich in organic carbons, dissolved salts, and heavy metals (15 – 30 %) and a small gaseous phase of mainly CO<sub>2</sub> (2 – 5 %).

This process is sometimes referred to as wet torrefaction in the literature, as opposed to the dry torrefaction used to get torrefied char.

There are other processes that allows a conversion of raw biomass into chars, like gasification, fast pyrolysis, hydrothermal liquefaction, hydrothermal vaporization and more; however, due to the fact that the desired product is often not the solid fuel (but gas or liquid), and that the conversion efficiency is so low, they have been excluded from the range of considered possibilities.

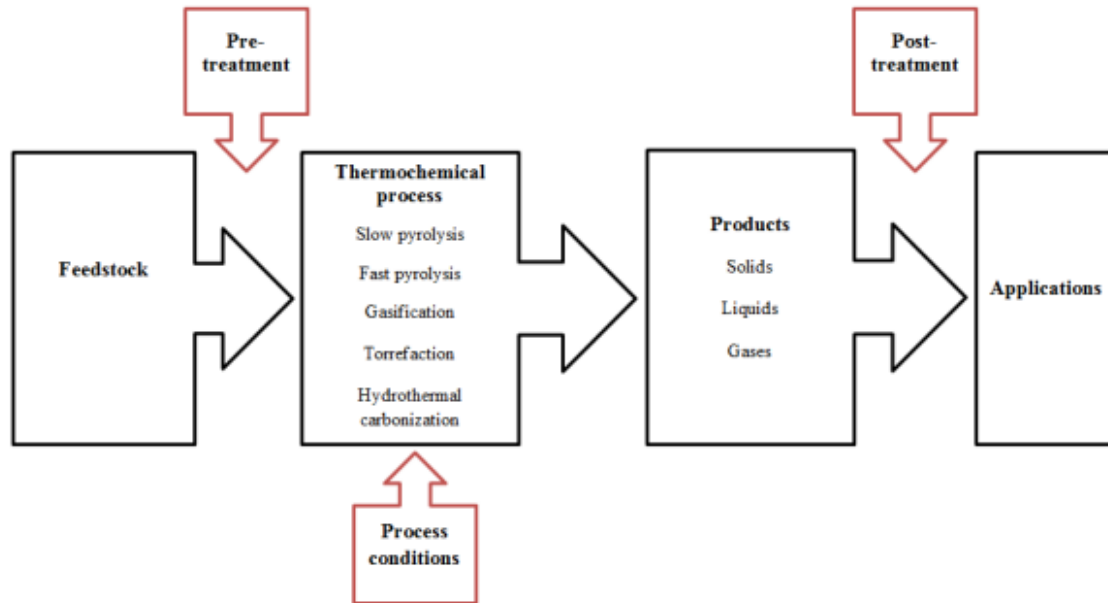


Fig. 3: General scheme of biomass conversion into biofuels.

Many feedstocks are available and suited to use for the conversion in biocoal: wood, green waste, municipal organic waste, agricultural products and leftovers, organic waste from food processing, sewage sludge digestate, microalgae. This work will explore in particular the microalgae from wastewater and the food waste options, given the lower attention received by these feedstocks for the production of char compared to other sources. Selection and requirement of the feedstock will be presented in the result section.

The possibility to transform a waste into a valuable product that can moreover reduce the carbon emission of a hard-to-abate sector represents the quintessence of the circular economy approach. Increasing the overall sustainability of such an important industry is an essential goal to tackle the global warming challenge of our time.

#### 1.4 STATE OF THE ART FOR BIO-CHAR USE IN THE EAF

Using bio-based coal instead of fossil one in the EAF is a quite recent field of interest and, to the author's knowledge, despite growing research and awareness, at the moment several trials have been done but no plant in the world is employing it for industrial operations.

Norgate et al. (2012) showed that charcoal obtained after pyrolysis of eucalypt biomass can replace from 50 to 100% of fossil carbon; <sup>(9)</sup> Fidalgo et al. (2014) compared the properties of two industrially-sources chars, originated from grape seed and pumpkin seed pyrolyzation to those of four coals currently used in EAF steelmaking and found them adequate substitutes. <sup>(10)</sup>

Bianco et al. (2012) carried out trials on different industrial electrical furnaces with carbonized biomass, used as injectable powder or charged in the basket with promising results as they could affirm that no negative influence on product quality is to be expected; however, the handling and the charging of the fine grains presents challenges. <sup>(11)</sup> Demus et al. (2016) used briquette of gasified wood biochar and pyrolyzed agricultural residues and the results showed no negative impact on the slag and steel chemistry with better handling. <sup>(12)</sup> Torrefied and pyrolyzed biomass has been used by Cirilli et al. (2017) with positive evaluation after more than 1500 heats, with recommendation of how to better place the charge carbon in the bucket. <sup>(13)</sup>

Robinson (2020) substituted a third of the charge anthracite with biochar from woody biomass finding no deviation from normal operating conditions in the EAF. <sup>(4)</sup>

A computational fluid dynamics model for combustion and electrode radiation inside an EAF was developed by Cardanelli et al. (2022) and used to analyze the behavior of three pretreated biomass via torrefaction, pyrolysis and hydrothermal carbonization and found that the use of biochars instead of fossil coal did not involve significant negative differences. For all biochars, the combustion reactions were fast and strongly exothermic, with extensive gas generation, especially CO. <sup>(64)</sup>

An important project developed and funded by the European Commission's Research Fund for Coal and Steel, Greeneaf2, was carried out to validate the utilization of chars from biomass as fossil coal substitute with overall positive results and indication on how to best use them in terms of pre-treatment and charging mode. <sup>(65)</sup>

As for the industrial use there is an active project, TORERO (Horizon 2020 Project), coordinated by Arcelor Mittal Belgium, that uses torrefied biomass for injection into the blast furnace. Operations are expected to start in late 2023 or 2024. <sup>(66)</sup>

Not all research achieved satisfactory results: Huang et al. (2019) found the interaction between biochars and slag to be poor compared to other carbonaceous materials, <sup>(67)</sup> and in the Greeneaf project hydrochar was not evaluated because of difficult handling and ignition at low temperature in the lab.

It's possible to reasonably conclude that treated biomass is suited for substituting carbon in electric arc furnace; although the composition of various biochars, result of biomass source and treatment conditions, and the charging modes are crucial and delicate factors that can make the difference in their applicability in this specific task.



## 2. Materials and methods

### 2.1 PRODUCTION OF BIOCHAR USING MICROALGAL BIOMASS AND WASTEWATER

In order to understand the characteristics of the cultivation modes and of the algal specie required it is necessary to first have an approximate idea of the quantity of biomass needed to replace the quantity of anthracite set, or its order of magnitude. Only after is then possible to select and design the most suited processes and to tune them into giving more precise estimations on expected productivity. For this task literature research has been employed.

The estimation was done following the equation:

$$\text{Carbon} = \% C \text{ anthr.} * \frac{1}{2} \text{ anthracite use} \quad (1)$$

equation:

$$\text{Algal biomass} = \text{Carbon} * \frac{1}{\% C \text{ in char}} * \frac{1}{\% \text{ Yield}} \quad (2)$$

and finally, equation:

$$\text{Volume} = \frac{\text{algal biomass}}{P * t} \quad (3)$$

to understand the volume of medium of growth required, given the algal productivity  $P$  and the operative time  $t$  of the plant in a year. The use of wastewater from an urban water treatment plant as medium was evaluated and accounted as an approach to decrease water withdrawal and employing a waste stream as a resource, increasing the sustainability of the process.

## 2.1.1. SCREENING OF PROCESS CONDITIONS

### Screening of most suitable algae species

Different species of algae were evaluated in order to find the most suitable for the project. Given the nature of the project, the two most important characteristics looked for were biomass productivity under optimal conditions and robustness or adaptability to grow on different substrates and conditions, since wastewater composition is likely to change during the year and large quantities of algal biomass are necessary to get a significant amount of biochar. A scientific literature review was performed, employing the most trusted search engines for publications like PubMed, Scopus, Google Scholar.

### Screening of the most suitable cultivation methods

Another literary review has been performed to understand the best method to cultivate the microalgae. The desired parameters for the system were high productivity, ease of scalability, ease of management, low cost, and consistency of operative conditions.

### Analysis of wastewater

The wastewater needed can come from different sources, with the most suitable being the streams coming from industries working with organic materials like breweries, food processing, slaughterhouses, dairy and cheese factories etc.... The source stream should be abundant, as homogenous as possible in its composition during the year, and closely located to the steel plant to avoid transportation burdens.

The closest source of abundant wastewater to ABS steel plant is the water treatment plant of CAFC S.p.a. located in Udine (46°01'37" N, 13°14'06" E), of 120'000 PE (population equivalent) of authorized capacity.



Fig. 4: Location of CAFC wastewater treatment plant (high left) and ABS steel plant (bottom right).

The distance is only 2 kilometers in a straight line, making this facility an ideal source of water with low cost of pumping and pipeline construction.

Following some meetings with plant operators, useful data have been gathered.

Literary research has been subsequently done to find the studies with the most similar growing medium on microalgae cultivation so to understand the removal rate of nutrients and design a system that matches the highest removal rates and productivity of the studies. HTC process water composition was estimated by averaging different studies and industry data. <sup>(69) (70) (91)</sup>

### Screening of downstream and conversion processes

To understand the best downstream process to transform the microalgae biomass present in the wastewater medium a combined approach of literature research, related industry's experts' meetings and other academic and internal company advisors'

opinions was employed. Also, in this section the desired traits of these steps were the low costs, ease of operability, high yield, and quality of the final product. Once all relevant information was collected, the entire process, material flow and equipment necessary could be calculated and designed and precise amount of water requirement by equations (1), (2) and (3) could be better estimated.

### 2.1.2 OPERATIVE COST ANALYSIS

Following the definition of all the processes necessary to obtain bio-coal from wastewater-grown microalgae, an analysis of the operative costs was performed in order to get to a price estimation of the char (€/ton).

The plant and the equipment have been set to work for 333 days per year for the entirety of the 24 hours. Cylindrical reactor size was set at 14 m of radius and height of 10 m for a working volume of 6000 m<sup>3</sup>. Electricity price was set at 0.1 €/kWh and the heating price from exhaust gases of the steel plant at 15 €/MWh.

Variables considered and calculation processes are presented:

#### Pumping:

The speed of the water flow in the tube is given by:

$$v = Q/A \tag{4}$$

Friction factor  $f$  is estimated using Moody's Diagram by intersection of Reynold's number and relative pipe roughness:

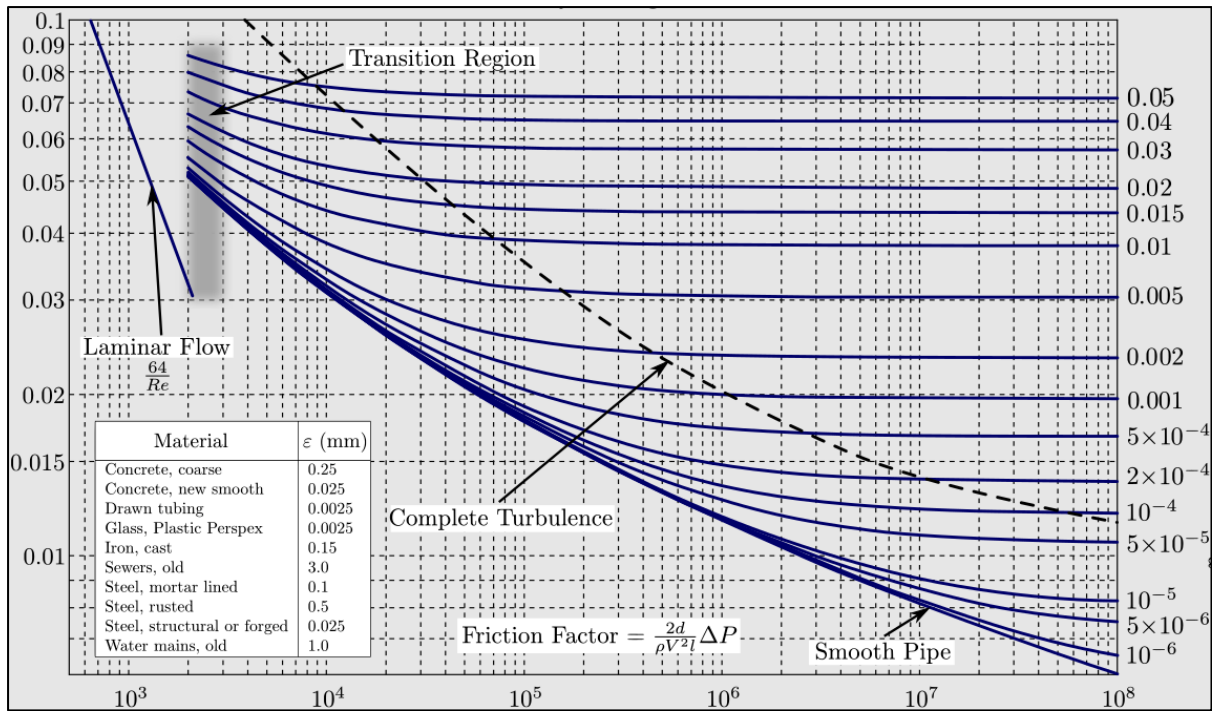


Fig. 5: Moody diagram: left and right axis represent the friction factor and relative pipe roughness; horizontal axis represents the Reynolds number.

Reynolds number is defined as:

$$Re = \frac{\rho * v * d}{\mu} \quad (5)$$

With  $\rho$  being the density of the fluid ( $1000 \text{ kg/m}^3$ ),  $v$  the velocity,  $d$  the diameter of the pipe ( $0.2 \text{ m}$ ) and  $\mu$  the viscosity factor.

By applying the following equation, the relative pipe roughness can be calculated:

$$\epsilon = \frac{\epsilon'}{d} \quad (6)$$

$\epsilon'$  representing the absolute pipe roughness, which in the case of hypothetical PVC pipe equals to  $0.0015 \text{ mm}$ .

Viscosity has been set at  $15 \text{ }^\circ\text{C}$  for a value of  $0.00114 \text{ Pa*s}$  (or  $\text{N*s/m}^2$  or  $\text{kg/m*s}$ ).

Reynolds number and relative roughness coefficient are combined in Fig. 5 to get the friction factor. Friction factor  $f$  is needed to calculate the pressure loss along the length of the pipeline (7):

$$\Delta P = \frac{f * \rho * v^2 * L}{2d} \quad (7)$$

Finally, the power requirement is known:

$$W = \frac{Q * \Delta P}{\eta} \quad (8)$$

With Q being the flowrate and  $\eta$  the efficiency of the pump;  $\eta$  was fixed at 0.75.

This procedure was applied to calculate the power required to move the water from the concentration stage back to the tanks of the cultivation (L = 200 m). The same calculations were used in the case of the pumping coming from the wastewater plant to ABS steel plant, with a length of 2000 meters. All piping routes were assumed perfectly straight.

The previous power requirement calculated was then added to the power required to pump the fluid on top of the cultivation reactors to be filled, which was calculated as:

$$W = \frac{Q * (\rho * g * h)}{\eta} * k \quad (9)$$

This is the minimum value of power to be applied in order for the fluid to reach the top of the reactor, it was therefore increased by 10 % for spilling (k = 1.1). Velocity was set at 4 m/s.

Pumping power to push the fluid from the bottom of the reactors to the concentration stage was not considered, as the pressure from the water column was deemed enough.

### Heating

To calculate the heating requirements of the culture, being the cultivation taking place outdoor, the average temperature for the municipality of ABS location, Pozzuolo del Friuli (UD), was taken from ARPA FVG, standing at 13.6 °C. It's possible then to calculate how many degrees day (DD) of heat need to be supplied to reach the optimal growth temperature for the algae at 42 °C in a year of operation:

$$DD = (42 - av.T) * 333 \quad (10)$$

Subsequently, heat to be supplied to the tanks was supposed to equal their heat loss and so, by calculating the latter, it's possible to know the heat required to maintain the optimal temperature.

Heat expressed in MWh equals to:

$$Q = \frac{DD * A * U * n * 24}{1000000} \quad (11)$$

$A$  being the area of the tank,  $U$  the heat transfer coefficient and  $n$  the number of tanks. The heat transfer coefficient changes based on the material, the conditions, and the fluid involved. For a concrete tank in contact with water and air it was set at  $4.5 \text{ W/m}^2\text{K}$  and it holds valid for the lateral surface of the tank, whereas the superior base where water is in contact directly with air the  $U$  value has been set at  $15 \text{ W/m}^2\text{K}$ . The inferior base in contact with the ground has been considered perfectly insulated. The total  $Q$  needed is therefore the sum of the  $Q$  dissipated from the concrete lateral surface and the superior face in contact with air.

Autogenous heat generated from cell respiration has not been taken into consideration given the scarce literature found for a meaningful analysis.

### Aeration and mixing

Regarding the aeration the literature report a significant variation of tested conditions, ranging from no aeration up to 3 VVM (volume of air insufflated for volume of the vessel per minute), with an optimum generally between 0.5 and 1.5 <sup>(86) (87) (88) (89) (90) (17) (Table1)</sup>. Given the very large energy requirement for the air blower and the scale of the cultivation, the parameters chosen have great influence over the final results, therefore particular attention is placed, and three scenarios of low aeration requirements are presented.

Scenario 1: VVM set at 0.17 (volume of air / volume of vessel per minute). Power is calculated using the formula for a compressor:

$$Power (kW) = mass\ flow\ rate \left( \frac{kg}{s} \right) * work \left( \frac{kJ}{kg} \right) \quad (12)$$

Isentropic compression work is got by:

$$Work = \frac{1}{\eta} * \left( \frac{k}{k-1} \right) * R * T * (P\ ratio^{\left( \frac{k}{k-1} \right)} - 1) / 1000 \quad (13)$$

$K$  being 1.4 (for air),  $R$  287.1 J/(kg\*k),  $T$  the temperature of air inlet, the  $P$  ratio necessary to overcome the water column 2.1 atm (pressure outlet / pressure inlet), and  $\eta$  0.8.

