BIOMASS CARBONIZATION IN FIXED-BED OXIDATIVE REACTOR: EXPERIMENTAL CAMPAIGN AND TECHNOLOGICAL DEVELOPMENTS

PhD THESIS

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Biomass carbonization in fixed-bed oxidative reactor: experimental campaign and technological developments

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To the person who has driven me in making charcoal.
My grandfather Angiolino,
the best charcoal maker of Montemaggio.
You are still alive in me, although I never knew you.

Alla persona che mi ha portato a fare tutto questo
Mio nonno Angiolino
il migliore carbonaio di Montemaggio
Ti porto sempre nei miei pensieri, sebbene non ci siamo mai conosciuti.

Declaration

I hereby declare that this submission is my own work, and to the best of my knowledge and belief, it contains no material previously published or written by another person, nor material which to a substantial extent has been accepted for the award of any other degree or diploma at University of Florence or any other educational institution, except where due references are provided in the thesis itself.

Any contribution made to the research by others I have been working with is explicitly acknowledged in the thesis.

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Me & Carbo during a daily work in NBM's premises

Me and my colleagues Andrea, David and Edoardo after long-day of successful test 12

(Marco e Renato weren't there but they were contributing with their joy)

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%wt	Weight percentage
ar.	As received
db.	Dry basis
AC	Alternate Current
ad	As determined
AFT	Adiabatic Flame Temperature
AIT	Auto Ignition Temperature
daf	Dry ash free
CAD	Computer Aided Design
CFD	Computational Fluid Dynamic
CO	Carbon Monoxide
DRE (or DE)	Destruction Removal Efficiency (or Destruction Efficiency)
EBC	European Biochar Certificate
ER	Air-fuel equivalent Ratio
EU	European Union
GHG	Green House Gas
GWP	Global Warming Potential
HP, HT	High Pressure, Temperature
HR	Heating Rate
HHV	Higher Heating Value (MJ/kg)
LHV	Lower Heating Value (MJ/kg)
IBI	International Biochar Initiative
LT	Low Temperature
LEL	Lower Explosive Limit
LOC	Lower Oxygen Concentration
LPG	Liquified Petroleum Gas
Mtoe	Million ton of oil equivalent (1 kg oil equivalent = 41.87 MJ)
NO_x	Nitrogen Oxides
RPM	Revolutions per Minute
UHC	Unburned Hydrocarbons
Wb	Wet basis
SV	Superficial Velocity
VOC	Volatile Organic Compound
UEL	Upper Explosive Limit
TLV	Threshold Limit Value

Summary

Nowadays charcoal can be considered an important vegetable solid matter product due to its large use in various markets, not only as a fuel in domestic cooking but also used for metal refining or solid amendment, and to produce high-value products, such as activated carbon, silicon and chemicals.

Biomass carbonization is the process of converting solid, lignocellulosic biomass into charcoal; it is currently operated at several scales, encompassing manual, rudimental batch methods and industrial, continuous systems, with reported throughput up to several tens of thousands ton per year. Reported yields range from 8-12% for traditional kilns, 12-17% for brick kilns, 14-20% for standard industrial facilities and 25-33% for advanced industrial processes [1]. A major concern with charcoal production facilities is related to volatiles released in the atmosphere: while larger plant operates either a post-combustion of the volatiles or recovers the organic compounds that are being produced, smaller and more rudimentary systems directly vent the off-gases, generating plenty of harmful emissions, e.g. product of incomplete combustion, and greenhouse gases. Along with improper post-harvest land and forest management, these emissions represent the main environmental impact of charcoal manufacturing in traditional systems.

The lack of coherent, sustained and secure supporting schemes for power generation from biomass can be regarded as an opportunity to promote the transition from energy to bioproducts in the conversion of biomass, and open new business prospects, independently from subsidies and feed-in tariffs. With this aim, since 2013 RE-CORD has been developing an innovative biomass carbonization process (CarbOn,

patent issued) for the small-to-medium sized forestry enterprises and is currently operating the first pilot plant, rated for a capacity of 50 kg/h and built from its proprietary layout.

The CarbOn pilot plant is a continuous biomass carbonization system based on open top, downdraft technology, operating in oxidative pyrolysis in the temperature range of 500 – 650°C and equivalence ratio (ER) between 0,1-0,2. The pilot is essentially composed of three sections: (1) loading and conversion of biomass; (2) charcoal discharge and cooling system; (3) extraction and combustion of pyrolysis vapours. The plant, made in stainless steel (AISI 304 and 316) and supported on a self-standing 6x2.5m structure, operates with biomass up to 20 %wt. moisture content.

The significance of the present work for the scientific community lies in having shown that high quality charcoal can be produced continuously in a cost-competitive, energy efficient and environmentally friendly pilot unit, even at small scale.

The first chapter offers a complete a state of the art on lignocellulosic biomass carbonization process as well as a pyrolysis vapour characterization based on existing literature experimental works. Principle information regarding environmental aspects and sustainability related to charcoal manufacturing, uses and charcoal characteristics and qualities are provided.

In the second chapter, it is explained in detail functioning and design of the CarbON pilot unit and are also reported the two most representative tests which validated the process. Some preliminary useful observations are described in order to design an industrial demo plant based on the same technology.

In chapter three is reported the experimental campaign were two different woodchips were used and where a full characterization of the input/output unit was carried out as well as vapour pyrolysis were sampled and compared to other experiment operating at similar condition. Conversion efficiency was measured by means of char samples characterizing and taking in to account test reactor temperature profile.

Using the data based on experimental tests, in chapter four, is evaluated the mass and energy balance of the technology. Based on test result, it has been investigated the combustion of pyrolysis vapour as well as VOC incineration, in view of design an industrial demo carbonization plant of 250 kg/h capacity. A complete system solution has been proposed with a layout and process scheme. Finally, an economic scenario of a possible adoption of the demo unit coupled with a SRF plot was studied to estimate the investment profitability.

Figure 1. Wood burning into the CarbON reactor (view through lateral flange)

1 From wood to char

1.1 Introduction

Global energy consumption have been constantly growing for a century and it is expected to grow parallel to the global population, that is expected to rise 9 billion in 2040, compared to about 9 billion in 2010 [2]. Nowadays, the challenges of building infrastructures to match the global needs for energy, mobility, housing and food are huge, and none of these challenges can be met without energy, whose demand will consequently grow. The energy needs are mostly covered resorting to fossil fuel with well-known environmental problems. In this scenario, pollution and greenhouse gas emissions remains the most serious issue, and global trends should be addressed towards cleaner electricity and higher energy efficiency.

Among the renewable energy sources, biomass is free from fluctuation of energy production with the time and can be stored as fuel, thus it is the only choice for sustainable fuels and chemicals production [3]. The world’s current infrastructure for these commodities is optimized around the production, distribution, and use of liquid hydrocarbons derived from petroleum. Producing liquid fuels and chemicals from alternative resources would not only reduce dependence on global fossil fuel reserves and potentially decrease greenhouse gas emissions, but will also have the benefit to allow the continued use of the existing infrastructure [4].

1.2 Lignocellulosic biomass as a feedstock

According to the RED, Renewable Energy Directive [5], with the term biomass is indicated the biodegradable fraction of products, waste and residues from biological origin, agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste.

Considering this so wide definition, a large variety of biomass types exist, but the one that has far more been exploited by mankind, due to its large availability, is the lignocellulosic biomass. In this particular kind of biomass, as well as in other types, i.e. green plants, the sunlight energy is stored in the form of chemical energy via photosynthesis [6]. The overall chemical reaction can be simply expressed as follows (in this example glucose is the product) [7]:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + O_2 \qquad (1)$$

Woody biomass, in general, is divided in two categories: hardwood and softwood. Actually, this distinction has to do with plant reproduction and not with the hardiness of the plant’s wood.

Lignocellulosic biomass, or wood, is an anisotropic porous material with different thermal and mass transfer properties in the radial, tangential and longitudinal direction. Its basic structure consists of three main components: cellulose, hemicelluloses and lignin; also extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash, and other compounds can be present.

Cellulose is the most abundant component of woody biomass as it constitutes the basic compound of cell walls and it can reach 48% wt. (dry and ash free basis) of wood. It is a linear polysaccharide composed of repeating anhydro-glucose units held together in a giant straight chain molecule [6].

The second major chemical species in wood are the hemicelluloses as they constitute the 24-35% wt (dry and ash free basis) of wood. They have a random amorphous structure composed of polysaccharides and monosaccharide units. Due to the amorphous morphology, they are partially soluble in water [6].

Lignin, being one of most abundant organic compounds on Earth after cellulose and chitin, is the third main chemical constituent of lignocellulosic biomass and it constitutes the 16-33% wt. (dry and ash free basis) of wood. Lignin is an integral part of the cell walls of plants, it holds the wood cells together and provides the extraordinary composite strength characteristics of wood. Lignin is a complex, high molecular weight polymer. It is relatively hydrophobic and aromatic in nature. Lignin plays a crucial part in water transportation in plant stems [6].