Scenario 2: keeping the same VVM and given the similarities between the microalgae cultivation system and the aerobic stage of a wastewater treatment process, power consumption has been gathered from the industry's data, scaled proportionately, and assumed continuous operation. Geometry of reactors was modified to equate the tank of the wastewater plant, which has a water head of 4,5 m.

Scenario 3: VVM aeration requirement (0.027) was taken from the wastewater treatment plant and power consumption was calculated as (12).

The mixing power need has also been gathered from wastewater plant aerobic tank equipment and scaled. The goal of the mixers is to increase the uniformity of the solution since aeration and some agitations are already provided by the blowers. Indeed, motionless, or inadequately mixed zones of the tank volume are possible to form. For this task propeller-type mixers have been chosen.

### Concentration and conversion

In the concentration stage electricity consumption has been calculated from the power requirement given by industry's experts. Chemical substances needed are also taken into consideration. The conversion method operative costs (identified in the hydrothermal carbonization process) have also been gathered by meeting with



industry's representatives and by adapting consumption values from Lucian et al. (2017), by eliminating the grinding stage, which accounts for 71.7 KW of power. <sup>(102)</sup>

### Labor

The employees' number were estimated based on academic and industry expert's opinion and identified in five for the cultivation and concentration stages and with an assumed medium salary cost for a company of 50'000 euros each; this expense has been aggregated at the cultivation phase in the calculations. All processes were supposed to be highly automated. Expenses for personnel of the conversion stage was given by the industry and included in the general conversion process.

#### 2.1.3 COMPETITIVENESS POINT

Price of anthracite plus carbon emission certificates (ETS) was compared to hydrochar price found in the three scenarios.

To do so, a conversion factor between anthracite and hydrochar based on the carbon content was established. Since anthracite contains more carbon than the char, more of the latter is necessary to achieve the same result in the steel plant. Acknowledged from company's data that percentage of C is 92 %, conversion factor is given by:

$$F = \frac{\% C \text{ anthracite}}{\% C \text{ hydrochar}} \quad (14)$$

By multiplying  $F$  by the cost of char production and dividing by its quantity obtained the substitution price of one ton of anthracite is given (thereafter known as anthracite equivalent).

Heat to be supplied to the microalgae tanks was assumed coming from the waste heat of the steel factory and valorized a 15 €/MWh. Electricity was assumed to come entirely from the Italian grid, with its relative price of 0,10 €/kWh.

After that it was calculated the price of a hypothetical carbon credit necessary for the

hydrochar to be competitive with the anthracite (these carbon credits are, as already mentioned, an extra cost incurred by whoever burns fossil fuels).

This hypothetical carbon credit was called ETS\* and defined in €/ton<sub>CO2</sub> by using the following formula:

$$ETS^* \text{ price} = \frac{A \text{ eq. Cost} - AC}{t_{CO_2}/t_A} \quad (15)$$

with *A eq. Cost* being the cost per ton of anthracite equivalent, *AC* the cost per ton of anthracite, *t<sub>CO2</sub>/t<sub>A</sub>* the quantity of carbon dioxide in tons emitted by the use of one ton of anthracite.

## 2.2. PRODUCTION OF BIOCHAR USING FOOD WASTE AND SEWAGE SLUDGE DIGESTATE

After evaluation of microalgal system results, an alternative feedstock option system based on a co-treatment of food waste and sewage sludge digestate has been given with related flowchart and operative cost analysis. The digestate is the solid byproduct of the anaerobic digestion for biogas production of the sludge coming from the wastewater treatment settling, whereas food waste represents the municipal organic fraction except for the green fraction. Given the quite large availability of this product, its location at a very short distance from the steel plant and the high revenue potential from its intake, its co-treatment by hydrothermal carbonization (co-HTC) with food waste was considered. This means that these two products are mixed and grinded together before entering the reactor vessel. Data and information for this alternative have again been gathered by industry's experts and scientific literature research.

From CAFC plant data the composition of their dewatered digestate is as follow (on dry biomass, or d.b.):

C: 25 % - N: 3 % - P: 1,8 %, and the humidity on wet biomass (w.b.) is 75 %.

Food waste composition was taken from Zheng et al. (2019), <sup>(112)</sup> from a paper where the authors co-treat mixtures of sewage sludge and food waste at different proportions and analyzed the resulting hydrochar, a quite similar situation of the present study. It's worth noticing that food waste composition varies in every study and in site sampling is necessary to reach more accurate values. In any case ultimate analysis chemical composition are quite similar in most of the studies. <sup>(108) (109) (110) (111) (124) (123) (130)</sup>

(On dry biomass) C: 49,6 % - H: 7,5 % - O: 33,5 % - N: 3,2 % - Fixed carbon: 12,6 % - Volatile matter: 81,3 % - Ash: 6,1 %, and the humidity on wet biomass is 55 %.

Exact data for hydrochar characteristics deriving from the co-HTC of these two waste sources at the required proportions to get the desired quantity of char do not exist and therefore only estimations are achievable. To get the most accurate result possible two methods has been employed to make predictions and then confronted and averaged.

### 2.2.1. FIRST METHOD

The first method used consists in the employment of a machine learning software developed by Djandja et al. (2022) <sup>(113)</sup> and accessible at <https://strategefil-cohtc-cohtc-fuel-n2lxgw.streamlit.app/>. The software requires to insert properties of sewage sludge and biomass (C, H, N, O, VM, FC, ash) and the operative condition under which the reaction takes place. By evaluating the inputs and confronting them with the database built by the researchers by analysis of many studies, the software then returns the expected char characteristics.

In a typical biomass composition, two relations must always be true:

- $C + H + N + O + \text{Ash} = 100$  (16)

- $\text{VM} + \text{FC} + \text{Ash} = 100$  (17)

Unfortunately, not all of these values were present in the analysis provided by CAFC, so they have been integrated using again the study of Zheng et al.

To satisfy both the equation (16) and (17), as required by the software, ash content was increased by 7 % and VM decreased by 7 %.

To summarize, the parameters used in the software are tabled:

%	Digestate	Food waste
C	25	49.6
H	4.7	7.5
N	3	3.2
O	18.5	33.5
VM	46.6	81.3
FC	5.1	12.6
Ash	48.2	6.1

Table 1: Input used in the online software developed by Djandja et al. <sup>(113)</sup>

Conditions set were: temperature 230 °C, reaction time 60 min, digestate/mixture ratio 5,8 %, solid loading 15 %.

Software outputs for many elements are given in their atomic ratio versus the carbon content (to easily interpret them in a Van Krevelen diagram), therefore, atomic ratios have been converted in weight percentage by:

$$\% X = \frac{\text{ratio} * \text{atomic mass } X}{\text{atomic mass } C} * \% C \quad (18)$$

And ash content has been estimated using equation (16).

### 2.2.2. SECOND METHOD

The same reaction conditions (temperature 230 °C, reaction time 60 min, digestate/mixture ratio 5,8 %, solid loading 15 %) were used for a regression analysis computed separately for all variables considered (content of C, H, O, N, S, FC, VM, Ash, HHV, mass yield) using data from Zheng et al. <sup>(112)</sup>

SS	FW	C (%)	H (%)	O (%)	N (%)	S (%)	FC (%)	VM (%)	Ash (%)	HHV (MJ/kg)	Yield (%)
0	100	68.6	7.3	14.8	3.4	0	25.7	68.4	6	30.8	0.43
100	0	22.7	3.2	6.1	1.8	0.3	4.9	26.4	68.1	9.8	0.59
70	30	31.9	4	8.8	2.3	0.2	9.6	37.6	52.7	13.8	0.52
50	50	42.2	5	10.3	2.66	0.2	15	45.4	39.7	18.7	0.5
30	70	51.3	5.8	12.1	3.1	0.1	19	53.4	27.6	22.9	0.47

Table 2: Data of hydrochar properties by different mixture ratio and raw feedstocks reported by Zheng.

An additional mixture option is added to this table (5.8 % SS and 94.2 % FW) and the resulting char characteristics reported.

Adjusted  $R^2$  values were considered for determining the accuracy of the results.

Subsequently the estimation done using the two methods described above, it was also considered the effects of the recirculation of the carbon-rich process water back into the reactor. To do so, relevant literature has been analyzed and the characteristics of the char modified according to the findings, and eventually adjusted to keep relations (16) and (17) valid. After that it was possible to gather enough information to deliver the best approximation regarding the hydrochar properties.

### 2.2.3. COST ANALYSIS

Downstream stages for the char, the process water and other byproduct after the HTC reactions have been designed and modelled following industry's data and guidelines, as well as the operative costs and consumption incurred by such a system. Heat was assumed coming from exhaust gases from the steel plant with a cost of 15 €/MWh. Contrary to the microalgal process, the grinding stage has been included, and the energy consumption estimated again by Lucian et al. (2017). Unitary cost of one ton of hydrochar has been derived by the total expenses and revenues and related to an equivalent anthracite ton using the conversion factor  $F$  (14). Earning from the disposal of digestate from the wastewater plant was set at 65 €/ton and the same from food waste at 65 €/ton.

Additionally, to understand the difference in terms of energy that may arise in the furnace by employing hydrochar, a comparison with the energy content of the two fuel was done.

Higher heating value (HHV) of anthracite was calculated using:

$$HHV = 0.349C + 1.178H + 0.1S - 0.1O - 0.015N - 0.021 Ash \quad (19)$$

The energy difference between charging the furnace with fossil coal and char (per ton of liquid steel) was instead calculated with (20):

$$\Delta = HHVa * kg - HHVeq * kg \quad (20)$$

HHVa being the higher heating value of anthracite and HHV eq the value of an equivalent quantity of char injected to replace the same quantity of carbon atoms of the anthracite.

## 3. Results

This study wants to examine two different ways of producing solid biofuel for its use in a steelmaking electric arc furnace instead of the fossil coal employed today. The first way is by cultivating highly-productive microalgae on organic-rich wastewater and then converting them into a hydrochar. The second way involves other suited waste streams, identified as food waste and sewage sludge digestate, converted into a solid char too. Equipment necessary, energy usage, carbon savings and operative economic calculations were assessed and evaluated in order to produce enough biocoal to substitute half of the anthracite demand for a million ton of steel output plant.

### 3.1. FEEDSTOCK REQUIREMENTS

The sources of waste organic material from which to produce char with are vast and diverse. A table summarizing identified criticalities and advantages of possible waste materials is given below, along with definitions of the parameters.

	Char Quality	Seasonality	Consistency	Collection density	Revenue
Agricultural leftovers	HIGH	HIGH	MEDIUM	LOW	NO
Sewage sludge	LOW	LOW	HIGH	HIGH	YES
Food waste	HIGH	LOW	HIGH	HIGH	YES
Garden waste	HIGH	HIGH	HIGH	HIGH	YES
WW Microalgae	HIGH	LOW	HIGH	HIGH	NO*

*Table 3: Characteristics of various waste feedstock with desirable traits highlighted.*

Char quality: the feedstock produces a biochar of good quality, with low impurities and high carbon content.

Seasonality: the feedstock is affected by the time of the year, and its availability inconstant.

Consistency: the feedstock source is constant in its elemental composition in time.

Collection density: it indicates the density of the material at the collection point or, in other words, the quantity of waste available in a single or few locations., allowing efficient collection and transportation.

Revenue: it suggests if the waste source has the potential to generate revenue from its disposal. Microalgae can generate revenue from wastewater treatment; however, at the moment it's not employed at a large scale and it's unclear whether it can be achieved with a single algal treatment or as part of a multi-step strategy. Moreover, as by request of the company, a high degree of recycling of the elements and materials employed in the overall process is desirable, thus reducing the primary wastewater intake and therefore the compensation. So, for the purpose of this study, revenues from microalgae has not been considered.

From the table it appears that the most suited feedstocks are microalgae and food waste, as they check positively all the most important boxes (revenues cannot be declared as a critical factor at this point).

Wood biomass have not been considered despite being an ideal and obvious candidate for the conversion in biochar given its high carbon content. The reasons are multiple:

- Thermochemical-converted wood has been already extensively researched and analyzed. <sup>(96)</sup> <sup>(97)</sup> <sup>(98)</sup>
- It cannot be considered a waste stream. Woody waste do exist, like pruning or sawdust from mills, but its availability is too seasonal, scattered and dispersed over large territories for any meaningful use in high quantity. Large industrial use of wood in fact, comes from trees plantation.
- It raises concern over the sustainability of the practice, especially if adopted on a wide scale. Forest biomass use is at an all-time-high and growing steadily, with supply competition heating up. <sup>(99)</sup> For the EAF size considered and by using torrefaction, assuming 70 % of carbon content in char and 60 % yield,



around 20 thousand tons of wood biomass is needed. The European Forest Institute states that it takes 0.045 hectares of land to grow 1 cubic meter of harvested wood in a year, in particular poplar in the Po Valley (which, according to the European Panel Federation, has a density of 400 – 480 kg/m<sup>3</sup>).<sup>(93) (94) (95)</sup> It's worth noticing that this is the lowest value of the trees considered, and by a wide margin (in other words it's a very productive species). By applying a simple equation it's possible to estimate the area needed yearly to collect the desired wood:

$$A = 0.045 * B * d$$

With *B* being biomass request (20 thousand tons) and *d* the density. The area needed would be of 2'045 ha, or 20.54 km<sup>2</sup>, a significant land requirement.

### 3.2. MICROALGAE AND WASTEWATER OPTION

Microalgae are a wide range of organisms that has attracted the attention of many research and industries due to their ability to produce valuable chemicals and to provide ecosystem services. They have high surface area-to-volume ratios, enabling rapid uptake of nutrients and metabolites and a much faster growth rate than land-based plants.<sup>(100)</sup>

Extensive trials were conducted in the 90's and early 2000's for mass algae cultivation with the purpose of producing biodiesel from the lipids stored in the cells, but high costs and technical difficulties have prevented the adoption of this route and many companies have switched to more high-value niche products like pigments, food supplements and other useful molecules.

Given their aquatic-based life environment, water supply for their growth is necessary. This supply can be a wastewater coming from human activities, coupling a waste stream with valuable final products while at the same time removing excess nutrients, enhancing the circularity of the system.<sup>(101)</sup>

Treating wastewater with microalgae allows for a reduction of substances harmful for the environment, such as nitrogen and phosphate (responsible of eutrophication of rivers, lakes, and coastal areas), organic molecules and heavy metals.

The resulting biomass, after the harvesting and conversion process, could be used as solid bio-coal (char) in the furnace.

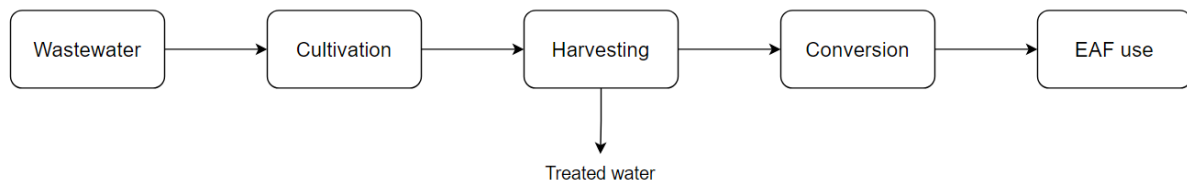


Fig. 6: Summary of process flow.

### 3.2.1. ESTIMATION OF BIOMASS NEEDED

According to ABS internal data, average anthracite consumption stands at 18 kg per ton of liquid steel produced. Anthracite is a high-grade carbon-based fuel, with carbon content of 92% as used by the company's electric furnaces. Therefore, in a medium-sized steel plant of a million ton of output the coal demand equal to 18'000 tons, for a carbon content of 16'560 tons. Half of it amounts to 8'280 tons.

The latter is the actual amount of carbon to be substituted with a low-emission and renewable source, as the remaining part comprises mainly ashes, moisture and small quantities of heavy metals and elements like nitrogen and phosphorus, for a predicted yearly saving of carbon dioxide emissions of 30'388 tons.

Amount of carbon present in a biochar depends vastly in relation to the conversion process considered, to its conditions (mainly temperature and residence time), and to the feedstock employed. It can range between 50% up to 80-90% adopting more extreme values, which in turns amounts to a biochar supply between 9'200 and 16'560 tons every year.

Based on the process of conversion moreover, different mass yield of solid biofuel will be obtained; more extreme conditions will lead to lower mass yield but higher carbon content, and vice-versa, going from 30% to 70% or more for milder conditions. <sup>(77)</sup> <sup>(79)</sup>

(80)

Microalgae dry biomass required is thus finally estimated to be between 17'000 and 30'000 tons.

To put this number in perspective, consider that the world's production of microalgae stands at 56'000 tons annually according to FAO (2019), mainly in China, with Europe producing around 500 ton. <sup>(14)</sup>

### 3.2.2. SCREENING OF PROCESS CONDITIONS

#### 3.2.2.1. METHODS OF CULTIVATION

Microalgae species can be divided in two main branches based on their metabolism: autotrophic and heterotrophic, with some species belonging to both.

Autotrophic cultivation currently accounts for more than 80% of world's microalgae production, mainly using the open pond system <sup>(17)</sup>. Other more advanced system involves the use of photobioreactors (PBR), that allows more precise variables control and higher productivity, but at higher costs. In this mode the organisms use light and CO<sub>2</sub> for their growth, with oxygen as a waste, effectively resembling a plant physiology. Heterotrophic cultivation on the other hand exploits the ability of some microalgae to uptake organic carbon sources plus oxygen to build their cell components without the need for sunlight and with CO<sub>2</sub> as a byproduct, resembling in this case the animal respiration process. This system allows a much higher growth rate and cell density with good system control, and lower risk of microbial contamination, but high nutrient inputs are required, which must be produced. <sup>(18) (19)</sup>

Mixotrophy mode is employed by some algae and it's a strategy to take advantage of different environmental conditions with performances usually between the two.

Cultivation type	Energy source	Carbon source	Metabolism
Autotroph	Light	Inorganic	$H_2O + HCO_3^- \rightarrow C(\text{biomass}) + 1/2O_2 + 3OH^-$ : pH increase
Heterotroph	Organic	Organic	$(1+a)CH_2O + O_2 \rightarrow C(\text{biomass}) + aCO_2 + (1+a)H_2O$ : pH decrease
Mixotroph	Light and organic	Inorganic and organic	$bHCO_3 + cCH_2O \rightarrow (b+(c-a))C(\text{biomass}) + 3OH^- + aCO_2$ : pH changes are inconsistent

Fig. 7: Different metabolism by microalgae. <sup>(20)</sup>

	Autotrophic Cultures	Heterotrophic Cultures
Advantages	<ul style="list-style-type: none"> <li>• CO<sub>2</sub> fixation ⇒ GHG mitigation</li> <li>• Efficient N and P removal</li> </ul>	<ul style="list-style-type: none"> <li>• Non-dependence of light and season</li> <li>• Efficient organic carbon removal</li> <li>• Simpler and cheaper conventional bioreactors than photobioreactors</li> <li>• High cell-density cultures ⇒ high intracellular product productivities</li> </ul>
Drawbacks	<ul style="list-style-type: none"> <li>• Light and season dependence</li> <li>• Low cell-density cultures due to light shadow</li> <li>• Photobioreactors are expensive and difficult to scale-up</li> </ul>	<ul style="list-style-type: none"> <li>• CO<sub>2</sub> emission</li> <li>• High contamination risk by other heterotrophic microorganisms</li> <li>• Sterilization requirement is an expensive energetic step</li> </ul>

Fig. 8: Features of different cultivation metabolisms. <sup>(21)</sup>

Cell densities of over 100 g/L have been reported for heterotrophic mode in the literature, whereas maximum values for autotrophic in PBR is around 5 g/L and in open pond usually values are lower than 0.5 g/L. This not only increases the equipment required to reach high biomass production, but also the energy and cost of the next harvesting step, which is correlated with cell concentration. <sup>(21)</sup>

Morillas-Espana (2021) have evaluated the productivity of the algae *Scenedesmus sp.* in raceway ponds placed inside a greenhouse in the south of Spain for a year and measured an average of 20 g/m<sup>2</sup>day, which equals to 56 ton of dry biomass per hectare. <sup>(22)</sup> To get to 17 kton and 30 kton calculated before, the area necessary would be between 300 and 535 hectares. However, more realistic numbers are reported by Lee (2001) <sup>(92)</sup>: in a well-managed pond 20 – 25 g/m<sup>2</sup>day are possible for short periods, while long-term productivity in large commercial facilities rarely exceeds 12 – 13 g/m<sup>2</sup>d (ca 35 ton/ha). More realistic estimates therefore put the area required in the range of 480 – 850 hectares (4.8 – 8.5 square kilometers). According to Fernandez (2020) there are not facilities larger than 100 ha currently in the world, <sup>(23)</sup> and less than 20 with area between 50 and 100 ha.

This huge land requirements and related equipment poses serious doubt about the feasibility and sustainability of any hypothetical plant, and so it has been discarded.

PBRs on the other hand requires less land, but the complexity of operations and cost increases, and they are mainly used to produce high or medium-value biomass, whereas biocoal is a low-value commodity.

As a general rule, and in most cases, heterotrophic cultivation is far cheaper, simpler to construct, and easier to maintain on a large scale. This capacity allows for expansion of useful applications that is now limited as a result of elevated cost of autotrophy; so that today's exploitation of microalgae is restricted to small volume of high-value product. <sup>(24)</sup> <sup>(27)</sup>

Since the requirements for a microalgae-based biocoal in EAF steel plant are broadly:

- High productivity
- Low cost
- Ease of operation
- Regularity of production

placing the desired product at the base of the typical value pyramid, the heterotrophic route looks the only possible one.

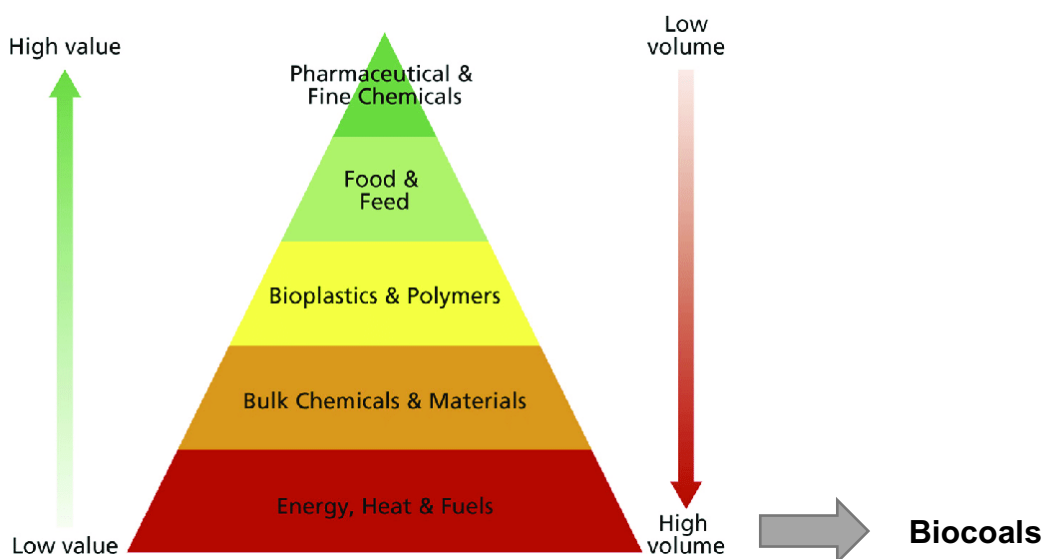


Fig. 9: Bio-based products value pyramid. <sup>(24)</sup>

Heterotrophic mode is not, however, without problems. One of the main costs in heterotrophic production is the carbon source; glucose, the most utilized, can account for up to 60 % of the overall production cost, <sup>(26)</sup> with an intake efficiency of about 50 %, or optimizing the feeding strategy, 60 %. <sup>(27)</sup> <sup>(23)</sup>

The intake efficiency measures the amount of biomass produced given a unit of nutrient input: an efficiency of 50 % mean that for every 2 g of glucose added microalgae biomass grows of 1 g.

Given that the price for glucose is around 450 €/ton, <sup>(28)</sup> the cost of dried algae biomass starts at 900 €/ton accounting only for feedstock supply.

Moreover, currently glucose is produced from food crops such as corn and this has sparked the old “food vs fuel” debate. <sup>(39)</sup> <sup>(40)</sup> That is why much research have

suggested to replace it with other organic-carbon sources, coming from a waste stream, with the double advantage to decrease cost and transforming a waste material in valuable product. Among the waste streams as algal feedstock, glycerol has received some attention <sup>(32)</sup> <sup>(33)</sup>: it's a waste product of the bio-diesel production via transesterification reaction; for every 10 kg of biodiesel, it is produced also 1 kg of glycerol. The sole Italian production of glycerol stands in 2017 at 70'000 tons, <sup>(30)</sup> and according to the brokerage firm Greenea <sup>(30)</sup> the EU waste-based glycerin market is estimated at 258 thousand tons and increasing. Today it is mainly incinerated, used for cattle feed or biogas generation. However attractive it may appear; it suffers from some of the same drawbacks of glucose: price and intake efficiency (50 %).

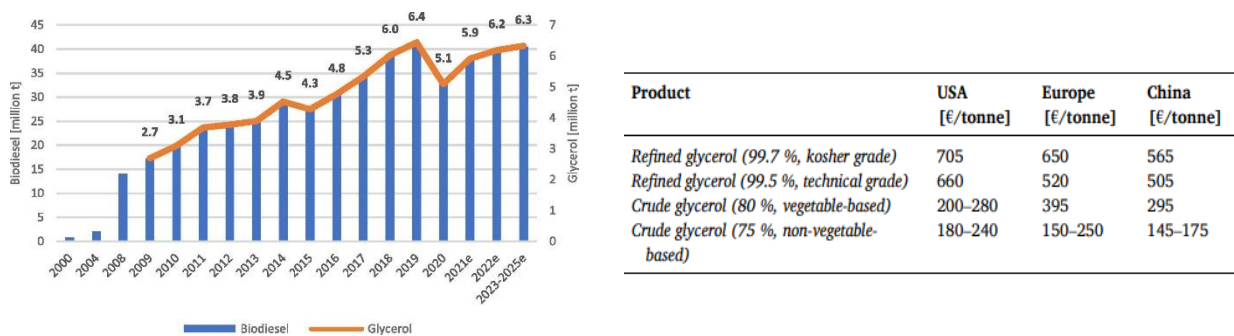


Fig. 10, 11: Trend of production and prices of biodiesel and glycerol. <sup>(31)</sup>

Moreover, the future supply of waste glycerol is questionable, as biodiesel production is predicted to gradually shift from transesterification of oils and fats to their hydrogenation to get the so called HVO biodiesel. This reaction does not produce glycerol as byproduct and the resulting fuel has better overall properties. <sup>(34)</sup>

Another waste stream which has received much attention is the wastewater coming from urban areas or industries, which could solve, at least partially, the problem of the source of carbon and medium for microalgae growth, while at the same time producing useful molecules and cleaning polluted water. <sup>(35)</sup> <sup>(36)</sup> <sup>(37)</sup> <sup>(38)</sup>

In addition, it can be safely assumed that despite producing CO<sub>2</sub> as part of the respiration process, all organic carbon atoms come from sequestered atmospheric ones at a previous stage, making the heterotrophic mode intrinsically carbon neutral. Clearly the growth in wastewater organic carbon compounds is lower than compared to optimal glucose or glycerol; a table summarizing a literary review about expected productivity in real or simulated wastewaters is presented below.

Specie	Medium	Productivity (g/L*day)	Source
Chlorella sorokiniana	Anaerobic sludge from sugar plant	0,11	[41]
Scenedesmus	Synthetic WW	0,34	[42]
Chlorella sorokiniana	Solutions of acetate, butyrate, lactate	0,50	[43]
Chlorella protothecoides	Solutions of acetate, butyrate, lactate	0,40	[43]
Scenedesmus	Untreated WW	0,13	[44]
Chlorella	Untreated WW	0,16	[44]
Chlorella protothecoides	Whey permeate	0,81	[45]
Chlorella zofingiensis	Various sugar monomers	0,68	[46]
Chlorella zofingiensis	Various sugar monomers	2,80	[46]
Mix of microalgae	Various combinations of VFA	0,11	[47]
Chlorella protothecoides	Brewer fermentation waste + glycerol	2,00	[48]
Scenedesmus r-16	Sludge from WW plant for df	0,16	[36]
Galdieria sulphuraria	Primary WW	0,25	[49]
Galdieria sulphuraria	Cheese WW	0,59	[51]

Table 4: Studies on heterotrophic cultivation of microalgae on real or simulated wastewater.

As a result of the research and following consultation with academic expert the productivity used in this study was set to be 0.5 g/L\*day.

The modality of cultivation has been decided to be the fed-batch mode (sometimes referred as semicontinuous mode); it's the most widely adopted in the world and acknowledged for its simplicity and low cost. When a cultivation cycle is completed and removed from the tank, a small quantity is left inside and mixed with the new medium to be introduced. In this way the necessity for large inoculum cultivation is avoided (except for the first cycle ideally; more realistically once in a while "fresh" culture is introduced, especially if the microalgae are outcompeted by other organisms), which brings down cost and complexity. For this reason, inoculum cost and equipment have not been considered relevant.

### 3.2.2.2. SPECIES SCREENING

The selection of the suited microalgae strain to be grown in wastewater should follow some criteria:

- Adaptability in different substrates
- Capacity to intake different carbon sources
- High productivity and cell density

Only a few microalgae can grow heterotrophically, as most of these organisms are photoautotroph. The most studied and well-established strains belong to *Chlorella sp.* and *Scenedesmus sp.* which are considered reliable, capable of good productivity and with high removal rate of N, P and COD. Another recently studied strain is the extremophile red algae *Galdieria sulphuraria*, which can grow at extremely low pH and high temperature, being also able to use autotrophy and to utilize more than 50 different carbon sources, withstanding toxic environments. <sup>(52) (53) (26)</sup> The thermophilic nature enable cultivation in closed reactors-fermenters without the need to a cooling system, as heterotrophic processes produce heat that can reach over 40 °C in closed systems.

Most industrial microalgae species have an optimal temperature situated between 15 and 35 °C, *Chlorella sp.* have been reported to best thrive at temperature of 25 °C, 29 °C and even 40 °C, <sup>(54) (55) (56)</sup> whereas *Scenedesmus sp.* seem to bare 35 - 37 °C as upper limit. <sup>(57)</sup> Being able to duplicate rapidly in more extreme conditions is also helpful in avoiding contamination, if needed.

According to Schonknecht et al. (2013) *Galdieria sulphuraria* is the most versatile alga known with respect to growth on organic carbon sources, <sup>(58)</sup> with optimal cultivation conditions being 42 °C and pH of about 2 or 3, but with good rates until pH 8; moreover Rossoni et al. (2019) showed its fast adaptation at lower temperature environment, observing even faster (30 % more) growth at 28 °C after only 100 generations of, for this species, cold exposure. <sup>(60) (61)</sup>

Another useful aspect is its ability to naturally acidify its growth medium from neutrality to optimum levels under heterotrophic conditions, <sup>(59)</sup> a property that will come useful in subsequential conversion step.



Despite the good performances of *Chlorella* and *Scenedesmus* species, for the purposes of this study the strain of choice was *Galdieria sulphuraria*, because of its versatility and the ability to avoid contaminations from other microorganisms, which would create sewage sludge and therefore, a char of lower quality as seen in Table 3.

### 3.2.2.3. ANALYSIS OF WASTEWATER

The volume available for usage as growing microalgal medium amount to 410 m<sup>3</sup>/d and comes from the water stripped from the sludge after primary treatment. Most of it comes from a first stripping in the dynamic thickeners (320 m<sup>3</sup>/d) and the remaining part is obtained from dewatering of the digestate (in this plant the sludge is processed in a biogas unit). These two streams are combined into a common underground pool, they have high load of COD, BOD, nitrogen and phosphorous and they are later sent back to the initial treatment unit.

A weighted average of the composition of this mixture (from now on simply treated as one) is given below:

	N total	P total	COD	Volume
	(mg/L)	(mg/L)	(mg/L)	(m <sup>3</sup> /d)
Stream 1	289	42	1171	90
Stream 2	1264	431	28'950	320
Weight. Average	1050	346	22'852	410

Table 5: Composition of available wastewater from the treatment plant.

### 3.2.2.4. CONVERSION

To convert the microalgal biomass coming from the cultivation fermenters into a char, as seen in the introduction, there are mainly three routes: torrefaction, pyrolysis, or HTC. With such a high-moisture type of feedstock, consensus about the most effective conversion method is quite large, in favor of the hydrothermal carbonization. This

process has the unique advantage of eliminating the pre-drying requirement of wet biomass, a very energy and financial intensive step, since the carbonization reactions happen in a liquid solvent, water precisely. An undesirable and costly to abate substance in pyrolysis and torrefaction is instead the necessary reaction medium in the HTC. The milder temperature conditions allow for further energy savings, especially compared to pyrolysis, which have the additional drawback of converting into solid fuel an inferior share of the initial carbon content of the feedstock, while a substantial part gets converted in tar and gases. This in turn means that a bigger quantity of microalgae is needed and more byproduct to be processed and disposed of are produced. This leaves only HTC (or wet torrefaction) and dry torrefaction as viable options, but generally, HTC is more suited for biomass with more than 50 % of moisture. Moreover, it removes a significant fraction of undesired inorganic elements that would otherwise contribute to additional slag: due to the formation of acetic acid in liquid by-product stream, acid solvation mechanism solubilize and leach out inorganic element such as calcium, magnesium, phosphorous, potassium, sodium, sulfur, iron, which is not possible in case of dry thermal pre-treatments. Other authors believe HTC produces a material with superior metallurgical properties compared with torrefaction biochar. <sup>(15) (72) (73) (74) (76) (128)</sup>

	<b>Dry torrefaction</b>	<b>HTC</b>
<b>Properties of process</b>		
<i>Inert conditions</i>	Yes	Yes
<i>Pre-drying unit</i>	Yes	No
<i>Moisture handling capabilities</i>	Low	High
<i>Solid mass yield</i>	Higher	Lower
<b>Properties of product</b>		
<i>Hydrophobic</i>	Yes	Yes
<i>Moisture content</i>	Lower	Higher
<i>Higher heating value</i>	Lower	Higher
<i>Storage at open air</i>	Possible	Possible
<i>Purity</i>	Medium	High
<i>Grinding energy</i>	Low	Low

Table 6: Summary of dry and wet torrefaction properties, extrapolated from Acharya et al. (2015) <sup>(72)</sup>

For all these reasons HTC was finally selected as conversion method.

During the HTC process the water is in subcritical phase and acts as a non-polar solvent enhancing the solubility of organic compounds of the biomass. Liquid water at high values of temperature and pressure behaves both as acid and base, as the degree of ionization is higher, and it starts dissociating into  $H_3O^+$  (hydronium ions) and  $OH^-$  (hydroxide ions).

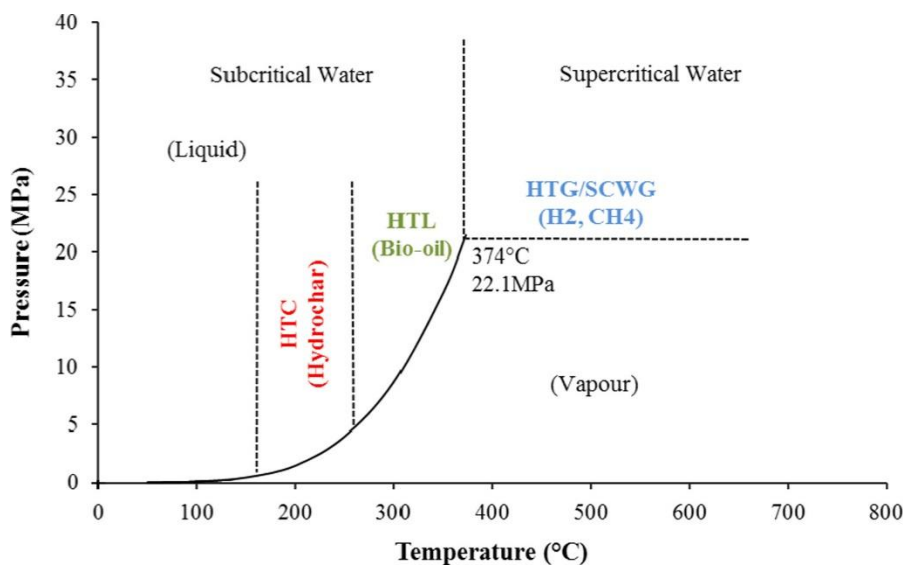


Fig. 12: Classification of hydrothermal processes with reference to the P-T diagram of water.