Biomass can be directly burnt to produce thermal and/or electric energy or can be processed by means of several conversion routes to produce biofuels or bioliquids. According to the RED, biofuels are defined as liquid or gaseous fuel for transport produced from biomass, whereas ‘bioliquids’ means liquid fuel for energy purposes rather than for transport, including electricity, heating and cooling, produced from biomass [5].

1.2.1 Biomass combustion for heat and power generation

Combustion is the first biomass energetic exploitation that mankind has ever experienced. The transition from passive to active use of fire had started somewhere between 500 and 300 thousand years ago and it marked the first great act of human interference with nature [8].

Biomass oxidation can be effectively considered as a thermochemical conversion process but, unlike in gasification, pyrolysis and hydrothermal processes, its main purpose is to produce heat and not a biofuel or a bioliquid, i.e. it is meant to totally transform the chemical energy of the organic material into thermal energy.

Biomass combustion is widely used for a large variety of applications: from log-fed stoves for domestic heating to large-scale steam-cycle power plant in the range of 100-3000MW. One of the best way to exploit biomass by means of combustion is co-firing in coal-fuelled power plant, in this way high conversion efficiency is possible with relatively low economical efforts [9]. Overall efficiencies to power tend to be rather low at typically 15% for small plants up to 30% for larger and newer plants [10].

There are five main steps which the biomass particle evolves during its oxidation: firstly, the organic matter heats up and loses its water content, then, as the temperature rises, devolatilization or pyrolysis starts and almost 80% of the particle’s mass vaporizes. As temperature increases part of the tarry vapours and the remaining solid biomass undergo homogeneous and heterogeneous gasification reactions, respectively, and, finally, residual charcoal and gas phase oxidation occur. These phases can be individuated by a thermo-gravimetric analysis (TGA) and its derivative which monitor the weight loss of a combusted sample.

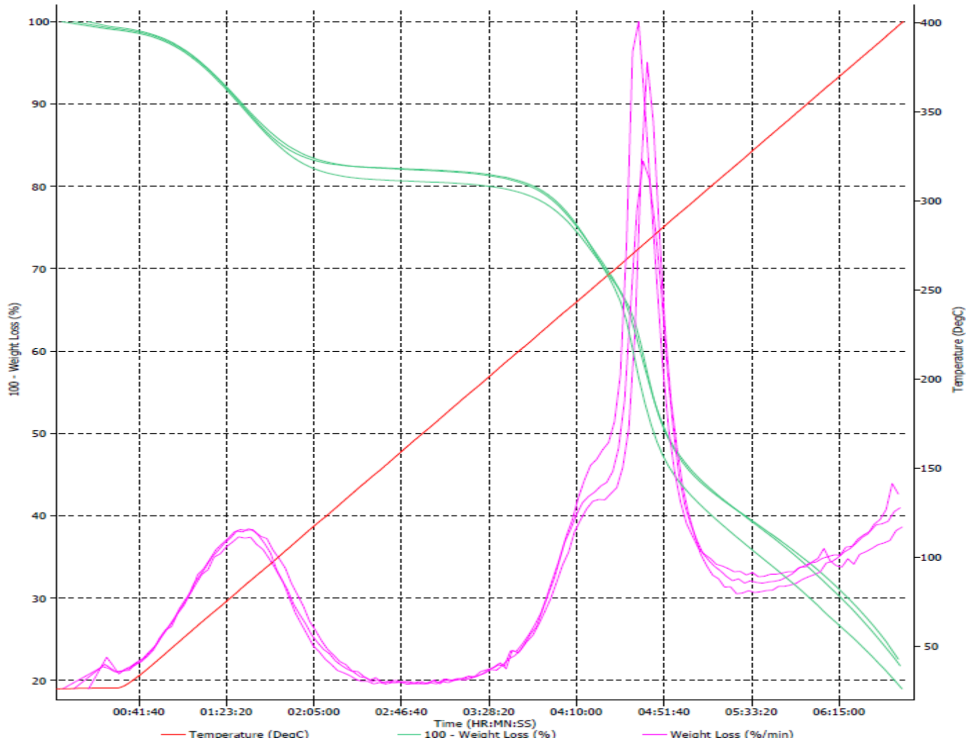

Figure 2. TGA at 1°C/min heating rate in oxidative ambient of 1.5 mg chestnut wood sample used during the carbonization tests

There are some drawbacks related to biomass combustion system with respect to solid fossil fuel like coal. Usually biomass has a considerable amount of absorbed/adsorbed water, which limits flame temperature and leads to higher flue gas volume, requiring a larger combustion chamber (with increased thermal inertia) and larger flue gas conditioning system. Furthermore, the inorganic elements that are present in the feedstock can form low-melting compounds, which, in addition to cause pollution, can sinter and deposit on surfaces, causing corrosion and combustion instability. The availability and sustainability of biomass supply is a very relevant issue, but not often it is taken in great consideration [11]. The power plant throughput should be designed in function of the locally available biomass and careful attention must be paid to ensure the continuous functioning of the facility

Fixed beds are absolutely the most widely adopted combustors as, in general, they can burn variable size feedstock with relatively high moisture and ash content. Usually they perform a two stages combustion: primary air flows through the biomass bed, carrying out drying, gasification and residual char oxidation, while combustion of gaseous products is obtained in a separated chamber by means of secondary air injection. The primary air is added in sub-stoichiometric amounts in order to achieve massive devolatilization and shift the majority of the oxidation reactions to occur in a homogeneous gas phase [12].

Fluidized bed combustors have limited flexibility as far as biomass size and impurities are concerned, but, due to their extremely high mixing action and heat transfer, combustion efficiency is enhanced and the amount of unburnt fuel is reduced. Because of their long start-up time and limited partial load operations, fluidized bed has been adopted for larger-scale plants: up to 100 MW and 300 MW in co-firing [13].

Pulverized bed is the combustor design which requires the most severe pre-treatment of the feedstock: biomass particle size should be less than 2 – 5 mm, in order to reach the desired bed suspension, and ash and moisture content should be lower than 2 and 20 %wt, respectively [14]. However, high efficiency is reached and low excess air are possible, leading to low NO_x emissions [13].

1.3 Thermochemical conversion of biomass

There are at least three main conversion technologies to exploit biomass as renewable source. Except for direct combustion process already described in the previous paragraph, thermochemical and biochemical processes provide multitude options to address the more efficient technology depending on boundary condition.

Biochemical processes, convert biomass using bacterial micro-organisms or organic enzymes for carrying out reaction, which can be very complex and usually occur at low temperature. Typical biochemical processes are: anaerobic digestion, fermentation and transesterification.

Thermochemical processes for the conversion of biomass are those technologies that involve use of elevated temperatures to feed the process. The energy necessary to reach and maintain the temperature of the system is supplied from external sources or from the combustion of part of the biomass itself. These thermochemical processes are: torrefaction, pyrolysis (fast, intermediate and slow), gasification and hydrothermal degradation (carbonization and liquefaction).

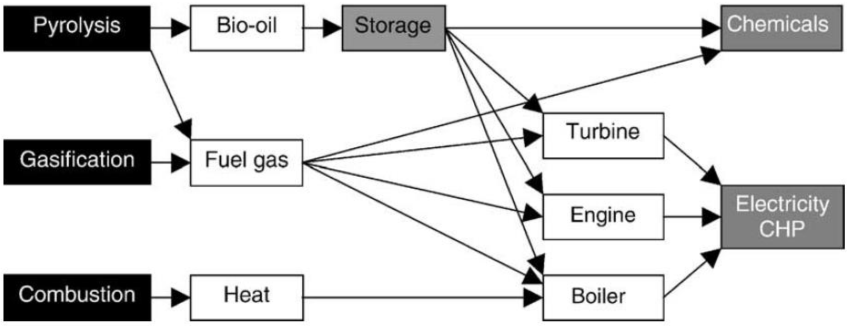

Figure 3. Products from thermal biomass conversion [10]

1.3.1 Gasification

Biomass gasification is a process where the organic material is converted into fuel gas at relative high temperature by partial oxidation to avoid complete combustion of the feedstock. Gasification is an endothermic process and requires an oxidising agent to occur, such as air, oxygen or steam. Heat is needed to dry inlet biomass, devolatilize though pyrolysis, to drive some solid-gas reaction and to compensate for heat losses though the reactor wall. Generally, heat is internally provided by partial oxidation of the biomass, but more complex external heating systems, which use heat exchangers or hot CO_2, exists. The producer gas generated is a low heating value mixture of carbon monoxide, carbon dioxide, hydrogen, nitrogen, methane and other low molecular weight hydrocarbons. Basically, the gas composition is influenced by many factors such as feed composition, water content, reaction temperature, and extent of oxidation of the pyrolysis products. However, the producer gas is contaminated with several compounds that need to be removed, accordingly to the end-use of the gas itself, by means of traditional cleaning methods (filtering, scrubbing and reduction). The most critical pollutant, tars are formed due to the not properly conversion of the liquid products. They are a complex mixture of substances ranging from mixed oxygenates to large PAH and are defined as compounds with molecular weight greater than of benzene. At temperature below 350°C [15] they start to condensate into sticky substances, causing filter and clogging, deposits, combustion problems and catalyst poisoning. Typical cleaning methods are condensation followed by physical removal and catalytic or thermal cracking.