Density and viscosity decrease, whereas solubility and heat capacity increase. Dielectric constant is reduced, making the subcritical water resembling a non-polar solvent behavior, and allowing free fatty acids and other hydrophobic substances to be dissolved.

Biomass polymers are broken down into smaller molecules first through hydrolysis, then decarboxylation, dehydration, decarbonylation, demethoxylation, condensation, aromatization, and other reactions (happening often simultaneously) rearrange the chemical composition in a manner still not well understood. <sup>(75)</sup> <sup>(74)</sup>

Residence time and temperature are the most important factors in determining the characteristics and ratio of the products, the latter being the most influential one. The range of products ratio are usually in favor of the solid char (accounting for 40 – 70 % of the mass yield), the desired goal, while the rest is mainly an organic-rich liquid and small quantities of gas. By increasing the reaction condition, the liquid fraction

increases, solid yield decreases (but with more carbon percentage), and solubilization of some elements, like N and P, is enhanced (the process is moving towards the HTL area of Fig. 12). The correct balance between the variables needs to be found to get the best possible outcome.

A useful tool to assess the HTC char properties compared to coals is the Van Krevelen diagram, where the axis represents the H/C and O/C ratios decreasing with increasing severity of the conditions to give a char placed in the lignin or sub-bituminous coal values.

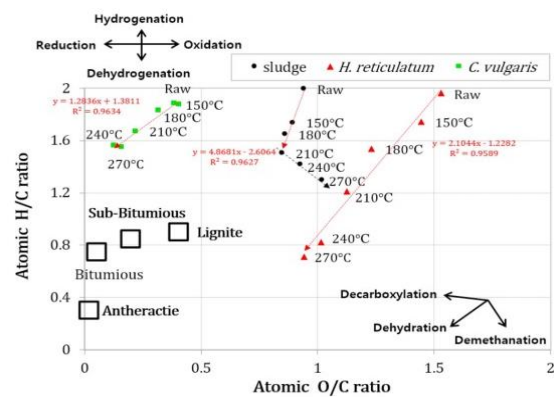
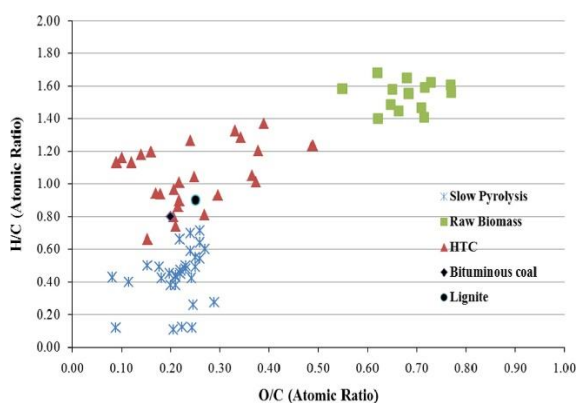


Fig. 13, 14: Van Krevelen diagram of various biomass and microalgae. <sup>(15)</sup> <sup>(77)</sup>

The other major product formed is a liquid phase called process water or HTC water. The main components consist of organic acids like formic, glycolic, propionic, levulinic.... along with many other molecules like phenols, and many of which represent potentially valuable chemicals: levulinic acid is a block for manufacture of chemicals, 2,5-HMF can be used to replace some fossil-based material and they have been identified as “top 12 value added chemicals for biomass” by US Department of Energy in 2004, <sup>(82)</sup> making the technology attractive also from a bio-refinery concept. It presents also high value of COD, TOC, N and P, therefore the disposal of this process water has been an issue, especially for biomass with very high moisture levels. Microalgae have been shown to grow on this medium, <sup>(71)</sup> <sup>(70)</sup> so it can be recirculated back in the cultivation tanks, with the additional benefit of acidify the solution and enriching it with organic acids, with beneficial effect on the mass yield and carbon yield thanks to their catalytic promotion of HTC reactions; moreover, organic acids can also directly participate in the formation of hydrochar through condensation and

precipitation on hydrochar matrix. <sup>(85)</sup> This concept will be explored further in the “food waste option”, as recirculation of process water is usually designed for direct input in the HTC reactor rather than in an earlier cultivation step.

Since studies about hydrothermal carbonization of *G. sulphuraria* has not been found and given the similar elemental composition with the more studied *Chlorella sp.*, results have been deemed highly similar and interchangeable, especially regarding the carbon content.

	<i>G. sulphuraria</i> <sup>(78)</sup>	<i>G. sulphuraria</i> <sup>(79)</sup>	<i>Chlorella sp.</i> <sup>(77)</sup>	<i>Chlorella sp.</i> <sup>(80)</sup>
C (%)	49.7	50	53	50.9
H (%)	7.7	5	8.4	7
N (%)	10.6	10.3	10	10.3
S (%)	1.8	1.1	0	0.8
O (%)	30.2	33.6	24.1	31

Table 7: Ultimate analysis comparison of *Chlorella* and *Galdieria sp.* in four studies.

According to experimental data from Park et al. (2018), who performed hydrothermal carbonization of *Chlorella vulgaris*, the best outcome would be to treat the microalgal biomass at 210 °C for maximum efficiency of product yield and carbon recovery, with one hour as the retention time.

The resulting hydrochar has a carbon content of 63.5 % and a product yield of 66 %.

	C %	H %	O %	N %	H/C	O/C	Ash (%)
Hydrochar	63.5	8.9	10.6	8.6	1.7	0.2	8.4

Table 8: Ultimate analysis of hydrochar from microalgae.

When the process is completed, the hydrochar is in a slurry form and moisture needs to be taken out, which is usually done with a mechanical filter press, followed by solar or thermal drying. A final briquetting or pelletizing step can be added to ease the storage and handling.

### 3.2.2.5. CONCENTRATION

Microalgae at the end of the cultivation stage are at a concentration of about 5 g/L of dry biomass in the medium, so that the moisture level of this feedstock is 99.5 %. This level of moisture is too high even for hydrothermal carbonization, which works best with levels at 80 – 85 %. An intermediate 30-fold concentration step is then needed before the microalgal biomass can enter the HTC reactor.

Following some meetings with industry's operators and experts a double step system is proposed: a first coagulation/flocculation process to bring biomass concentration to about 30 g/L and a second passage consisting of an innovative but proven tangential pressure membrane filtration called Dynamos from TMCI Padovan for the final increase to 150 g/L.

### 3.2.3. DESIGN AND FLOW

Following equation (1), (2) and (3) the water requirement have been calculated in 118'658 m<sup>3</sup>, this is the operative volume constantly operative to produce 19'757 ton yearly of dry microalgal biomass, which transformed generates 13'039 tons of hydrochar. With an HRT (hydraulic retention time) set at 10 days the cultivation system has an output of 11'866 m<sup>3</sup> daily and with an estimated dry biomass microalgae productivity of 0,5 g/L\*d, a final concentration of about 5 g/L is likely reached. To put this volume into perspective, it amounts to the volume of 20 large biogas plant digesters of 6000 m<sup>3</sup>, or to 475 large fermentation tanks of 250 m<sup>3</sup> used in the winery industry.

In order to design the best possible water flow system, the most similar study on the subject, written by Henkanatte-Gedera et al. (2015) has been taken as reference for the composition required of the medium. <sup>(49)</sup>

	Concentration	Removal rate
	(mg/L)	(mg/L*d)
BOD	59,4	18,6
N total	48	15,5
P total	11	3,6

Table 9: Composition of wastewater and removal rate of nutrients recorded according to Henkanatte-Gedera (2015).

For an HRT of 10 days this means a removal of 186 mg/L of BOD, 155 mg/L of N and 36 mg/L of P every cycle. These quantities represent the minimum concentration of nutrients to be present in the medium at day one. The ratio between BOD, N, P to be achieved is therefore 5,4 / 4,4 / 1.

In the data from CAFC (Table 5) however, COD is given instead of BOD. The conversion of these data has been done following industries guidelines <sup>(68)</sup> obtaining a value of BOD equal to 9936 mg/L. The ratio of nutrients (organic carbon, nitrogen and phosphorous) is then 29 / 3 / 1, and the limiting factor compared to the study is seen to be the nitrogen.

However, given that BOD value is usually referred in the span of five days (BOD<sub>5</sub>) and the HRT chosen was ten, BOD was assumed to be completely consumed at the end of a cycle, but since its ratio with the other nutrient is way higher than the study, it is deemed as not limiting and of not particular concern, and so not considered. In other words, carbon sources for microalgae are plentiful. Eventual accumulation of not-biologically degradable remaining COD can be lowered artificially later in the process like in the recirculation phase, if deemed useful for algal growth.

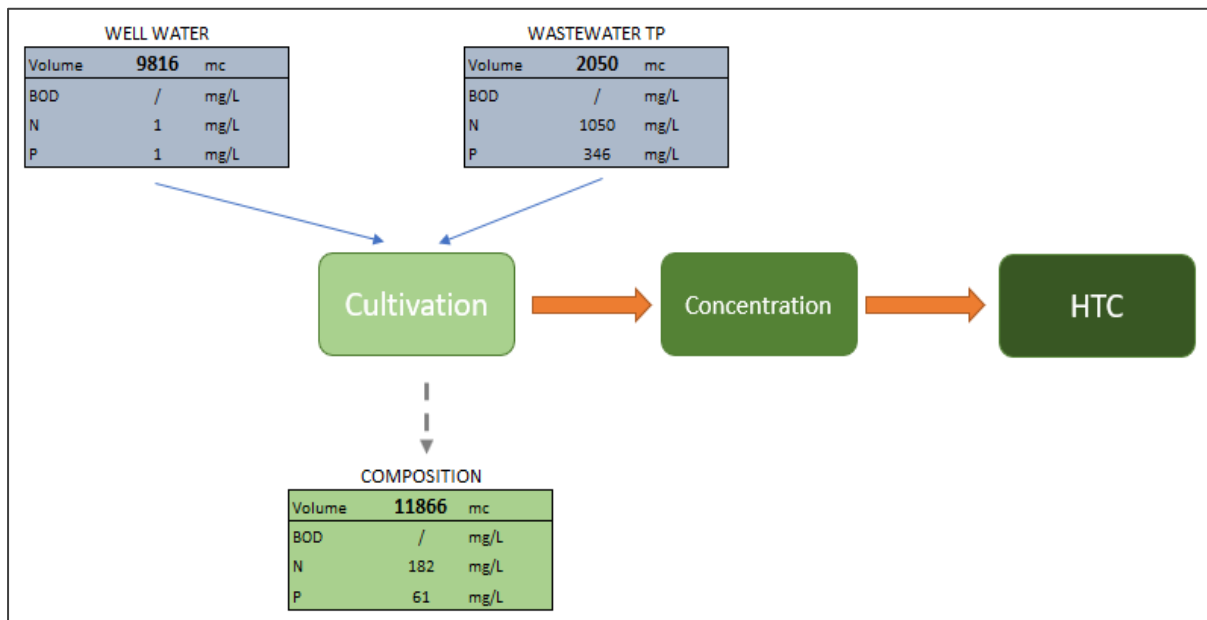


Fig. 15: Wastewater streams flowchart and composition at day 0.

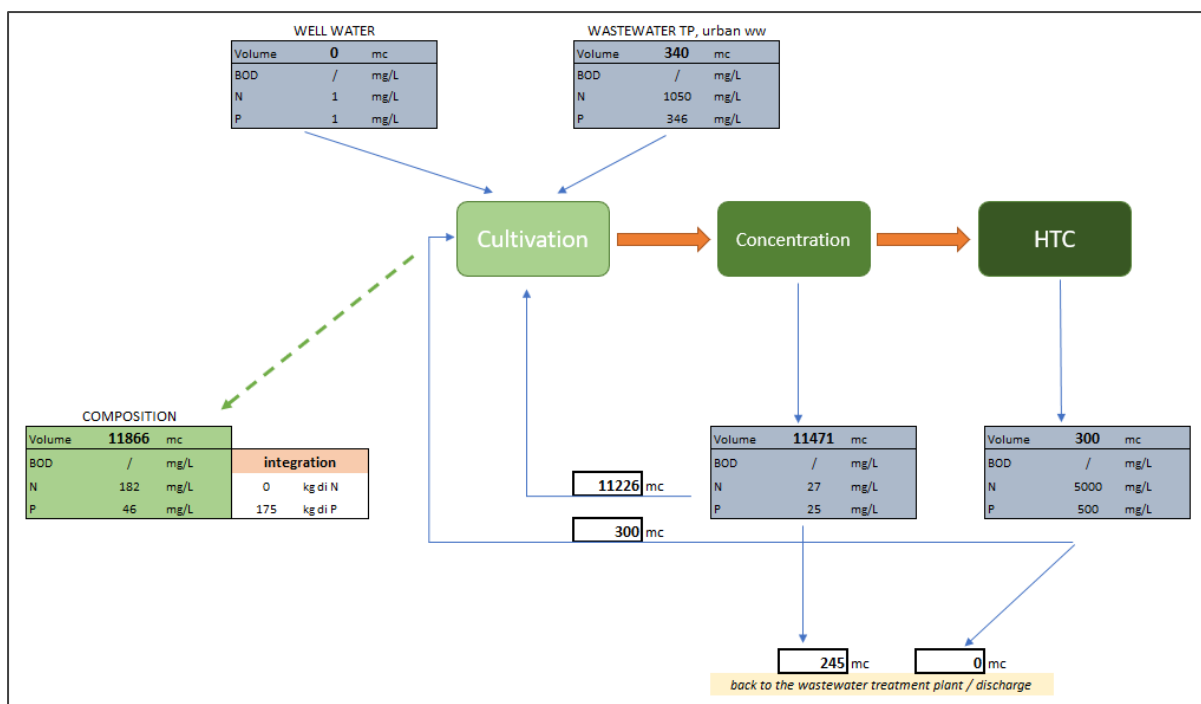


Fig. 16: Wastewater streams flowchart and compositions at a regular day of operation.

In Fig. 15 is represented the initial filling, done in five days of complete withdrawal of the available wastewater from the treatment plant. This stream is joined by the well water of ABS with extremely low value of nutrients and together they form the closest medium composition to the study possible. Amount of nitrogen, the limiting factor, have been tuned with an excess of 10 – 15 % to ensure microalgae would intake it at the maximum possible rate. In Fig. 16 is represented instead a normal day of operation for the water flow of the system: 340 m<sup>3</sup> of wastewater are withdrawn and mixed with the stream coming from the concentration step of the previous cycle, where nutrients have been depleted according to the removal rate of Table 9, and the stream coming from the hydrothermal carbonization reactor, called process water of HTC water, with instead very high N, P, and organic carbon values. The flowchart is designed to minimize the discharge of water (245 m<sup>3</sup> per day) and the usage from the ground well (effectively zero). The discharge water can be sent back to the treatment plant or released into surface water or public sewage, which will depend on its composition and alignment with parameters stated in Tab. 3, All. 5, D.Lgs n. 152 of 03.04.06. Composition of HTC water varies wildly in the literature based on feedstock, medium, reaction conditions, and precise values could not be found. The estimation used was applied by aggregating data from some studies and industry experts. <sup>(69) (70) (71)</sup>



Moreover, a phosphorous integration of 175 kg was found to be necessary to ensure the correct ratio of nutrients.

To follow there is the concentration step:

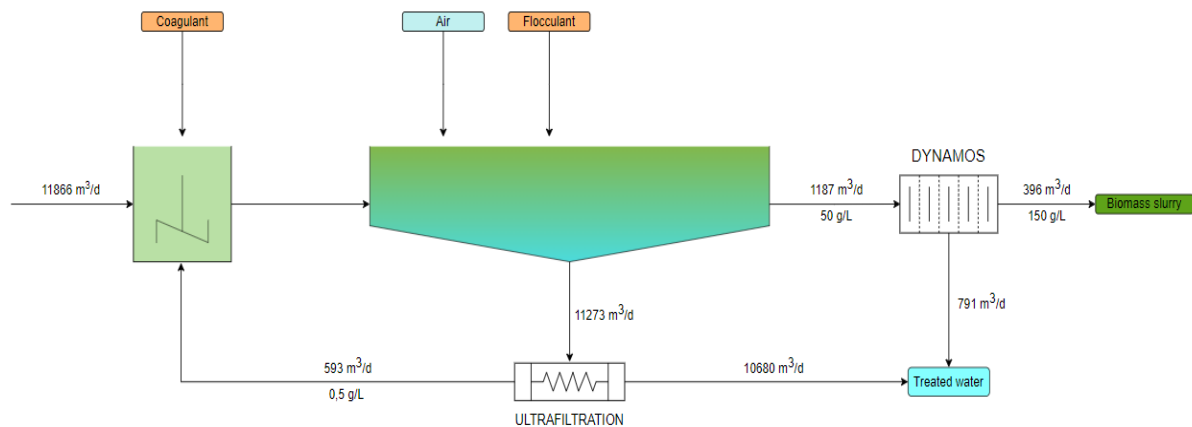


Fig. 17: Design and material flow of the concentration system on a daily basis.