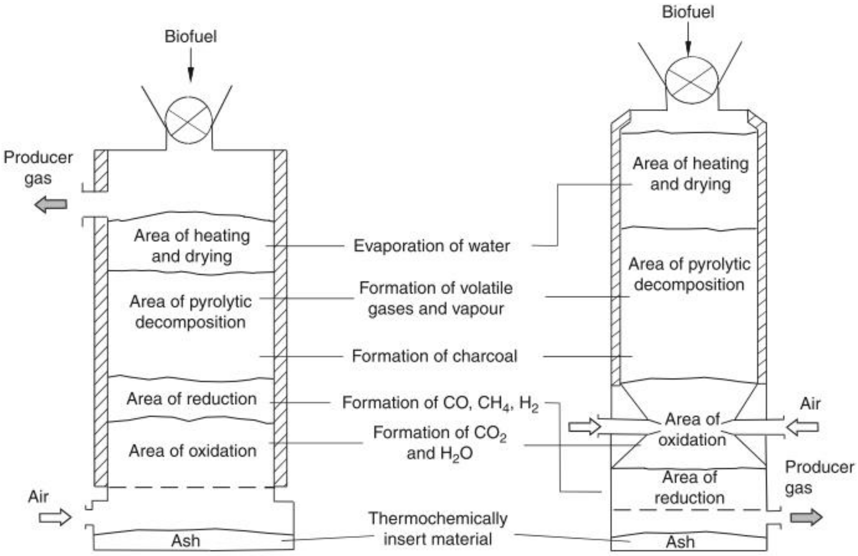

Figure 4. Fixed bed reactors: left updraft, right downdraft [16]

There are many several types of reactor depending the size and the configuration. The main distinction can be done between fixed bed and fluidized bed. Fixed beds are the oldest kind of reactors that have been adopted for gasification, the conversion steps occur at distinct different heights, depending on the reactor design, and therefore, temperature profile is not homogenously distributed. Among all the fixed bed reactors, another sub-definition is regarding the gas flow direction through the bed and the most used designs are downdraft and updraft.

Although, biomass gasification industry has limited operating experience and limited confidence in the technology [10], today, this technology is largely used mostly in small scale application.

1.3.2 Torrefaction

Torrefaction is process where biomass is heated at temperature between 200 and 300°C, in absence of oxygen for a long residence time. During torrefaction, the fibre structure of biomass material is destroyed through the breakdown of hemicellulose and to less cellulose molecules, so that the material becomes brittle and easy to grind. The material then changes from being hydrophilic to becoming hydrophobic. Although the weight loss is about 30%, the energy loss is only 10%. The main product is the solid, torrefied biomass. With the removal of the light volatile fraction that contains most of the oxygen in the biomass, the low heating value of torrefied biomass is 18–23 MJ/kg dry [17]. The mass and energy in the torrefied biomass is preserved in the solid product for a long time, as the material does not degrade with time. During the torrefaction process a combustible gas is released (about 15% wt.), which is utilised to provide heat to the process.

1.3.3 Pyrolysis

Pyrolysis is thermal decomposition occurring in the absence of oxygen at near atmospheric pressure and in the temperature range between 300 and 600 °C. It is always also the first step in combustion and gasification processes where it is followed by total or partial oxidation of the primary products [10]. It is a versatile thermal conversion technology, which produces a range of products: a solid (char), a mixture of non-condensable gases (CO, H_2, CO_2, CH_4 and higher C_2+) and condensable vapours resulting from the thermal fragmentation of the feedstock constituents, which, once condensed, form the biocrude or bio-oil. Operating conditions, mostly in terms of residence time, temperature and heating rate, affect the yield, quality and relative number of products: longer residence time, slow heating rate and low temperature promote the production of charcoal, short hot vapor residence time and moderate temperature in combination with high heating rate lead to high liquid yield, longer residence time and high temperature increase the non-condensable gas fraction. Relatively, to final scope and process condition of pyrolysis process, this can be divided in: (1) fast, (2) intermediate, and (3) slow. The latter is also traditionally called carbonization process.

Table 1. Thermochemical conversion process type:
typical process parameters and yields for biomass [10,18]

	Fast pyrolysis	Slow pyrolysis	Gasification	Torrefaction
Temperature	~500°C	>400°C	600-1800°C	<300°C
Heating rate	Fast/ up to 1000°C	< 80°C	-	-
Reaction time	Few seconds	Hours - days	-	< 2 h
Pressure	Atmospheric (and vacuum)	Atmospheric (or elevated up to 1MPa)	Atmospheric / pressurized up to 1MPa	Atmospheric
Medium	Oxygen-free	Oxygen-free / Oxygen limited	Oxygen limited	Oxygen-free
Liquids (bio-oil)	75 %	30 %	5 %	5 %
Non-condensable gases	13 %	35 %	85 %	15 %
Char/solids	12 %	35 %	10 %	80 %

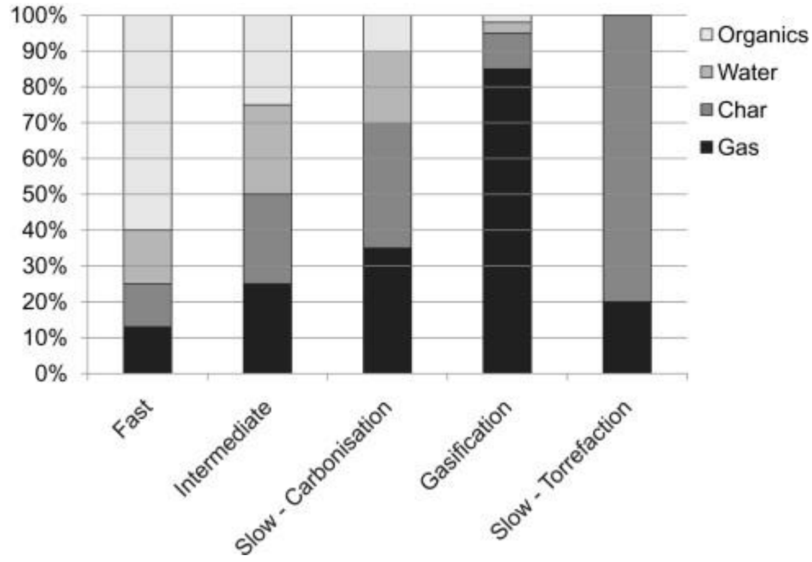

Figure 5. Products yield according to the type of pyrolysis [19]

In Table 1 and Figure 5 are reported product yields and process parameters relatively to the diverse types of pyrolysis in comparison with gasification and torrefaction.

Pyrolysis is considered the main step in thermochemical process, which occurs within almost all processes also in combustion, is also true that studying and modelling pyrolysis is not a trivial pursuit and is common to find in literature plenty of experimental study.

Since the aim of this work is to experimentally study and characterize carbonization, pyrolysis is described in the next paragraph 1.4 focussing on processes which maximize char content in final product.

1.3.4 Introduction to biorefining

Nowadays, thermochemical conversion of biomass can be seen in a wide context which is called the biorefinery concept. IEA Bioenergy Task 42 has developed the following definition:

Biorefinery is the sustainable processing of biomass into a spectrum of marketable products and energy [20].

More general, the biorefinery (or also thermochemical biorefinery), can be considered as a facility that processes and converts biomass into several marketable products, emphasizing fuels and chemicals production [21]. The goal is to obtain a no-waste self-sustainable industry. These infrastructures could constitute the focal point of different industrial sectors, being at the convergence of various scientific fields and market segments. Notably, petrochemical and chemical companies, automobile makers, electronic appliance and portable device makers, food companies and agricultural companies are all poised to be affected by the new technology paradigm [22].

Biorefinery considers, therefore, several possibilities to convert biomass into bio-products via combinations of different processing technologies, including biochemical and thermochemical processes. Biorefinery concepts can be classified according to platforms, products, feedstocks and processes. Intermediates from biomass can be substances such as syngas, biogas, sugars, lignin, and bio-oil. These intermediates constitutes the building blocks for the final products of the Biorefinery, including fuels, chemicals and value-added materials [23].

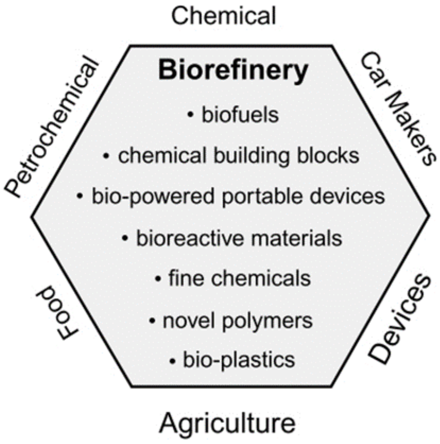

Figure 6. The biorefinery concept: marketable and related industries [22]

1.4 Carbonization as slow pyrolysis

Carbonization is a well-known process that allowed humans to produce charcoal, the first biofuel that has been used by humans to step out of the stone-age by refining ores into metals. Carbonization represents the commercial name of the process which is chemically identified as slow pyrolysis or dry distillation. In slow pyrolysis process, the residence time of the feedstock goes from 1-2 hours up to 2-3 days. With this high solid retention time, secondary reactions of condensable vapours cracking take place, thus largely reducing the tar content in the end products (even more reduced at temperatures higher than 600°C). The carbon content of the obtained char is very high (up to 85-90 %wt.), while a small amount of pyrolysis vapours mixed with gases is produced. Charcoal, acetic acid and pyrolysis gases are the end products of this process [24].