The system is composed by a first coagulation tank, followed by a larger one where flocculation of the biomass is achieved using air bubbling and polyelectrolytes. The aggregated biomass accumulates on the upper part of the liquid layer and 1187 m<sup>3</sup> are then sent to the Dynamos system with a concentration of about 50 g/L. This is a rotary dynamic cross-flow filter constituted of a filtering bell with a set of high-velocity rotating discs fixed on a series of hollow shafts, and the passage of the filtrate happens by differential trans-membrane pressure. At last, 396 m<sup>3</sup> of dense algal slurry leave the process unit and this is the quantity that will be sent into the HTC reactor. Excess water from the flocculation tank is pumped into an ultrafiltration machinery able to effectively separate the remaining suspended solids (mostly microalgal cells) sending them back to the coagulation tank, from most of the water, which should have low level of contaminants. In this way it's increased the overall yield and efficiency, as no dry biomass is lost. The ultrafiltrate water is joined by another smaller clean water stream coming from the Dynamos filter and together they are recirculated back into the cultivation fermenters as seen in Fig. 17, while a little fraction is discharged into the sewage system (if its composition falls within the regulations) or it can be sent back to the wastewater treatment plant.

Lastly, the microalgal slurry is ready to feed the HTC vessel:

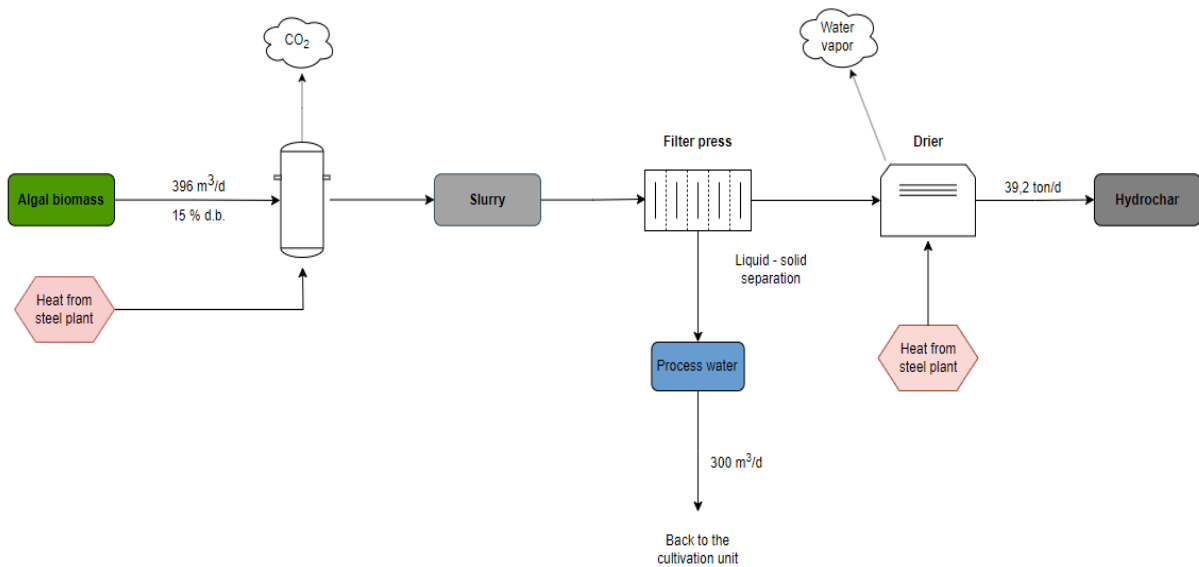


Fig. 18: Hydrothermal carbonization process for microalgal biomass.

The reactor is sealed and under autogenous pressure from the gases liberated from the biomass transformation. Heat can be provided by the steel plant in both the carbonization stage and in the drier. After an adequate time, identified previously in 1 hour, the carbonized slurry exits the vessel and is pumped into a filter press for mechanical dewatering of the hydrochar. Extracted water (process water), rich in organics and nutrients, is sent back to the cultivation stage, whereas the hydrochar undergoes a final drying process to reduce further the moisture content. An extra pelletizing step is possible and recommendable to ease the handling and storage.

### 3.2.4. OPERATIVE COST ANALYSIS

Operative costs are below presented, subdivided in the various phases of the process, with a final price per ton of char and of anthracite equivalent.

#### *Cultivation stage*

	<b>Power installed</b>	<b>Power use</b>	<b>Cost</b>
	<i>(kW)</i>	<i>(kWh)</i>	<i>(eur)</i>
<b>PUMP (wwtp)</b>	5,2	41'766	4'177
<b>PUMP (concentration)</b>	18,5	147'573	14'757
<b>PUMP (top tank)</b>	21,4	171'029	17'103
<b>SUM PUMPS</b>			36'014
<b>MIXERS</b>	209	1'666'634	166'663
<b>BLOWERS (scenario 1)</b>	53'075	424'175'400	29'369'542
<b>BLOWERS (scenario 2)</b>	34'437	275'221'192	27'522'119
<b>BLOWERS (scenario 3)</b>	8'303	67'952'899	4'705'001

	<b>Yearly use</b>	<b>Price</b>	<b>Cost</b>
	<i>(kg/y)</i>	<i>(eur/kg)</i>	<i>(eur)</i>
<b>Nutrient integration</b>	58'369	1	58'369

	<b>Q</b>	<b>Cost</b>
	<i>(MWh)</i>	<i>(eur)</i>
<b>HEATING (sides)</b>	17'960	269'339
<b>HEATING (top)</b>	41'906	628'597
<b>Sum heating (scenario 1 and 3)</b>	59'866	897'995
<b>HEATING (sides)</b>	12'123	181'844
<b>HEATING (top)</b>	94'289	1'414'342
<b>Sum heating (scenario 2)</b>	106'412	1'596'186

Concentration stage

	<b>Daily use</b>	<b>Price</b>	<b>Cost</b>
	<i>(kg/d)</i>	<i>(eur/kg)</i>	<i>(eur)</i>
<b>FeCl<sub>3</sub></b>	494,4	1	164'635
<b>Polyelectrolyte</b>	24,7	2	16'464
<b>NaOH (30%)</b>	652,6	0,5	108'659
<b>HNO<sub>3</sub> (50%)</b>	296,6	1	98'781
<b>NaOCl</b>	74,2	0,5	12'348
<b>HCl (30%)</b>	39,6	0,5	6'585
<b>Sum chemicals</b>			407'472

	<b>Specific consumption</b>	<b>Power use</b>	<b>Cost</b>
	<i>(kWh/m<sup>3</sup>)</i>	<i>(kWh)</i>	<i>(eur)</i>
<b>Coagul./flocicul.</b>	0,2	790'276	79'028
<b>Dynamos</b>	6,5	2'569'262	256'926
<b>Ultrafiltration</b>	0,1	375'391	37'539
<b>Sum electricity</b>			373'493

Conversion stage

	<b>Cost</b>
	<i>(eur)</i>
<b>HTC</b>	2'713'700

*Total by stages*

	<b>Cost scenario 1</b>	<b>Cost scenario 2</b>	<b>Cost scenario 3</b>
	(eur)	(eur)	(eur)
<b>Cultivation (scenario 1)</b>	30'778'583		
<b>Cultivation (scenario 2)</b>		29'629'352	
<b>Cultivation (scenario 3)</b>			6'114'042
<b>Concentration</b>	780'965	780'965	780'965
<b>Conversion</b>	2'713'700	2'713'700	2'713'700
<b>SUM</b>	<b>34'273'248</b>	<b>33'124'017</b>	<b>11'548'674</b>

<b>Hydrochar quantity (ton)</b>	13'039	13'039	13'039
<b>Hydrochar cost (€/ton)</b>	2'629	2'540	737
<b>Anthr. eq. cost (€/ton)</b>	<b>3'811</b>	<b>3'684</b>	<b>1'069</b>

*Table 10: Cost analysis of microalgae-produced hydrochar*

In order to get the same amount of carbon in the EAF 1.45 tons of hydrochar are necessary (14) to replace each ton of anthracite (conversion factor  $F$ ). By following this calculation, we obtain the cost to replace 1 ton of anthracite with microalgal-growth hydrochar: 3'811 € in case of “scenario 1”, 3'684 € in case of “scenario 2”, and 1'069 for “scenario 3”.

In the next graph, it's considered a price for a ton of anthracite being 300 € and the price for CO<sub>2</sub> credits emissions of 90 €/ton. Every atom of carbon burned is oxidized to carbon dioxide, increasing its weight by exactly 3.67 times. Since this kind of anthracite contains 92 % of carbon, every ton burned equals to 3.38 tons of CO<sub>2</sub> released into the atmosphere, so that additional 304 € must be accounted for every ton of anthracite consumption.

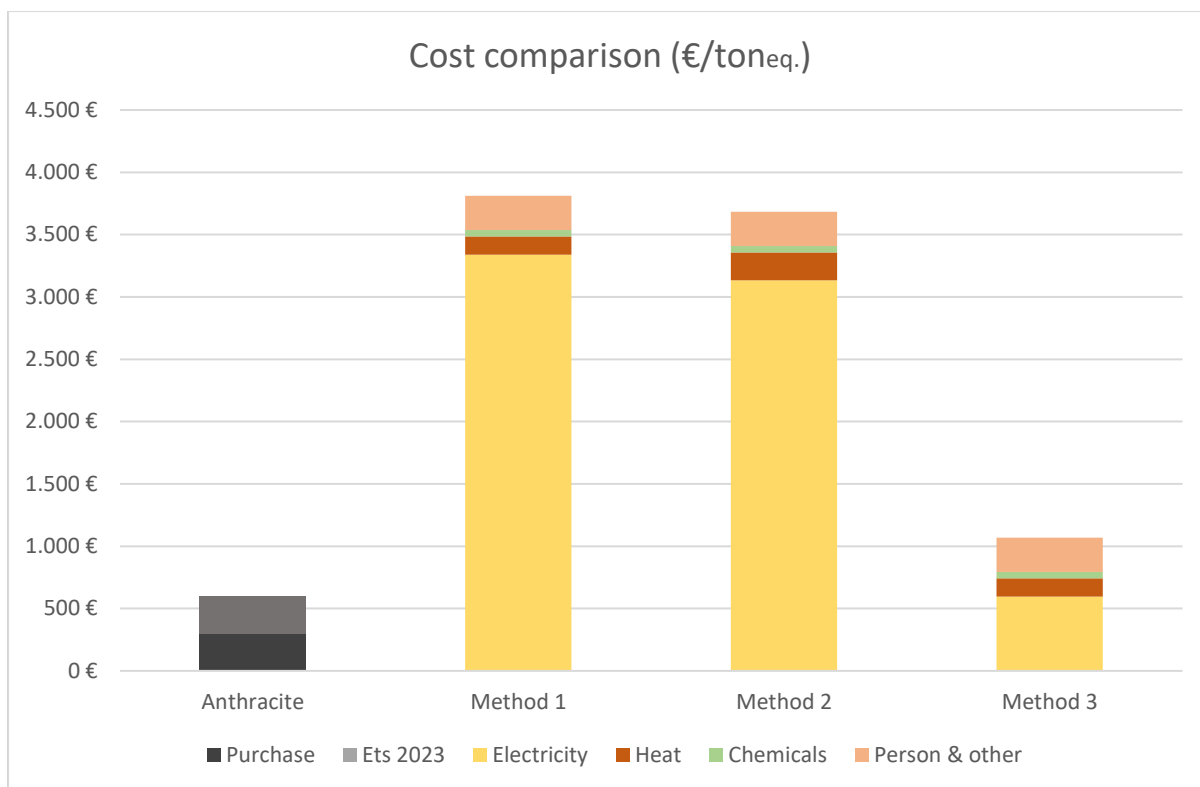


Fig. 21: Comparison of purchased anthracite and hydrochar (equivalent) costs, from Table 10.

The cultivation phase weights the highest in the first and second scenario (89.8 and 89.4 %) and decreases for the third (63.6 %). Concentration phase is minority in all of them (respectively 2.3, 2.4 and 8.1 %), whereas the HTC conversion is the most significant in the third scenario (28.2 %), and the less significant in the first (7.9 %), while it accounts for 8.2 % in the second.

As displayed by the following figure, electricity is by far the largest operative cost, mainly driven by the aeration requirement, even considering these low aeration scenarios.

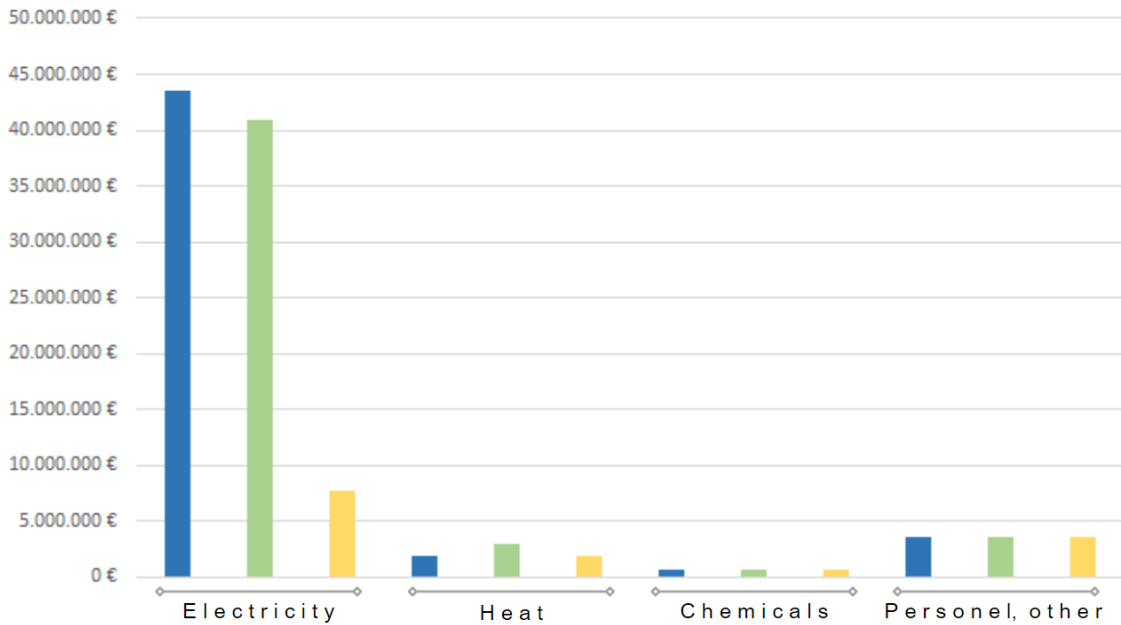


Fig. 19: Cost breakdown for different sources, converted in anthracite equivalent. Blue bars represent “scenario 1”, green bars represent “scenario 2” and yellow bars “scenario 3”.

The prices for hydrochar found (0.7 – 2.6 €/kg) differ significantly, with the third scenario belonging to the lowest estimation range, caused by the extremely little VVM injected. The accuracy of the results is also validated by comparing its cost structure with a typical wastewater treatment plant. Gu et al. (2017) <sup>(105)</sup> report the following expenses for a typical conventional activated sludge treatment plant. Given that a wastewater-based microalgae cultivation is similar in design as an aerobic treatment process, it’s possible to exclude many items from the graph like anaerobic digestion, lightning, thickening, press etc... to end up with an overwhelming share of cost drove by the aeration requirements. Blowers’ consumption comprises the 86 % of the total production cost in “scenario 1”, 84 % in “scenario 2” and 41 % of “scenario 3”.

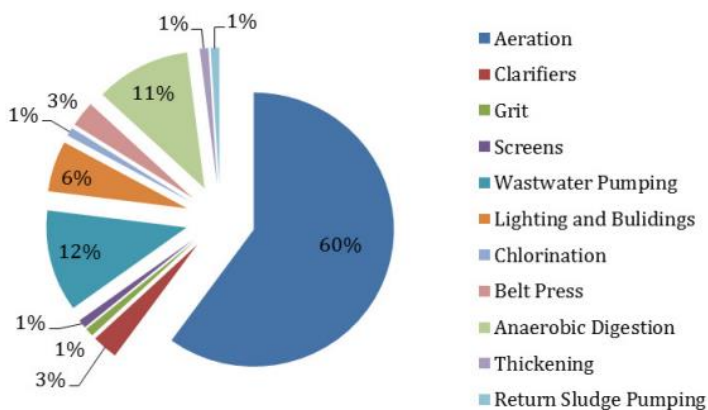


Fig. 20: Cost structure of a typical wastewater treatment plant. <sup>(105)</sup>

It's worth remembering that only operative cost are accounted for in this paper, and capex is excluded. However, given the scale of the system, it's likely very consistent.

### 3.2.5 COMPETITIVENESS POINT

It's then calculated using equation (15) the carbon credit price necessary for this technology to be competitive or, in other words, how much taxes should be added to the fossil coal emission for this particular biogenic fuel to reach price parity:

	Purchase	Production cost	ETS* price
	(€/ton)	(€/ton)	(€/ton <sub>CO2</sub> )
Anthracite	300		
Hydrochar 1		3'811	1'039
Hydrochar 2		3'684	1'002
Hydrochar 3		1'069	228

Table 11: ETS\* price for cost parity between chars obtained with different scenarios, referred as anthracite equivalent.

The European Central Bank, reporting the Net-Zero-Scenario for 2050 of the IEA, <sup>(103)</sup> forecast a price for carbon credits of 140 €/ton by 2030, and even higher in later years. Further carbon emission price forecast is difficult to estimate, but according to LSEG Carbon Research <sup>(104)</sup> it could reach 400 €/ton by 2040. Even by taking the best-case scenario and only from an operative point of view, cost parity is forecasted well into the next decade, with high uncertainty of the carbon credits. The middle and worst-case scenario instead, does not predict a cost parity under the current circumstances and carbon market analysis.

Hydrochar from heterotrophic microalgae cultivation is clearly not competitive with current fossil anthracite coal prices, costing between over 1.7 and six times more. It's possible to observe that even accounting for a carbon dioxide price of 140 €/ton forecasted for 2030 the cost of its substitution with an equivalent hydrochar is quite surely out of reach for any scenarios. Electricity consumption is very high and absorbed for the vast majority during the cultivation phase, which in turn is driven



mostly by the aeration requirements provided by the tank's blowers. In order to make them competitive, either the energy consumption or its cost should decrease substantially, or a combination of both. Heat savings from insulation of the tanks and autogenous cellular generation can help in lowering some expenses but they cannot change the overall picture as cost distribution is very unbalanced.