Slow pyrolysis steps can be resumed as follow [25,26]:

- 20 – 110°C: drying and pre-heating of biomass. Temperature remains constant at 100°C until moisture is evaporated;
- 110 - 270°C: thermal decomposition starts gradually with release of gas (CO and CO_2) and condensable gases;

- 270 – 290°C: starting of endothermic decomposition, with spontaneous generation of heat and increasing of gas and vapour release;
- 290 – >400°C: decomposition of biomass continues, with larger tar production.

Pyrolysis gas produced is composed mainly by CO2, CO, CH4, minor quantities of H2 and hydrocarbons. Such as for every pyrolysis process, liquid phase produced is plenty of various compounds and yield varies depending on operative process parameters: temperature and residence time. Liquid phase is also composed of oxygenated compounds and a certain quantity of water formed during the dry distillation as well as resulting from wood moisture content [27]. Pyrolysis vapour produced during thermal degradation of wood, is subjected to secondary cracking reaction when in contact to hot char surfaces, generating secondary char and gas [28]. For this reason, in order to limit tar production and avoid facing any problem in handling tar, is better to design the reactor to maximize gas travelling time through hot char.

The solid output residue of slow pyrolysis of lignocellulosic biomass is charcoal, which has a fixed C content around 60 – 90 % wt. and the rest is inorganic matter formed by ash and organic compounds [24]. Charcoal is a bright dark solid fuel, similar and lighter than coke and with cellular morphology described and compared to carbon foams.

Heating value of wood charcoal is normally around 28-30 MJ/kg and bulk density between 106 and 190 kg/m^3. Specific heat at ambient temperature is around 670 – 1350 KJ/kgK, while at temperature of 800°C it is rated 100 – 3000 kJ/kgK [28]. According to Byrne and Nagle, charcoal is 82% of the bulk density of the precursor wood and it is 28% stronger [29].

Carbonization efficiency and char properties are strictly related to process parameters, type of reactor and physical properties of the feedstock itself. In general, carbonization efficiency, express as char yields on dry matter, can vary from 8-12% wt. for a traditional process, to up to 25-33 % wt. for advanced systems [30].

Considering carbonization of cellulose, which is the principal component of woody biomass, Antal calculated the maximum char yields obtainable derives directly from the following stoichiometric formula:

$$C_6H_{10}O_5 \rightarrow 6C + 5H_2O \quad (2)$$

This means, that the char yields is 44.4% wt. (only carbon) and considering a high quality char which contains about 82% of fixed C, the max charcoal yields is about 54% [31]. This limit leads to consider that there is still a wide gap in technology in term of conversion efficiency.

Charcoal yield seems to be independent to wood specie utilized despite some studies affirm that softwood has a slight higher conversion efficiency due to the higher lignin and resin content. Basically, biomass with higher lignin content has a high char yield. Wood specie influences properties of charcoal obtained. Char produced from hardwood biomass, is more hard, resistant and bulky and it burns slowly with slow pollutant emissions. Charcoal from softwood, on the other hand, is more friable, burns at higher temperature and it is easy to ignite [28].

1.4.1 Influence of process parameter on char properties

Charcoal is composed by fixed carbon, volatile matter and ash. Its quality is essentially related to the fixed carbon content, since it means a higher heating value. Fixed carbon represents well the main quality to be taken in account to compare processes and it can be expressed with the following formula:

$$\%fC = 100 - \%m_{VM} - \%m_{ash} \quad (3)$$

Peak temperature, that is the maximum temperature reached into the reactor, largely controls quality and other properties of char. In Figure 7 are reported trends (all values are approximate) of many important properties.

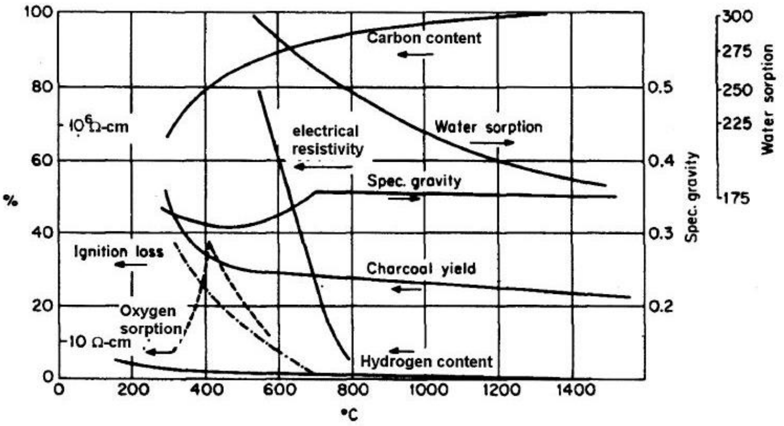

Figure 7. Temperature effect on char properties [32]

Higher peak temperature increments carbon content and heating value and char is also energy densified with advantages in term of transportation and storage. Lower temperature, instead, increases char yield and for this reason in an industrial process is important to adopt a compromise.

Heating rate is a crucial parameter because is related to reactor size and capacity, as well as, the residence time and to the conversion efficiency. Many experimental studies [28,33,34] have shown that a slow carbonization process associated to a low heating rate allows to increase up to 10% wt. db. and char results more hard and heavy.

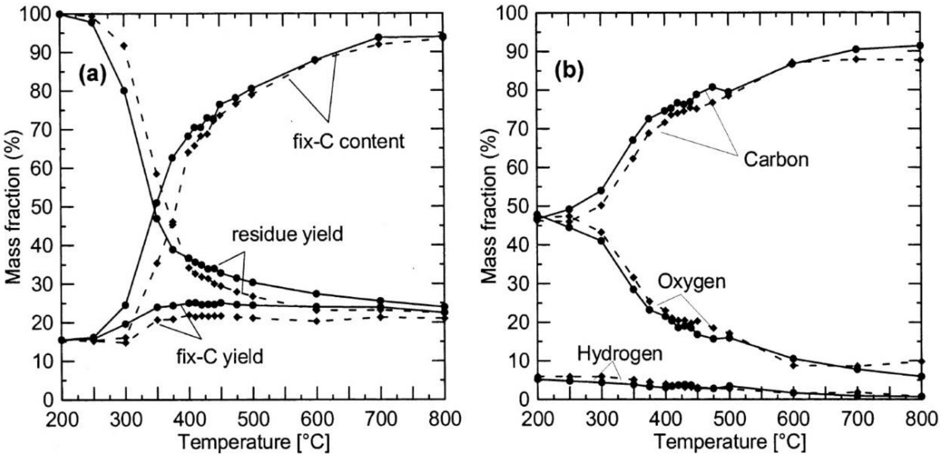

Figure 8. Heating rate and temperature effect on charcoal properties resulting from Antal's experiment on beech wood [1] [28]

Cracking of particles effect is well known in pyrolysis process and this happens at high heating rate. Byrne and Nagle [29] demonstrated that below 15°C/min fibres cracking disappeared or is very limited.

Size of wood particles has a significative effect on char yield for temperature up to 520°C [28]. Larger sizes increase the residence time of vapour into the particle itself with grater possibility of secondary tar reaction with char formation, however, it would be necessary to increase residence time to transfer uniformly heat into the wood piece.

Gas flow or superficial velocity (SV) inside the reactor has a negative result on char production. Slow flow increases the interaction time between vapour and solid phases allowing to favourite secondary cracking reaction with char deposition. This effect is

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[1] The solid and dashed lines represent heating rates of 2 and 10°C/min respectively

more amplified for pressurized carbonization. Mok and Antal observed a char yield growth from 12 to 22 %wt. of cellulose carbonization, increasing pressure from 0.1 MPa to 2.5 MPa at low flow gas [35]. Basically, at high pressure pyrolysis vapour has a smaller specific volume and of consequence the residence time into the wood piece is longer, increasing secondary char formation. In Figure 8 is reported the effect of flow gas and pressure on char yield measured by Antal.