### 3.3. CO-TREATMENT OF FOOD WASTE AND DIGESTED SEWAGE SLUDGE

This next part of the study will consider a co-treatment of municipal food waste and of digestate of sewage sludge coming from the same wastewater treatment plant seen previously.

As seen in Table 3, other than microalgae the most suited waste source to be employed for the production of biochar is represented by the food waste. This stream is part of the organic fraction, amounting to more than 7 million tons in 2021 in Italy (the largest municipal waste source) and according to ISPRA its growth is constant. Since 2010, its collection has increased by 40 %. <sup>(107)</sup> A significant portion is composed by green waste (grass, leaves, pruning...) which is not constant during the year and needs to be excluded to get a constant and homogeneous char throughout the year. The percentage of food waste over the total organic fraction is finally identified to be 69.6 %, which brings the figure of yearly collected Italian food waste to 5.14 million tons. The high moisture content (generally over 50 %) makes it a good candidate for the hydrothermal carbonization process and has indeed attracted the attention of researchers and industries working toward its valorization and transformation into a resource, following circular economy principles. <sup>(108) (109) (110) (111)</sup>

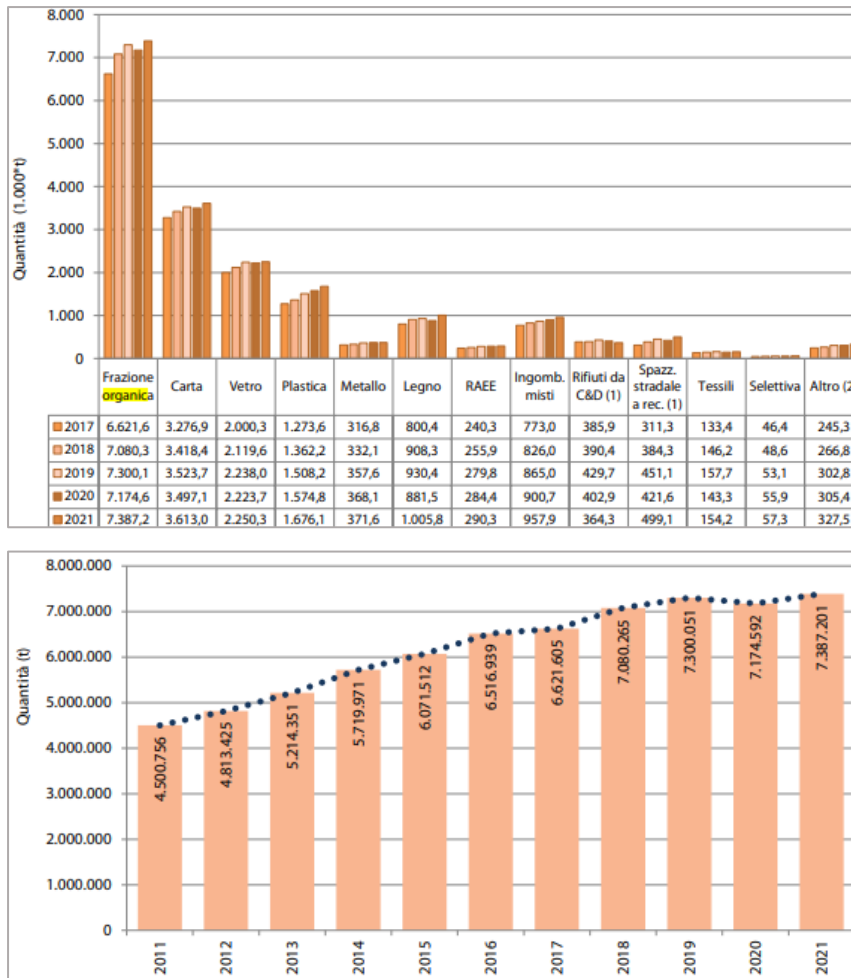


Fig. 22: Separate waste fractions (up) and last 10 years trend of organic waste collected (down), according to ISPRA. <sup>(107)</sup>

Currently food waste is treated in three ways: aerobic composting (47,6 %), anaerobic digestion (4,8 %) and integrated aerobic-anaerobic treatment (47,6 %), but interest in thermal upgrading is growing due to the possibility of obtaining more valuable end-products and together reduce GHG emission. HTC in fact, is believed to emit less harmful gases than more widespread treatments like composting: not all the waste mass in fact, is aerated properly and formation of CH<sub>4</sub>, N<sub>2</sub>O, NH<sub>3</sub>, VOC and H<sub>2</sub>S are inevitable and highly dependent on the type of management in place. Some of these compounds are harmful for human health or potent GHG's with a GWP several times higher than carbon dioxide. Exact quantification are difficult to estimate and varies wildly but many studies report an order of magnitude of few hundreds' kg of CO<sub>2</sub> eq per ton of treated waste. <sup>(147) (148)</sup>

Sewage sludge digestate instead is the product of the anaerobic treatment in a biogas unit of sewage sludge extracted from the wastewater. CAFC S.p.a. plant considered produces annually 7000 tons of digestate and its disposal is done by farmers who come to the facility with trucks to collect and scatter it gradually in the fields. This practice can increase the fertility and structure of the soil as digestate contains high amounts of nutrients however, it contains also heavy metals and pathogens, and the overall advantage is controversial. Moreover, its spread into the soil may be a source of greenhouse gas emission (especially due to N<sub>2</sub>O, that has a GWP 100 of 298 CO<sub>2</sub> eq.) and eutrophication, so regulations on modality and timing of this kind of disposal are in place. Literature has not reached an agreement whether this practice is beneficial or harmful in terms of emissions, as a lot of factors influence the results, such as system boundaries, feedstock type, biogas plant parameters, sparging type, soil type, crop cultivated, climate, etc. <sup>(137) (138) (139) (140) (141) (142)</sup> Other widely used choices of disposal are incineration and landfilling. <sup>(143)</sup> Despite its conversion in bio-coal through hydrothermal carbonization is possible and currently operative in some facilities, its quality as solid fuel is not excellent as the amount of ash is particularly high and the carbon content and the calorific value quite low compared to other feedstock hydrochar. In order to get a bio-coal of better quality, many studies propose to co-treat the digestate with other feedstock, mixing them together in the reactor and obtaining a char with much better characteristics.

### 3.3.1. FIRST METHOD

This method involves the use of the machine learning software mentioned in paragraph 3.2.1. with the input given as stated in Table 2 and operative conditions set at 230 °C, one hour of treatment, 15 % of solid loading, 5.8 % SS/FW ratio.

The predicted hydrochar properties output are summarized below:

C (%)	H/C ratio	O/C ratio	N/C ratio	HHV (MJ/kg)	Mass Yield (%)
60.4	1.1	0.2	0.05	24.6	45.6

Table 12: Output predicted of hydrochar from co-HTC.

The fuel ratio is 0.67: this parameter represents the ratio between fixed carbon (FC) and volatile matter (VM) of the biofuel. Combined with equation (17) fixed carbon percentage stands at 34 % and VM at 51 %.

By transforming the ratios in weight % using equation (17) a final table for the first method is given:

C (%)	H (%)	O (%)	N (%)	Ash (%)	HHV (MJ/kg)	Yield (%)
60.4	5.4	16.9	3.2	14.5	24.6	45.6

Table 13: Hydrochar properties estimated.

### 3.3.2. SECOND METHOD

Here a regression analysis was performed for all variables considered in the paper by Zheng et al. (where the team obtained biochar with different sludge/food waste mixture). For this study requirements, a different SS/FW ratio of 5.8 % was considered, and results presented:

SS	FW	C (%)	H (%)	O (%)	N (%)	S (%)	FC (%)	VM (%)	Ash (%)	HHV (MJ/kg)	Yield (%)
0	100	68.6	7.3	14.8	3.4	0	25.7	68.4	6	30.8	0.43
100	0	22.7	3.2	6.1	1.8	0.3	4.9	26.4	68.1	9.8	0.59
70	30	31.9	4	8.8	2.3	0.2	9.6	37.6	52.7	13.8	0.52
50	50	42.2	5	10.3	2.66	0.2	15	45.4	39.7	18.7	0.5
30	70	51.3	5.8	12.1	3.1	0.1	19	53.4	27.6	22.9	0.47
5.8	94.2	63.8	6.9	14.2	3.4	0.02	24	64.7	11.3	28.6	0.43
Adjusted R <sup>2</sup>		0.980	0.985	0.999	0.986	0.989	0.992	0.99	0.993	0.978	0.971

Table 14: Hydrochar properties estimation from regression analysis.

Adjusted R<sup>2</sup> is very high for all variables considered. The more it approaches 1, the more valid the result; the results are therefore considered fairly accurate.

### 3.3.3. COMPARISON

Results indicate that both methods provide very similar results, strengthening the likely outcome to expect such a process (and feedstocks used) were to be implemented. Variations of some percentage points are common in these mechanisms, as feedstocks and equipment design are never exactly the same.

Fixed carbon and volatile matter are the only values where there is a significant difference between the two methods, therefore more uncertainty is expected. Averaged fuel ratio stands at 0.5, which is high but not unseen in other studies. Also, the percentage of sulfur is not considered by the software which so doesn't return this value. The higher heating value of the second method could be explained by the use in that paper of sewage sludge data instead of digested sewage sludge, which in the first method software were substituted with first-hand data from the biogas plant unit. Digestate in fact, has lower carbon content, higher ash, lower HHV, due to the fact that there are fewer organic compounds as the anaerobic digestion have "consumed" them to generate biogas. Using undigested sewage sludge, other raw biomass or simply 100% food waste would surely slightly improve the hydrochar properties. If characteristics from the two methods were to be averaged for increasing robustness of the results, the hydrochar would have the following composition and properties:

C (%)	62.1
H (%)	6.2
O (%)	15.6
N (%)	3.3
S (%)	0.02
FC (%)	29
VM (%)	58
Ash (%)	12.9
HHV (MJ/kg)	26.6
Yield (%)	44.3

*Table 15: Averaged estimated characteristics of hydrochar.*

### 3.3.4. EFFECT OF RECIRCULATION OF PROCESS WATER

The previous estimation of the hydrochar properties were based on scientific experiments that analyzed its elemental and proximate composition after one thermal treatment, or one passage through the reactor. But this is not the case during industrial operations: process water is in fact recirculated back into the HTC vessel and this influences the reaction. PW water in fact, is rich in organic molecules that can participate both directly (by condensation and precipitation in the char matrix) and indirectly (by promoting other reactions) in the carbonization process. Examples of the most abundant are acetic acid, formic acid, lactic acid, 5-HMF, phenolic compounds (such as guaiacol, syringol), which are not present in a first-round experiment solvent. Amount of TOC (total organic carbon) can reach the order of tens of grams per liter. The effect of these organic molecules in the reaction medium, present in non-trivial quantities, was studied by many scholars,<sup>(114) (115) (116) (117)</sup> with generally consistent and favorable results: mass yield, carbon content, fixed carbon increase by some percentage points, at the expense of the oxygen content which instead decreases.

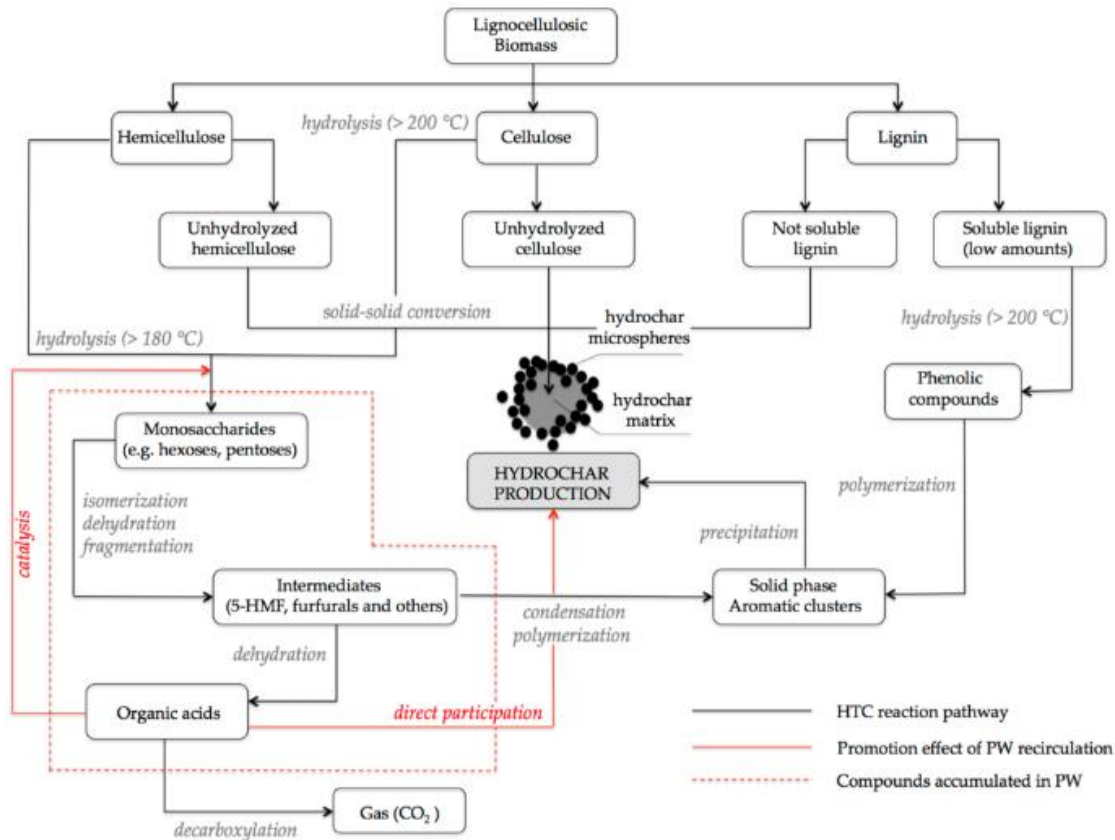


Fig. 23: Highlights of PW recirculation effect during hydrochar matrix formation. <sup>(117)</sup>

By reviewing the data from Picone et al. (2021) it's seen that the average mass yield increases by 5.8 %, HHV by 0.7 MJ/kg, carbon content by 1.6 %, ashes by 0.5 %, H by 0.1 %, N by 0.2 %, while oxygen decreases by 1.7 %. <sup>(117)</sup>

It's expected that the mixture analyzed will behave in a similar way, bringing the values of the hydrochar of Table 15 to:

	C (%)	H (%)	O (%)	N (%)	Ash (%)	S (%)	HHV	Yield (%)
Hydrochar	63.4	6.2	13.8	3.4	13.2	0.02	27.3	50.1

Table 16: Expected hydrochar composition after recirculation of process water. HHV unit is MJ/kg.

It's interesting to note that the expected chemical composition following recirculation of PW is very similar to the result obtained by the regression analysis (second method), especially for the most important value: carbon. Yield of the process instead is closer to the output of the first method (the software).

Accounting for all these expected positive effects it's possible to finally estimate the amount of annual feedstock requirement for a production of 13'060 tons of dry char in:

- Digestate: 6'048 ton
- Food waste: 54'569 ton

To put this quantity in perspective, the region of Friuli Venezia-Giulia produces annually (according to ISPRA) 164'810 tons of organic waste, and by taking off the green fraction the available feedstock in the region amounts to 114'012 tons.

An hydrochar plant of this scale will, therefore, take up 48 % of the FVG regional food waste output, or 33 % of the entire organic fraction.

Composition and properties are all in line with literature, as most of the studies treating food waste carbonization found heating values in the range of 20 – 30 MJ/kg, or even higher, and similar elemental and proximate analysis. <sup>(123) (124) (111) (126) (127) (122)</sup> The resulting carbonaceous material can sometimes be referred as bio-lignite by the industry, and it's regulated by the "Attachments to part five – Annex X – Regulation of fuels". <sup>(119)</sup>

### 3.3.5. DESIGN AND FLOW

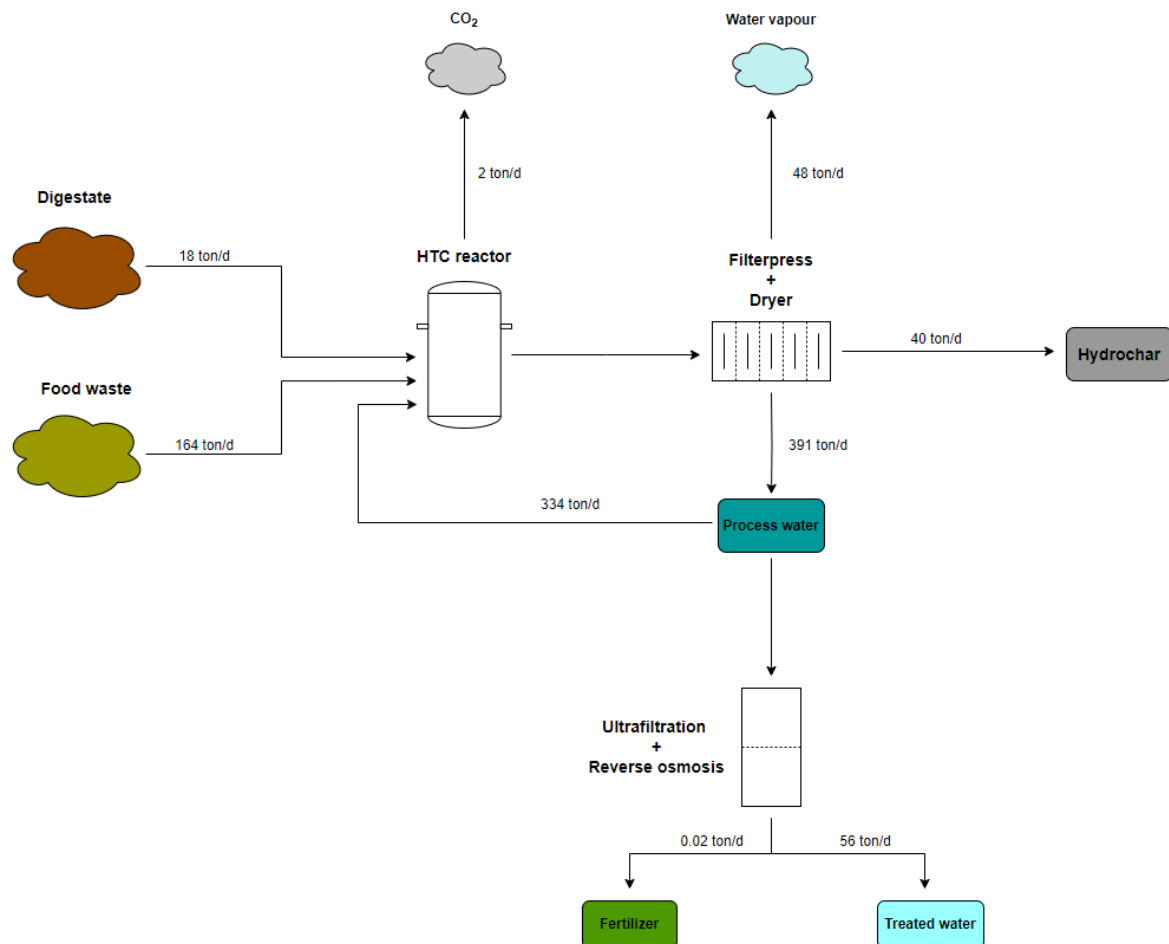


Fig. 24: Process flow of the co-HTC system.

Process water coming from the liquid-water separation happening in the filterpress gets, for the most part, recirculated back into the HTC reactor to raise the moisture level of the feedstock mixture to the desired level. The excess process water passes through a double stage treatment made of an ultrafiltration part and a reverse osmosis one, resulting in a treated water suitable for discharge as it is compliant with the regulation limits set by Table 3, All 5, D. Lgs n° 152 of 03/04/06. The byproduct of this two-stage treatment is a high-nutrient liquid fertilizer containing nitrogen and phosphorus in high percentage, tested for agricultural use, and included in D. Lgs n° 152 (the same decree), Art 184-bis, as agricultural byproduct eligible for field usage. The overall process also emits a small quantity of carbon dioxide from the carbonization reactions (precisely 546 ton/year and considered carbon neutral given the biogenic origin) and some water vapor from the drying stage. It's very efficient as



no external water intake is required, and the biggest waste produced are put back in at the start of the cycle as reaction medium, whereas the other much smaller waste streams are innocuous or have easy market application (some pre-sorting might be necessary to ensure only the right organic materials enters the reactor, even though HTC process works very well also with plastics and paper). The drying stage, moreover, does not eliminate entirely the water content of the char of a standard process, and industry's source claim a 7 % moisture level in the final product.

The plant occupies an area of around 5'000 m<sup>2</sup>, and for the volume of feedstock considered 8 – 10 reactors are needed, each of about 10 m high and some meters in diameter, although size of reactors varies among industries and requirements.

### 3.3.6. COST ANALYSIS

	<b>Cost</b>	<b>Revenue</b>
	(eur)	(eur)
<b>HTC system (opex)</b>	3'171'711	
<b>HTC system (capex)</b>	2'000'000	
<b>Digestate disposal (6'048 ton)</b>		393'120
<b>Food waste disposal (54'569 ton)</b>		3'546'985
<b>SUM</b>	5'171'711	3'940'105
<b>TOTAL</b>	1'231'606	

<b>Hydrochar quantity (ton)</b>	<b>13'060</b>
<b>Hydrochar cost (€/ton)</b>	<b>94</b>
<b>Anthr. eq cost (€/ton)</b>	<b>137</b>
<b>Anthracite cost (€/ton)</b>	<b>604</b>
<b>Net gain (€/ton)</b>	<b>467</b>

Table 17: Cost and revenue summary of the co-HTC system.

In this cost analysis HTC industry’s executive provided an estimation for capex cost too, which amounts to 2 million per year for a plant lifetime of 15 years. Even with this addition, the price of this kind of hydrochar is substantially inferior to microalgal char, standing at 137 € per ton of anthracite equivalent (anthr. eq. calculated again using the conversion factor  $F$  (14)). But, more importantly, it’s inferior to standard anthracite. Considering, as in the previous case, fossil coal and carbon credit purchase accounting for 300 and 304 €/ton (for a total of 604 €/ton), this option seems viable and economically sustainable, with a net gain of 467 €/ton. Waste streams such as food and digestate are valorized by its hydrothermal conversion in place of more “traditional” disposal methods. They both have been considered priced at 65 €/ton; however, revenue from food waste could be higher: according to A&T 2000, one of the largest waste operator in FVG region, the cost of treatment of the municipal organic fraction is 86 €/ton.

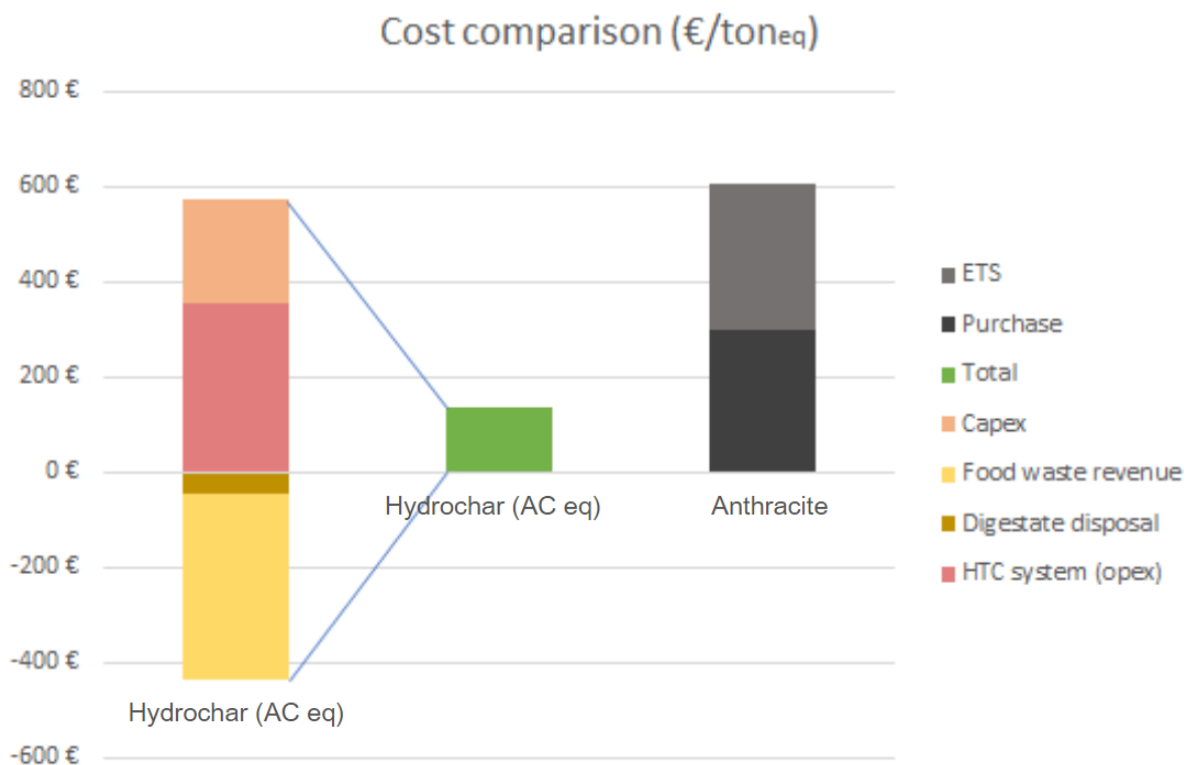


Fig. 25: Cost and revenue of anthracite equivalent per year with the co-HTC treatment option, from Table 17.

It’s also possible to notice that the system appears economically advantageous even without compensation for the disposal of the waste streams, as the red and orange

bars together (capex plus opex) are inferior to the anthracite bar. Indeed, these costs amount to 575 €/ton of anthracite equivalent.

### 3.3.7. FURTHER CONSIDERATIONS

#### Heating value and ash composition

The higher heating value of the hydrochar is expected to be 27.3 MJ/kg (Table 16), whereas anthracite one was calculated using (19), with composition from company's data (C: 92 %, H: 2 - 2,5 %, O: 3 %, N: 0,5 - 1 %, S: 0,5 - 1 %, Ash: 0,5 - 2 %) and found to be about 34.2 MJ/kg. HHV of fossil coal is 1.25 times higher and therefore, by loading in the EAF with 1.45 tons of char for every ton of anthracite it's expected a higher energy input inside the furnace from the charging and injecting coal; precisely by 5.4 MJ/kg. Applying (20), for every ton of liquid steel an excess of 48.8 MJ is estimated, 48'758 GJ annually. This could mean that less methane is to be supplied in the furnace as energy input; under these circumstances 1,24 million m<sup>3</sup> of gas could be avoided (assuming 39,4 MJ/m<sup>3</sup> of gas energy density, as stated by Snam). As a general rule, it's achieved an energy surplus if:

$$\frac{HHV \text{ char}}{HHV \text{ a}} > \frac{\% \text{ C char}}{\% \text{ C a}}$$

The ash content and composition are of great importance for the intended char use in the EAF, as its elements will contribute to slag and gases formation or solubilize in the liquid steel. Predictably, composition varies substantially across the literature, as it's closely related to the type of feedstock and solvent, reaction condition, solid loading etc... However, some similarities emerge: Hitzl et al. (2014) <sup>(120)</sup> conducted HTC experiments in an industrial plant for over two years using garden pruning as feedstock and obtaining a biocoal with very similar composition to this finding. Ash composition are summarized in the following figure:

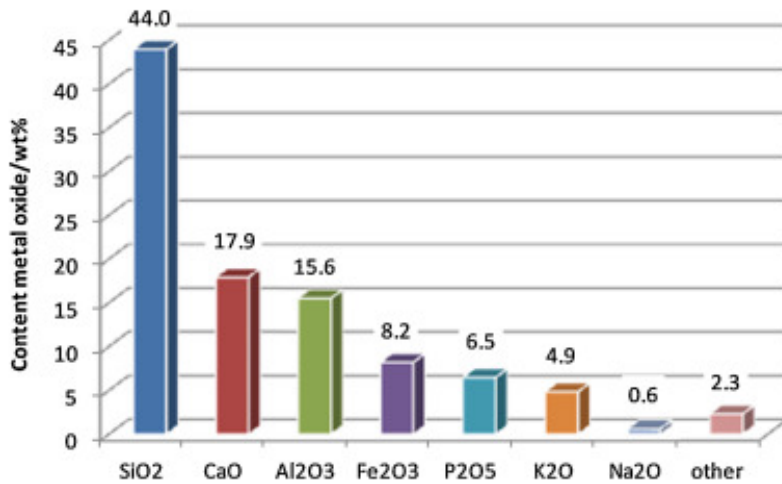


Fig. 26: Ash composition of garden pruning-derived hydrochar.

Reza et al. analyzed ash components after 230 °C HTC of, among other feedstocks, corn stover and rice hulls. <sup>(121)</sup> Predominant elements are Si and Ca.

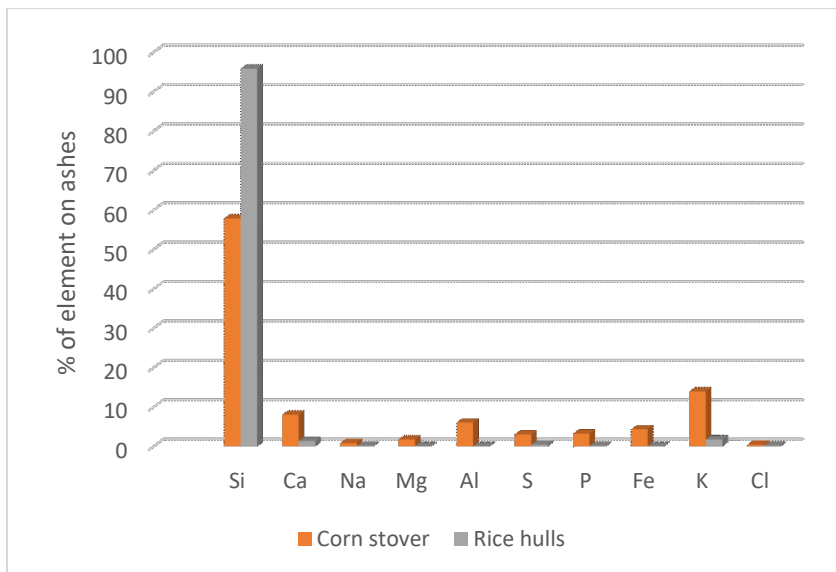


Fig. 27: Elemental ash composition of two feedstocks hydrochars.

Similar compositions to Hutzl study are reported on food waste-derived ashes by Smith et al. (2015); <sup>(122)</sup> Zhang et al. (2020) on rice straws found over 70 % silica, very little CaO and significant Al, K, P and Fe oxides, and comparable percentages when co-treat them with sewage sludge. <sup>(131)</sup> Instead, Lu et al. (2022) found that ashes of hydrochar from HTC treatment of lemon peel were composed mainly by CaO (48 %), Fe<sub>2</sub>O<sub>3</sub> (17 %) and SiO<sub>2</sub> (16 %); CaO predominance over silica is reported also by

Burguete et al. (2015).<sup>(129)</sup> The food-waste derived char ash of Wang et al. (2018) is even different as the elemental distribution is much more balanced: silica is still predominant but P<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O are significant.<sup>(130)</sup>

Since anthracite ashes consist generally and almost exclusively of SiO<sub>2</sub> and CaO in ratio 80/20 and other alkaline earth metals, plus all the ashes from the metal scraps, CaO (lime) is added in the furnace to maintain a certain pH level, reached with a lime – silica ratio of about 2.5. By adding 13 kg of hydrochar (9 kg \* *F*) for each ton of liquid steel, and assuming composition as reported by Hitzl, more ashes, more slag, and more lime are going to be present in the furnace. To investigate this amount, the quantity of ashes from 13 kg of char has been calculated (0.76 kg of SiO<sub>2</sub>, 0.31 of CaO and 0.65 of other) For the 2.5 ratio to be maintained, only silica and lime has been accounted as the third most important, aluminum oxide, has amphoteric behavior. To maintain the desired ratio and understand the amount of CaO to be added, the following calculation has been done:

$$Kg_{CHAR} * \%_{ASH} * \%_{SiO_2} * 2.5 - Kg_{CHAR} * \%_{ASH} * \%_{CaO}$$

resulting in 1.59 kg of CaO and an increase of ash in the furnace of 3 kg, or 2.5 % of the total slag present (assumed at 120 kg per ton of steel). But since 9 kg of anthracite and respective ashes are avoided, these must be taken off. In 9 kg of anthracite are present 0.11 kg of silica and 0.027 kg of lime: to reach the defined basicity 0,24 kg of CaO are normally added. To conclude, switching anthracite to hydrochar will increase the demand of lime for each ton of liquid steel of 1.34 kg, for a total of 2.65 kg of additional slag present in the furnace. Considering the average amount of slag in an EAF, this equals to an increase of 2.2 %, which could be acknowledged as manageable.

Sulphur is one of the undesirable elements in the steelmaking process, responsible for the formation of pollutant fumes like SO<sub>2</sub> in the EAF and its presence in the liquid steel has unwanted consequences. Desulphuration is therefore necessary to avoid the formation of sulfides like MnS during the cooling after the spilling, which gives steel different strength in transversal and longitudinal direction and fragility. It's carried out by adding CaO during the spilling and eventually in the ladle furnace, agitation with Argon is provided to enhance the kinetic of the reaction to form the so-called "synthetic

slag”: CaO switches an oxygen with a sulphur atom and becomes CaS. This element comes from the scrap metal charged in the EAF and from the coal added in there. Anthracite has usually less than 1 % of S in its composition, however, it’s quite certain that hydrochar (and generally all biocoals) contains less of it, sometimes at non-detectable levels. All hydrochars analyzed by Smith et al. (2015) contain maximum 0,2 % of S in the dry biomass, Reza et al. (2012) report as highest value a 3,5 % of the ash and Zhang et al (2022) found 0.32 % on d.b. <sup>(121)</sup> <sup>(122)</sup> <sup>(143)</sup> Sulphur, in fact, like many other elements, passes into the liquid phase during the HTC treatment

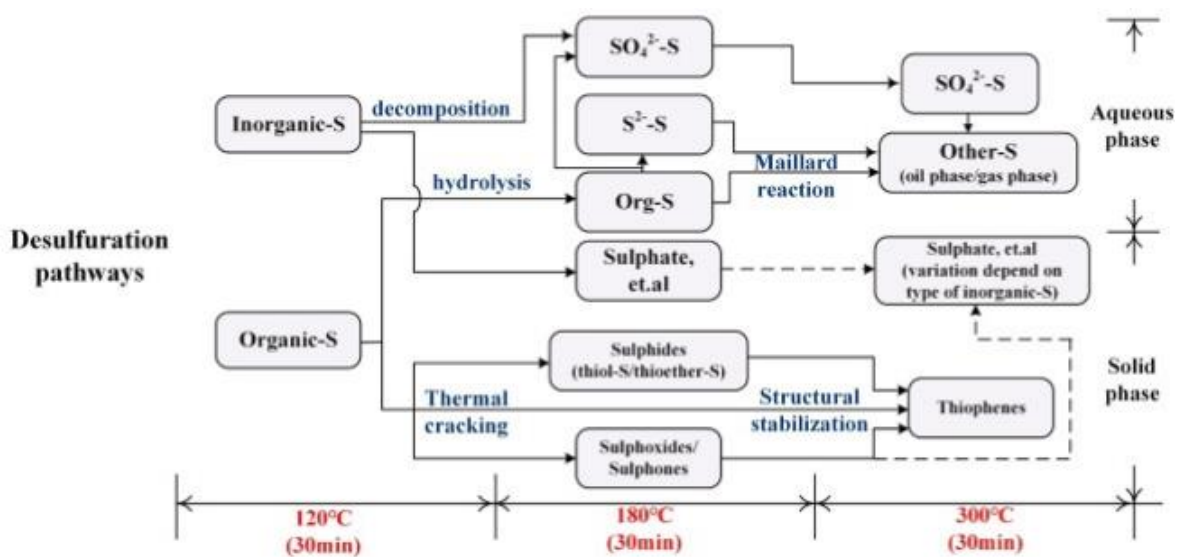


Fig. 28: The evolution pathways of S species in biowaste during hydrothermal process, from Zhuang et al (2018). <sup>(145)</sup>

Level of S is one of the main differences between hydrochar and low-ranking coal like lignite to which is often compared to. This property might be useful in steelmaking for both environmental (lower SO<sub>2</sub> in the fumes) and technical-economic reasons (less lime used and slag formation). To summarize, switching this type of hydrochar with anthracite should present an improving or, at worst, negligible effect from the point of view of sulphur.