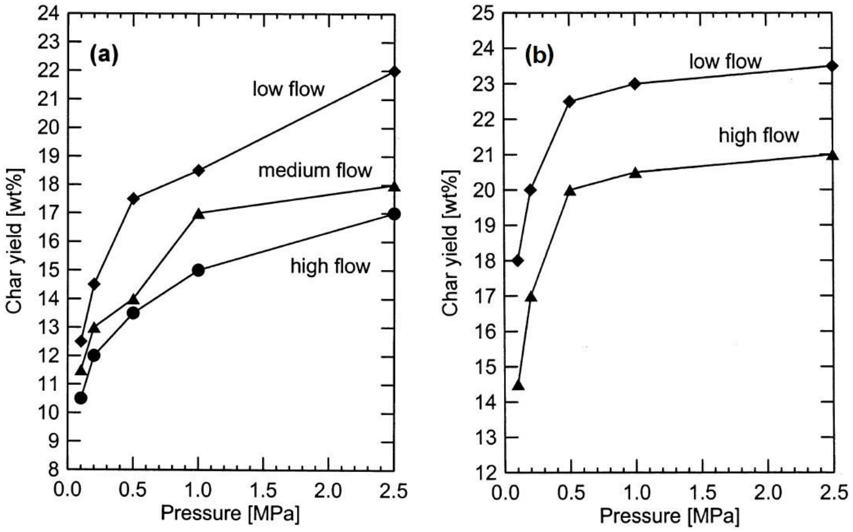

Figure 9. Effects of pressure and gas flow on char yield of: (a) cellulose), (b) oak [28]

With pressurized carbonization is possible to drastically reduce the residence time from 300 min of traditional furnace to 70 min of pressurized retort [36].

Last parameter to be taken in to account is moisture content of biomass feedstock. Moisture content retained into biomass requires more energy to evaporate and of consequence more biomass input, for the most used autothermal reactors, and it means that the process has a lower char yield. Moisture content has a positive effect only for pressurized allothermal carbonization due to water acts a catalyst for secondary reactions.

In order to study process carbonization objective of this work, is also important to clarify better the exothermicity or endothermicity of heat of reaction (or heat of pyrolysis). Generally, on the literature, carbonization process is considered exothermic but it depends mainly from the process. Mok and Antal showed (Figure 10) that increasing pressure, heat of reaction of wood cellulose moved from 230 J/g (endothermic) to -130 J/g (exothermic). At high pressure without any gas flow using a closed crucible, heat of reaction reached 600 J/g (exothermic) with a char yield of 40%.

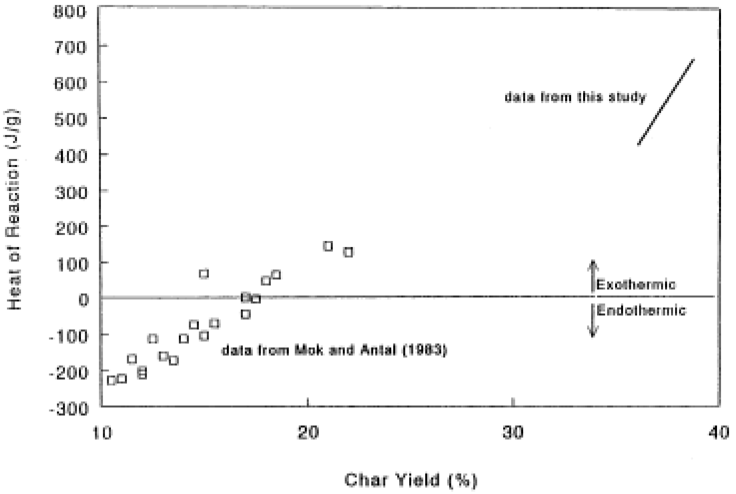

Figure 10. Pyrolytic heat of reaction vs char yields over a wide range of pressures [37]

1.4.2 Oxidative pyrolysis

When heat is generated by partial oxidation of biomass itself, the pyrolysis works in autothermal process and it is called oxidative or flaming pyrolysis.

This process is typical for stratified fixed bed gasifiers, where at steady state condition a flaming zone takes place between unburned fuel zone and reacting char zone [15]. Pyrolysis undergoes therefore in presence of a limited oxygen concentration, which influences thermal degradation of biomass and its by-products final yields. Heat of reaction released during oxidative pyrolysis is definitely an exothermic process. Oxidative reactions take place on the external surface of biomass piece, while internal oxygen concentration is extremely low or even absent and consequently oxygen does not significantly influence biomass pyrolysis behaviour [38]. In general, it must be recognized that data available on pyrolysis of solid fuels under inert conditions can be extended to pyrolysis under oxidizing condition only provided that either of the following condition holds [39]:

- oxygen cannot reach the surface of a pyrolyzing particle due to severe boundary layer diffusional resistances, or due to efflux of volatiles;

- the kinetics and the mechanism of pyrolytic processes are not affected by the inert versus oxidizing nature of the gaseous environment where they take place.

Oxidative pyrolysis depends on process parameters, such as, particle size, temperature and oxygen partial pressure.

Although char yield obtained can be at the same level of inert pyrolysis, grater differences in gas and vapour yields and composition occur.

An extensive literature review on chemical composition of slow pyrolysis vapour and gas characterization for oxidative processes is presented in the next paragraph.

1.5 Chemical composition of slow pyrolysis vapour: literature review

Biomass pyrolysis process produces, other than char and water, a large variety of chemical compounds which are included in the vapour phase. Product yields are strictly depended to process parameters, reactor type and biomass specie. Although on the literature is plenty of experimental results of pyrolysis products yields [40], tar characterization is not consistent as we could think, with some exceptions [41,42]. For this reason, is difficult to find a benchmarking among all the experimental results already existing in the literature, which address exactly the corresponding process conditions under investigation. Fully understanding chemical composition of slow pyrolysis vapours is complex and Milhé in his study [43] underlined the lack of results in biomass pyrolysis in continuous fixed bed reactors.

This paragraph aims to make a benchmarking among all the existing experimental studies considering both inert and oxidative slow pyrolysis of lignocellulosic biomass, focussing in continuous processes with parameters related to Re-Cord carbonization reactor. Some consistent batch processes are also present in this paragraph to complete the scenario. In the specific, this literature review addresses process parameters, mass fraction yields and distributions of the whole chemical species, liquid and gas, formed during biomass degradation in slow pyrolysis condition.

This survey focuses especially in the investigation of the chemical composition and quantification of tar existing in pyrolysis vapour because represents main issue in the technological developing and industrialization of biomass continuous systems. Tars, in facts, represent operative issues in terms of handling and pollutant emissions, and they must be incinerated before discharged in the atmosphere. Energy can be retrieved from tar combustion for the benefit of the system.

1.5.1 Continuous oxidative slow pyrolysis

Experimental studies on oxidative pyrolysis are less frequent than those in inert atmosphere, and rarely they report detailed information regarding chemical composition of products. Milhé (2013) and Daouk (2015) studied oxidative pyrolysis in a continuous fixed bed reactor at CIRAD (France) and they provided the most characteristic studies which can be taken as a reference for this work of thesis due to many characteristics in common with Re-Cord carbonization reactor. These studies allowed to correlate input and outputs characteristics with operating parameters.

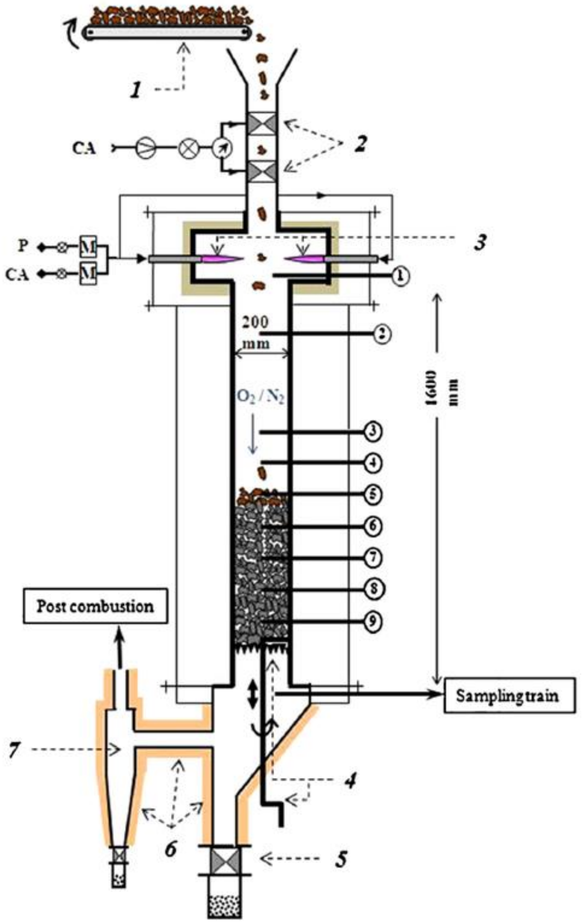

Figure 11. CFiBR downdraft reactor scheme: 1) loading belt, 2) inlet valves, 3) propane burner, 4) mixer, 5) char collector, 6) anti-condensed heating systems, 7) cyclone [43]

The reactor CFiBR (Continuous Fixed Bed Reactor) was developed by CIRAD in 2003 at first to understand and model the first stage of two stage gasifier NOTAR by Xilowatt [43] and later to study the fixed bed pyrolysis reactors and associated products.

The reactor is a downdraft with a diameter of 20 cm and a 160 cm height, capable of working in autothermic and in allothermal condition (using a LPG burner), and even in batch mode. The maximum capacity is 6 kg/h maintaining a bed height of 450 mm and the suitable woodchip dimension is between 3 – 13 mm. Reactor is closed at top and air flow inlet is controlled during the process. Char is manually discharged, and vapour are extracted by through a heated ducting system with a cyclone and sent to a post combustion system.

Both studies tested maritime pine woodchip as a feedstock in similar conditions, monitoring all the operational parameters such as: bed temperatures, oxidant air flow rate and residence time. A fraction of pyrolysis vapours was condensate before incineration by means of a tar sampling line similar to CEN/TS 15439 and outlet permanent gas was analysed. In Table 2 are listed process parameters of the two experiments.

Table 2. Oxidative pyrolysis process parameters of Milhé and Daouk experiments[43,44]

Paramters	**Milhé** [43]	**Daouk** [44]
Biom. specie	Maritime Pine	
Biom. granulomtery [mm]	5-10	4-12
Temp. max. [°C]	675	650
Residence time [min]	60	90
Biom. capacity [kg/h]	6	3,8
E.R.	0,10	0,12

Mass yields of the two experiments (Table 3) were affected by inevitable measurement errors. The sum of products % wt. on biomass input is above 100 because it considers oxidant air fed in the reactor. Milhé observed a 2% lower char yield compared to inert pyrolysis experiments and he ascribed this facts to higher temperature and not to the char oxidation [43].

Table 3. Yields of experimental results of Milhé and Daouk [43,44]

	Milhé [43]		**Daouk** [44]	
Product	*% wt. On biom. input*	*% wt. yields*	*% wt. On biom. input*	*% wt. yields*
Char	21	18,6	17,2	15,5
Condensate (no water)	15	13,3	8,5	7,6
Water	26	23,0	25,1	22,6
Permanent Gas	51	45,1	60,4	54,3
Total	113	100	111	100

Milhé and Daouk agreed with partially oxidative environment influences liquid and gas yields determining higher gas and water production, while organics compounds are instead limited by phase gas oxidation and secondary cracking reaction in char bed [44].

It was observed, that the presence of the oxidation zone in the reactor decreases O2 and N2, in favour of formation of other species, mostly CO, CO_2 and a good production of CH_4. Temperature and residence time don't seem to influence permanent gas composition of continuous oxidative pyrolysis [43]. In Table 4 are reported permanent gas composition and the list of the main identified organics compounds constituting the condensate.

Table 4. Detailed gas and tar yields of experimental results of Milhé and Daouk [43,44]

	Milhé [43]	**Daouk** [44]
Permanent Gas	*% wt. of tot perm. gas*	
CO	39,8	37,9
CO2	50,8	52,6
CH4	5,5	5,0
H2	1,9	2,1
C2H6	0,60	0,69
C2H4	1,40	1,79
Organics compounds	*% wt of total condensate*	
Levoglucosan	6,89	3,00
Acetic acid	5,66	5,90
Propionic acid	1,24	0,90
Furans	2,06	2,80
Phenols	3,27	7,30
Guaiacols	1,11	0,23
Aromatics	0,29	8,14
Formaldehydes	1,82	0,60
Acetaldehyde	2,27	3,70
Glycolaldehyde	10,17	0,41
1 hydroxy -2 propanone	5,89	-
Hydroxyacetone	-	2,00
Others	3,33	25,56
Identified organic compounds	**44**	**40**

Note: organics compounds < 1% are not listed

Oxidative environment seems to promote aromatics and phenols production, although is difficult to impute to oxidation or cracking reaction due to high temperature. According to Milhé, cracking reactions are generally favourite in oxidative environment.

1.5.2 Batch oxidative slow pyrolysis

Zhao's experiments on oxidative pyrolysis of pinewood were performed in a lab scale fixed bed reactor using pine biomass, analysing output product yields at different process conditions: temperature and oxygen concentration. The reactor called “hot rod” has an internal diameter of 12 mm and length 200 mm. It is capable to convert 1 g of biomass with heating rate of 20°C/min [45] despite actually Zhao didn’t mention it in his work.

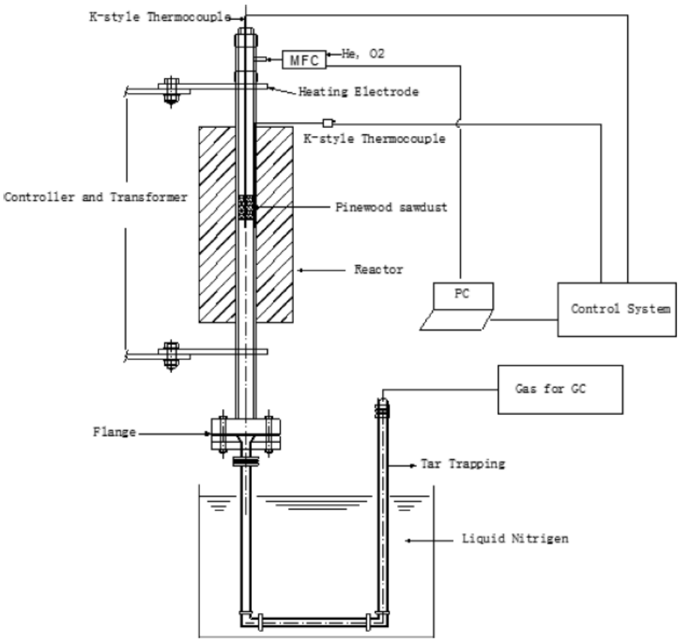

Figure 12. Zhao's experiment test bench for oxidative pyrolysis

Tests were conducted at different ER according the parameters listed in Table 5 in order to highlight yields trend of gas, water, char and tar.

Table 5. Process parameters of Zhao's experiment [46]

Parameters	**Zhao** [46]
Biomass specie	Pine
Granulometry [mm]	0,10 - 0,15
Temperature max [°C]	500
Mass biomass converted [kg]	1 · 10^-3
E.R.	0,08 – 0,18

Pyrolysis product yields depend on oxygen concentration ratio in the reactor and from Zaho’s result we note an evident trend with decreasing of char and tar contents and opposite increasing of water and gas. In particular, the pyrolysis products yield on biomass input at ER of 0.15 in respect to inert environment: char dropped from 31 to

27, tar dropped from 33 to 28, gas went from 30 to 53 and water from 6 to 11. Complete result of the test is shown in Figure 10. It is therefore important to underline that any increment of ER leads to tar reduction due to conversion of primary tar in secondary [46].

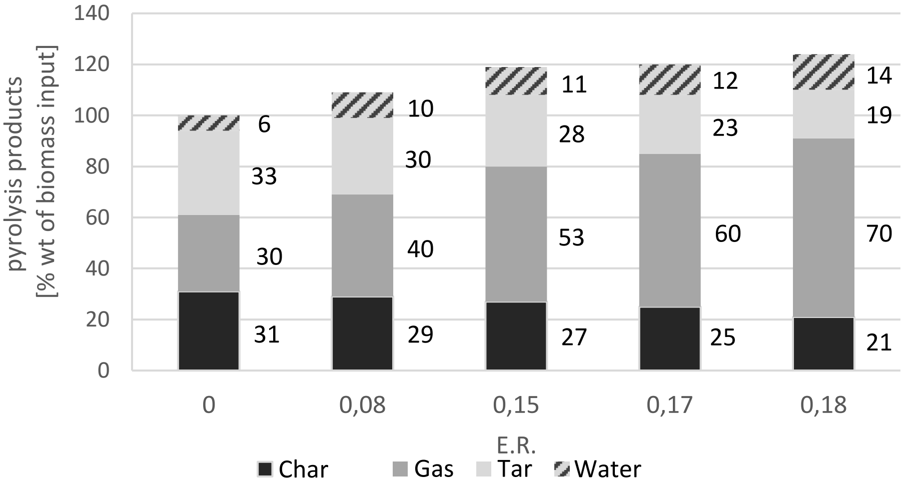

Figure 13. Slow pyrolysis output yields at different ER in oxidative batch experiments [46]

Oxidative pyrolysis of biomass at temperature above 300°C, favourited CH4 and CO production in comparison to inert pyrolysis, CO2 production increased even at low temperature. Above 400°C, at ER between 0.1 and 0.2 there was no substantial increment of CO and CH4 production, CO2 increased instead (Figure 11).