Nitrogen is another critical element as it’s associated with poor mechanical qualities, and degassing units are employed to remove it from the liquid steel when high-quality steels are desired, by lowering the partial pressure of the target gas to remove (not

only N<sub>2</sub>, but also CO and H<sub>2</sub>) the solubility of the gas in the solution is lowered too, and it bubbles out.

Its expected level as seen in Table 16 is 3,4 % which is higher than the usual < 1 % of anthracite. During HTC reactions, part of the nitrogen content of the biomass passes into the liquid phase, with higher liquid fraction slightly related to reaction severity conditions, in the form of mostly ammonium ions due to the degradation of proteins. Nitrogen gets incorporated into the char matrix by cyclization or ring condensation, in forms such as Pyrrole-N, Pyridine-N, Quaternary-N, as studied by HTC treatment on food waste by Wang (2017).<sup>(146)</sup> It appears that, contrary to most of inorganic elements, a relevant part of nitrogen gets incorporated into the aromatic rings that constitutes the char, making its reduction partial and an eventual upgrading post-treatment challenging.

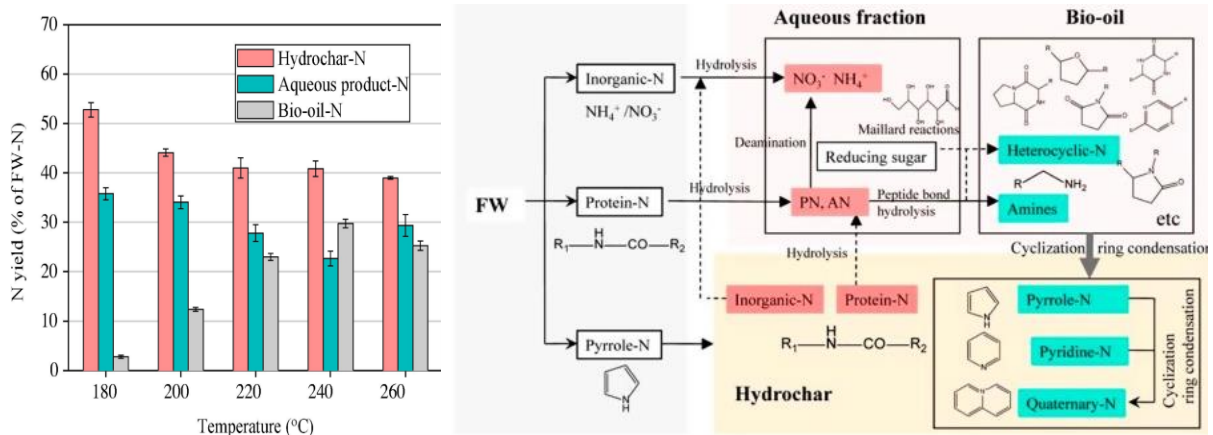


Fig. 29, 30: N yield in different phases (left) and evolution pathways during HTC (right).

Most of the nitrogen in the liquid steel comes from the scrap metals introduced in the furnace and to a lesser extend from air and anthracite; on the other hand, most of the nitrogen included in the charging/injecting carbon ends up in the liquid steel bath and minorly gets oxidized and becomes gas (NO<sub>x</sub> or N<sub>2</sub>O). The latter part is in any case a small percentage of the air volume present in the furnace cask and should therefore present little issues in subsequent fumes treatment. A more important issue is the part remaining in the liquid bath: nitrogen pickup of steel is to be checked with pilot test, as the issue is clearly present, especially for high-grade steel, but effects remain to be evaluated as the quantity involved are still relatively small.

### 3.6.8. HYDROCHAR UPGRADE

Since the economic advantage of hydrochar from co-HTC of food waste and digestate appears to be relevant, a significant “budget” is available, and it could be allocated to few additional processes or treatments to improve the biocoal characteristics without particular concerns.

Reducing moisture and ash content is very important for the proper functioning of the electric furnace. Some techniques may help in achieving a significant reduction and, since the hydrochar is comparable with lignite, its same proven method already employed by the industries to clean this kind of fossil coal can be exploited.

One option is to lower the pH in the reaction vessel: an acidic environment can solubilize many metal ions and so leave a char with less incorporated ashes in the matrix. The same principle can be applied at a later stage on the solid fuel: this is called leaching, and it can be both acid and basic, as the different conditions can solubilize different and more ash-forming elements. Common compounds involved are HCl, HF, HNO<sub>3</sub> and NaOH. This is particularly important for elements like nitrogen and phosphorous: their presence is associated with poorer steel mechanical properties like inter-granular cracking, non-metallic intrusions, and toxic gases formation. <sup>(129)</sup>

Steel et al. (2001) <sup>(132)</sup> investigated the chemical demineralization of bituminous coal with 7.9 % of ash content by employing a two stage treatment: first by employing aqueous HF and later HNO<sub>3</sub>, both for 3 hours and at 65 °C. With the first step ash was reduced to 2.6 % and after the second to only 0.6 %. The same author in another study reached under 1 % of ashes from a bituminous coal by using ferric ions in the second stages, derived from FeCl<sub>3</sub> and Fe(NO<sub>3</sub>)<sub>3</sub>. The second stage is useful not only to demineralize more elements, but also to eliminate some fluoride crystal that can form during the first treatment, like calcium fluoride. <sup>(133)</sup>

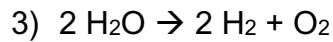
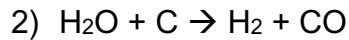
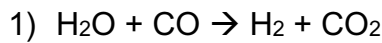
Mukherjee (2001) obtained a 50 % ash reduction from two Assam coals by employing a 16 % NaOH solution followed by a 10 % HCl solution at 90 °C. <sup>(134)</sup>

Given the aqueous environment where these reactions take place, it makes sense to add these steps before the filterpress or the subsequent drying stage of Fig. 24.

Moisture level is another parameter which may be necessary to lower compared to current industrial hydrochar-level, but it shouldn't be too challenging as it may only need higher retention time in the drier.



In the furnace water reacts mainly with carbon, carbon monoxide or undergoes splitting:



For all these cases hydrogen gas is one of the main product, an undesirable molecule in the EAF for its high explosivity. The threshold trigger is reached when about 10 % of the furnace atmosphere is composed of hydrogen, a significant level. Air volume in a medium-size electric arc furnace is 30 m<sup>3</sup>, so at least 3 m<sup>3</sup> must be present at the same time; accounting for the density of hydrogen at high temperature it means about 0.5 kg. H<sub>2</sub> comes mainly from water dissociation, and it weighs only 2 a.m.u. or 9 times less than a molecule of water. So, 4.5 – 5 kg of water and, in turn, 64 – 71 kg of hydrochar. Considering an EAF operating cycle with load of 130 tons, for a total coal input of 2.34 ton, 1.7 ton of hydrochar d.b. are expected to be present alongside 130 kg of water. Hydrogen is also another element which contributes to structural defects in the steel and given its low weight it's difficult to extract from the liquid bath, and strong vacuum chamber is necessary during the degassing phase. If water is injected together with the char into the lower part of the furnace it can form bubble of gas; pressure from above is high so it doesn't immediately rise and can therefore increase the pressure on the side of the furnace. When pressure is high enough, it burst suddenly to the surface, and this can cause problems in process management.

In any case some water is already present inside, as it is used to cool down the temperature of the electrodes, moreover, some hydrogen burns in the furnace, lowering its concentration, and some other gets aspirated by the suction hood. Risk could be managed especially if hydrochar is used as injection carbon as it can be inserted gradually and monitoring the parameters.

In any case, the lowest the water content, the better.

Much literature is available, as drying of high-moisture coal is a common problem in many countries. For example, Rao et al. (2014) <sup>(135)</sup> report the many methods that can be used, among which: rotary drying, fluidized bed, hot oil immersion, microwave irradiation, solvent extraction etc. Less water and ash will also raise the relative

content of carbon in the mixture, getting closer to high-grade coals. Another option among the thermal treatments is to pyrolyze the char: Garlapalli et al. (2016) conducted experiments consisting of applying pyrolysis of different temperature to hydrochar obtained by HTC of digestate at different temperatures. Even the mildest conditions induced a double digit increase in carbon content at the expense of hydrogen and above all of oxygen percentage, and HHV grew too. However, this approach present two issues: content of ashes increases substantially (but this as seen previously can be reduced later) and, more importantly, total mass yield plummets: by treating the feedstock at 220 °C during HTC and at 400 °C during pyrolysis, yield stands at 30.7 %. By analyzing Table 1 of the paper, it's possible to observe that a pyrolysis step at least halves the final product yield. This in turn means that more feedstock needs to be collected and treated. <sup>(136)</sup>

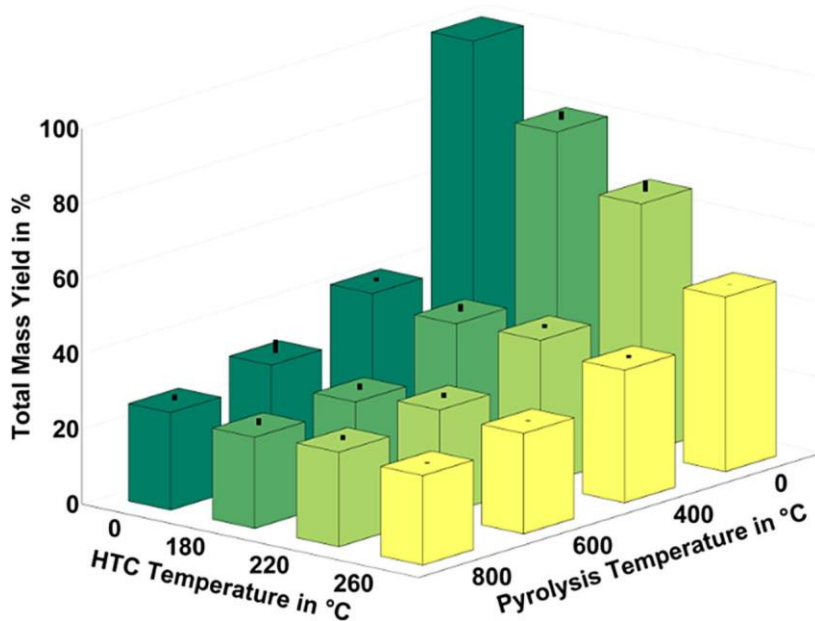


Fig. 31: Mass yield for combined HTC and later pyrolysis treatment of digestate at different temperatures.

Zhang et al (2022) <sup>(144)</sup> instead investigated the pyrolysis treatment of hydrochar obtained from kitchen waste (organic) of similar composition as the simulation of this study and a similar pattern emerges: lower solid yield, higher carbon and ash content, and formation of other by-product as typical of pyrolysis reactions like liquid tar and gas in greater quantities.

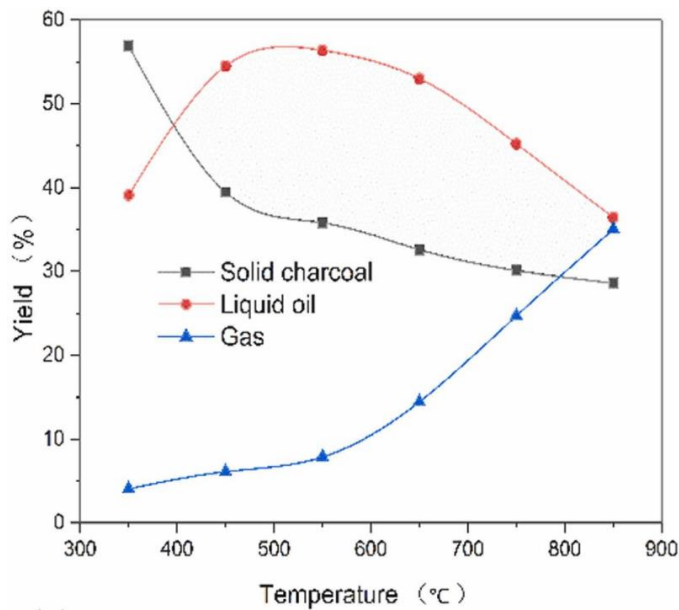


Fig. 32: By-product formation of pyrolysis of hydrochar from kitchen waste at different temperatures.

Another more immediate method to decrease the ash content and in parallel improving carbon purity and heating value is to employ only food waste in the HTC treatment: digestate-derived hydrochar is a low quality fuel and its co-reaction with food waste lowers the latter qualities proportionally to its mixing ratio. Even its substitution with untreated sewage sludge will deliver better result. However, digestate is available and unvalorized in large quantities at a location very close to ABS steel plant, and simply substituting this amount with food waste will surely have negative consequences as feedstock batches need to travel farther. Besides, since more food waste is to be acquired, the FVG regional quota seen earlier (page 60) will increase even more.

## 4. Discussion

Hydrothermal carbonization is an old technology that has been rediscovered as a tool to produce biogenic coal and curb carbon emission in the face of the climate emergency. This novel technology has been developed at industrial scale during the last 10 years and represents a very stable and simple process which simulates an accelerated process similar to the natural formation of coal. Among the many biomass-upgrading processes it has the unique advantage of working with high moisture feedstocks and produces a char with comparable characteristics to lignite. This renewed interest is exemplified by the number of studies and patents on the subject, strongly on the rise in recent year, especially in China. <sup>(149)</sup>

Microalgae grown on wastewater is one of these possible inputs, but the economic outlook looks grim as even accounting only for the operative costs and adopting highly productive strategies, the resulting hydrochar price is several times the price of the anthracite. Blowers power use to aerate the growth medium are the major obstacle to the sustainability of this option. Unless major breakthrough in algal technology is achieved, a system designed to produce high-quantity low-value commodity such as coal is unlikely to succeed at medium term, even in the face of higher ETS\* price.

The option to employ other waste streams such as food waste and digestate appears more interesting: a substantial economic advantage is expected over the use of fossil anthracite, as ETS are no longer purchased and disposal of this kind of waste generate substantial revenues. Even assuming very low disposal compensation the system shows competitiveness. It has been noted that the second method used to estimate the hydrochar properties (the regression method) is quite valid to provide composition values, whereas the second method (the software) seems to forecast better accuracy for the yield, even accounting for the process water recirculation effect.

The synergies between this process and the steel industry are very positive: one of the biggest expenses (and carbon emission sources) of the traditional HTC treatment is the heat supplied to the reactor, which can be substituted by the abundant waste heat generated in a steel plant. The quality of the hydrochar obtained is inferior to the high-grade coal typically employed in an EAF, but not by a huge gap, and post-treatment upgrades to lower ash and moisture are possible and generally well

understood. The nitrogen content is probably the biggest issue and pilot trials are needed to understand exactly how it affects the steel quality and eventually how to lower it. Another issue might be represented by the large feedstock required to generate significant amount of hydrochar: an Italian region of more than a million inhabitants produces yearly little more than double the required food waste to substitute half of the coal in a medium-size steel plant. Securing the supply does not seem a trivial task, although the economic incentive by this unique upcycle should enable the steel manufacturer to outcompete other waste treatment companies. Not only the end-product is better valorized than in today widely popular composting plants, but less pollutants and GHG are formed for the disposal of the waste. Furthermore, the major by-product of the process is beneficial for another sector like agriculture as it acts as a fertilizer, reducing the consumption of traditional ones, mostly made by fossil-fuel.

If this new 50-50 anthracite-hydrochar blend is adopted, the theoretical carbon dioxide reduction is substantial, decreasing by around 30-35 % a typical EAF carbon footprint.

The whole process fits very well on the pathway to a clean circular economy and EU policies support the construction of HTC plants with: <sup>(150)</sup>

- EU Circular Economy Action Plan <sup>(151)</sup>
- Waste framework directive <sup>(152)</sup>
- Waste landfilling
- Sewage Sludge directive 86/278/EEC
- EU climate action <sup>(153)</sup>

## 5. Conclusion

To summarize, the main findings are:

- The hydrothermal carbonization process (HTC) offers a unique way to recover materials from organic wastes which are otherwise difficult and expensive to be valorized. The products generated within the HTC treatment can be adapted to the industry's requirements by applying further post-treatments, enabling many industries and in particular steel plants, to substitute fossil coal, reducing the CO<sub>2</sub> emissions and encouraging circular economy.
- Two waste streams have been analyzed to be transformed into a char that could substitute half of the coal consumption in an EAF: microalgae and a mixture of food waste and digestate.
  - The first stream does not appear sustainable economically at the moment, nor in the foreseeable future. In fact, to produce a ton of hydrochar capable of substituting an equivalent amount of anthracite, operative costs range between 1'069 and 3'811 €/ton.
  - The study of the second stream instead highlights its feasibility from an economic perspective, the main findings summarized in:
    - 13'060 tons of hydrochar production with 63.4 % carbon content at a cost of 94 €/ton, capex included.
    - 137 €/ton of production cost for an equivalent amount of standard anthracite.
    - 467 €/ton of net gain from the hypothetical coal-char switch, if only carbon content is taken in consideration.
    - 6'048 tons of digestate and 54'569 tons of food waste are disposed.
    - Some perplexities from the technical part remains given the different chemical composition, in particular the nitrogen content for the possible effect on steel quality, to be further investigated.



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