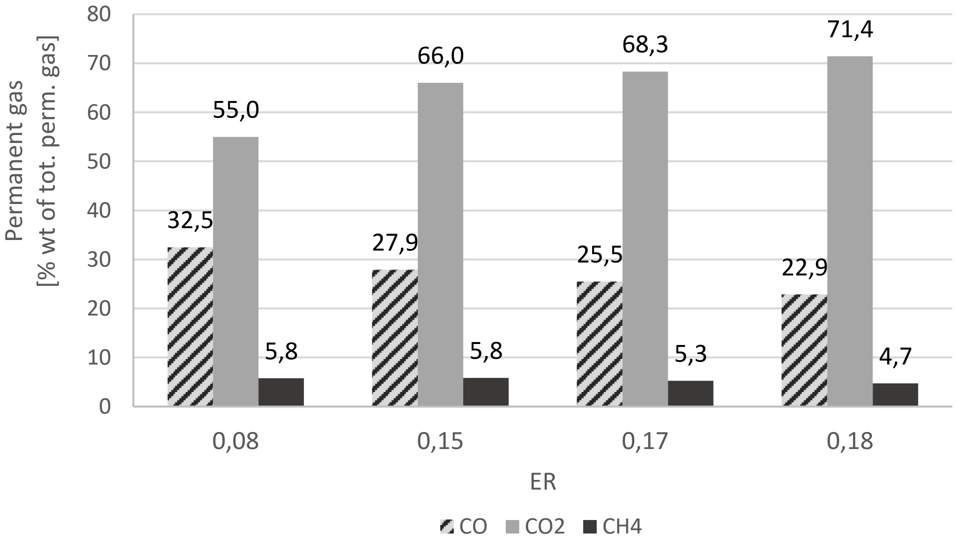

Figure 14. Permanent gas yields from slow pyrolysis oxidative batch experiment at different ER ratio [46]

Batch experiment complied with continuous experiments before mentioned, although it showed more production of CO_2 rather than CO, the CH_4 was for all the experiment around 5 %wt.

Levoglucosan, anhydrous sugars and other acid compounds concentration in condensate decreased at higher ER ratio and temperature, while furans, alcohols and chetons production was favourited. Phenols presence in condensate was also massive around 40 %wt. of total condensate and was quite constant at different ER.

1.5.3 Continuous inert slow pyrolysis

The lack of complete experimental studies on continuous oxidative pyrolysis of lignocellulosic biomass at similar condition of this present work, led to consider also some experiments in inert environment in order to depict the actual state of the art of continuous process. In addition, carbonization process scope of this work addressed low oxygen (ER 0.1-0.2) concertation not far from inert condition.

Fassinou studied pyrolysis of woodchip pine in a screw reactor unit correlating a wide range of temperatures and residence times with output products. Milhé experience was to study inert pyrolysis of maritime pine in the same reactor described in paragraph 1.5.1 set in allothermal configuration heated through 2 LPG burners. Although Milhé test had a residence time of 60 min, both studies were performed at similar conditions (Table 6).

Table 6. Continuous inert pyrolysis process parameters relative to Milhé and Fassinou experiments

[43,47]

Parameters	**Fassinou** [47]	**Milhé** [43]
Biomass specie	Pine	Maritime Pine
Granulometry [mm]	Woodchip	5-10
Temperature max [°C]	450 -750	475-575
Residence time [min]	30-60	60
Reactor type	Screw	Fixed bed
Biomass capacity [kg/h]	15	6

Char yields were approximately 30 %wt. and decreased at higher temperature as expected. Both studies were in compliance with the literature regarding gas and tar yields trend with temperature variation. Fassinou noted that residence time had a benefit effect on char production, this was due to hot char favourited secondary tar cracking reduction of pyrogas on char surface itself depositing additional carbonaceous residues. In the following chart (Figure 15) are listed char, liquid (water + tar) and gas yields at different temperatures.

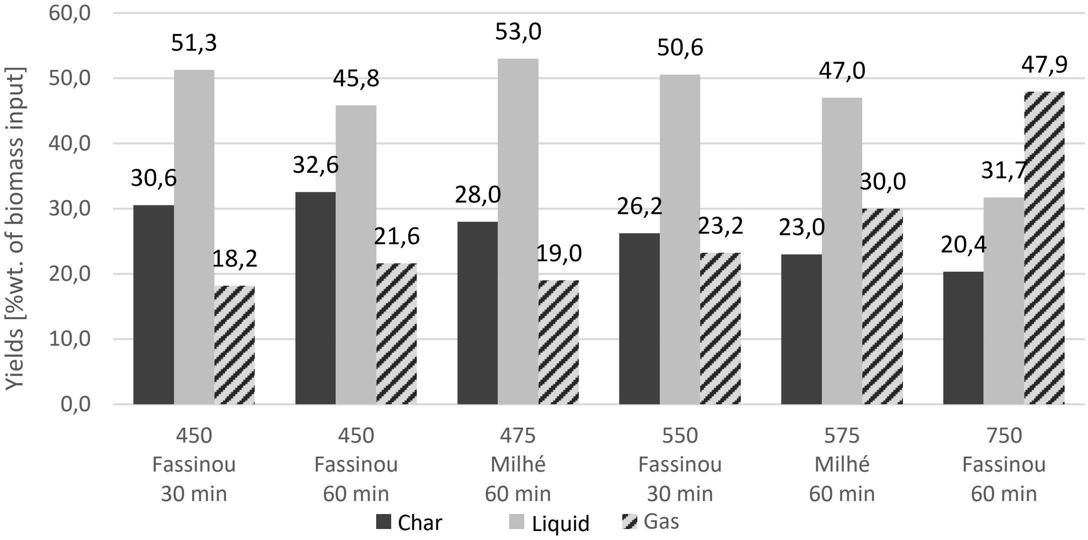

Figure 15. Product distribution of continuous inert pyrolysis [43,47]

As observed in oxidative pyrolysis, both experiments showed high production of CO and CO2 which constituted together around 85-90 %wt. of total produced gas. At similar temperature, reactor type seemed to influence also CO2/CO ratio: screw reactor gave a ratio of 2, while fixed bed gave approx. 1. Methane production increased with maximum temperature, as well as Ethane and Ethylene with yields of 1 – 2 %wt. above 550°C. Both authors found Hydrogen formation up to 2.1 %wt. at 575°C [43] and 2.9 %wt. at 750°C [47] respectively.

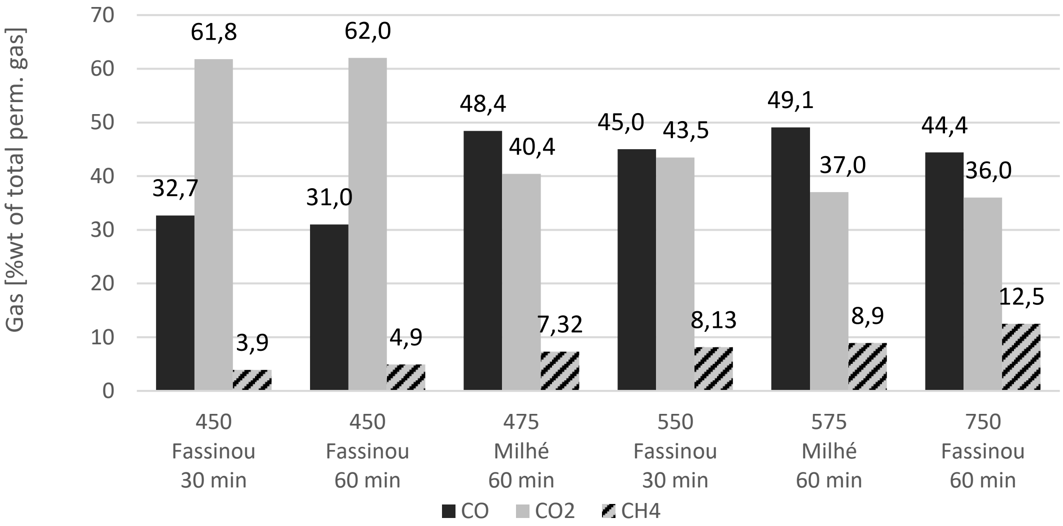

Figure 16. Gas composition of lignocellulosic biomass continuous inert pyrolysis tests [47][48]

Regarding tar production the main chemical compounds founds were: levoglucosan, acetic acid, furans, phenols, guaiacols and methanol. Table 7 reported the yields for main compounds. Tar yield for both studies gave similar values. At temperature of 750°C, Fassinou amplified and showed the phenomena which high temperature influenced tar cracking with formation of light species such aromatics, in particular benzene.

Table 7. Identified tar classification of continuous inert pyrolysis [47][48]

Parameters	**Fassinou**			**Milhé**
Temperature max [°C]	450	550	750	475
Residence time [min]	30	30	60	60
Identified TAR [%wt. of total organics]	24%	26%	64%	40%
Tar[2] [kg /kg of total organics]				
Levoglucosan	6,85	7,15	-	10,65
Acetic acid	3,41	3,26	-	5,90
Furans	3,18	2,54	-	0,94
Phenols	1,20	2,74	10,54	1,12
Guaiacols	3,42	-	-	2,15
Aromatics	1,04	2,00	33,20	0,54
Methanol	2,54	2,35	5,45	3,59
PAHs	-	-	4,73	0,11

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[2] Organic compounds with concentration less than 1% wt. are not listed.

In conclusion to this review I can state that literature is plenty of interesting works with a full characterization of input and output regarding carbonization of wood in inert batch process. In reality this process, even at pre-industrial scale, is the simplest as possible to be carried out and doesn't require any special equipment apart from instrumentation. Some extensive and interesting studies taken as a reference for this work of thesis were made by: Bajus [49], Branca [42], Fagernas [50], Williams and Besler [51], Ku and Mun [52].

1.6 Bio-based char products: definitions and market application

Wood charcoal is as a hard porous, highly carbonaceous product, obtained by slow pyrolysis process and commercially produced in furnaces and retorts, or even in rudimentary earth kilns. Emrich proposed the following definition: " charcoal is the residue of solid non-agglomerating organic matter, of vegetable or animal origin, that results from carbonization by heat in the absence of air at a temperature above 300°C" [37]. A recurring definition of good charcoal was made by Chaturvedy as follow: "Charcoal of good quality retains the grain of the wood; it is jet black in colour with a shining lustre in a fresh cross-section. It is sonorous with a metallic ring, and does not crush, nor does it soil the fingers. It floats in water, is a bad conductor of heat and electricity, and burns without flame" [53,54]. In addition, being an inert matter, it is not subjected of aging, microorganisms and mildew attack and it can be stored for long term periods.

There is no a clear distinction between charcoal and biochar definition. Sometimes char matter coming from converters and pyrolysis process refers to biochar when char is transformed in powder or small granules and could be potentially used as a soil conditioner. According to the European Biochar Certificate, biochar is defined as a heterogeneous substance rich in aromatic carbon and minerals. It is produced by pyrolysis of sustainably obtained biomass under controlled conditions with clean technology and is used for any purposes that do not involve its rapid mineralisation to CO_2 and may eventually become a soil amendment [55].

1.6.1 Industrial application

Charcoal is a valuable energy and carbon source for different industrial and domestic uses. Physical properties and chemical composition of the char determine its applicability as carbon source for a wide range of market sectors (Table 8).

The most known usage of charcoal is for food cooking. Most rural villages in poor countries use exclusively wood or wood charcoal in stoves for food and feed cooking and drying. In developed countries, instead, charcoal is no longer used as main domestic cooking fuel but has become a symbol of affluent lifestyle through its use in leisure activities as a fuel in open air barbequing (BBQ) and grilling meat. Standard EN 1860-2 [56] prescribed characteristics that a good charcoal for BBQ should have in terms of: calorific value, Fixed Carbon content, Ash, bulk density, moisture, volatiles and granulation.

Table 8. Charcoal industry sectors potential application [57]

Chemical Industry	Iron and Steel	Metallurgy	Activated Carbons	Energy	Fertilization
carbon disulphide	iron smelting	foundry operations	water and gas purification	District heating	Terrapreta fertilizer
sodium cyanide	high purity irons	copper smelting	catalysts and pollution control	Co-firing	Soil conditioner
metallic carbides	ferro silicon	tin smelting	solvent recovery	100% combustion	
silicon carbide	silicon	metal smelting	Batteries	Electricity	
	sintering and ore beneficiation	electric furnace electrodes	food, sugar industry	gas for motor vehicles	

In energy sector, charcoal has a less developed market due to the high competitiveness of fossil fuels and low cost of raw biofuels. Charcoal can substitute coal, coke, petroleum coke or lignite and it is largely better than wood pellets, however, the high cost reduces its consumption.

Charcoal has been largely used as a reductant in iron industry as partly or entirely substitute of coke in blast furnace. For metallurgical application char should have 85-90% fixed C [37]. Despite the high cost of char, it allows to manufacture a high-quality steel thanks to low sulphur and impurity content. Other advantages compared to coke are: higher reactivity in combustion, lower ash content, higher heating value, higher fixed C. In addition, replacing coke with charcoal provides a secure reduction of CO_2 emission and O_2 absorption from the atmosphere [58]. Brazil and Norway steel industries are currently largely using charcoal thanks to their vast forestry biomass available [59,60].

Bio-based char matter is used as a soil conditioner and fertilizer, with a name of biochar, however, market is at early stages and prices are overrated (up to 10-15 €/kg). Charcoal presents high fixed carbon content and a very low H/C ratio, therefore, it is a very stable product, resistant to the biodegradation. For this reason, it certainly represents a valid product for long-term carbon storage in soils and it could seem a possible solution to reverse the constant decline of organic carbon content in soils. Many scientific investigations of diverse agronomic properties of charcoal as soil conditioner is being conducted around the world. Recent studies have showed that soil charcoal amendments are indeed capable to increase soil fertility [61]. Due to its porous structure and large surface area (m2/g), biochar applications showed to positively influence soil field capacity, nutrient availability, and pH amelioration. Additionally, char has been demonstrated to increase water holding capacity and microbial activity, reducing nutrient leaching and to promote cation exchange capacity [61]. These results have been demonstrated by char application as soil conditioner tested by different studies worldwide [62]. The PAHs content and heavy metals content represent the binding condition to consider this product as a sustainable soil conditioner. Specific standards have been addressed by EBC and IBI [63,64] and are continuously under development in order to facilitate a sustainable market growth.

The use of charcoal for producing activated carbon is fairly new when compared to its utilisation in metallurgy or chemical industry. The first markets started to develop in Europe around the beginning of this century. Activated carbons are carbons which have undergone a post treatment (chemical or thermochemical activation) to increase their adsorption properties. The application of Charcoal in activated carbon industry depends on the surface area of the material, which must be in a range of 100-200 m^2/g to be considered of good quality before the activation process [65]. The process temperature, as well as the quality of the wood used to produce charcoal influence the micro-porosity of the product and automatically its application as activated carbon fuel. Additionally, the usability of wood charcoal depends on its low ash content and availability in consistent quality. Exceptionally good activated carbons can be produced with charcoal made from coconut shells, hardwood and even, sawdust and wood waste (depending on the process used). On the basis of its quality and structure, activated carbon can be used for the purification of a wide range of industrial effluents, like liquids, hot gases, etc..

1.6.2 Market overview

According to FAO the global production of charcoal in 2014 was more than 50 million tonnes. Africa is the continent counting the world largest production, which accounts for over 56% of the total production. In Africa, charcoal is often made by traditional earth mound and pit kilns, and charcoal making is frequently practised by farmers or villages citizens. Brazil is the world largest charcoal producer country accounting for about 13% of the total production (2014). In Brazil, charcoal is frequently used in metallurgy to produce pig iron and the most used technologies are brick kilns. Recently, new retort facilities are attracting the interest of investors for their environmental sustainability, but they are still not economically viable. Nigeria and Ethiopia are the second and third largest producers, both accounting for approximately 8% of the total production. According to Antal charcoal has been sold in in Europe and North America between 0.55 and 2.20 $/kg [31].

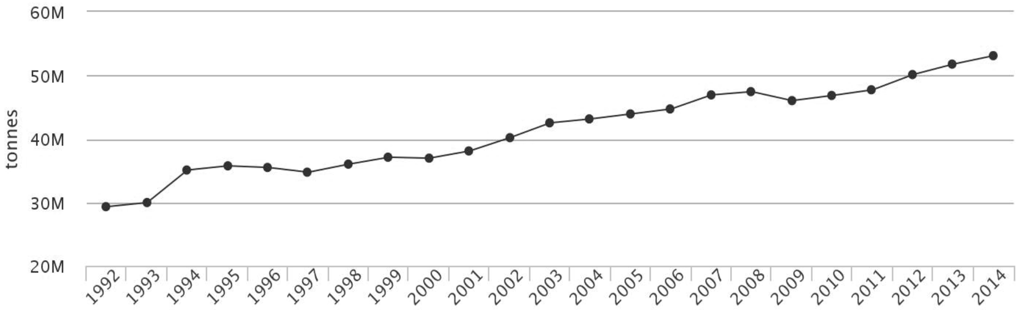

Figure 17. Wood charcoal global production trend at 2014 [66]

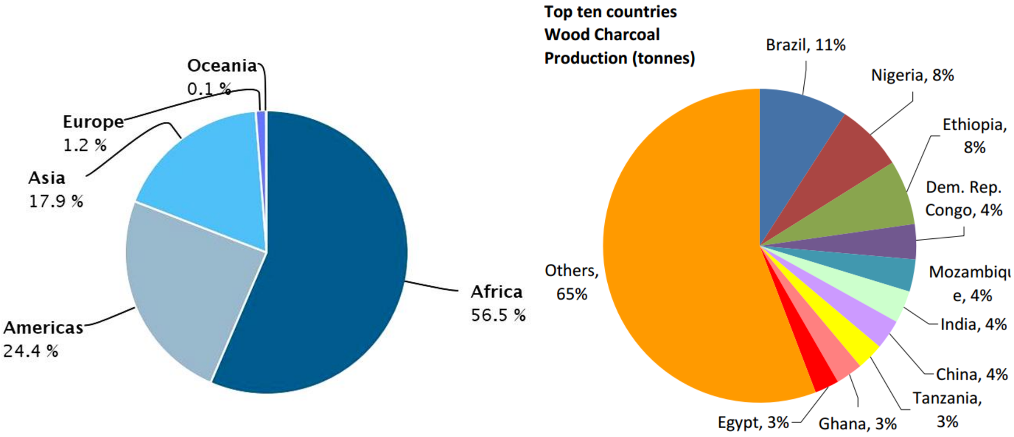

Figure 18. Global charcoal production distribution by continent (left) and country (right) [66]

In Europe, more than 1,4 million tons of charcoal is used every year. Despite the large availability of woody biomass and a very long history and tradition of charcoal production in the Europe, around 67% of the charcoal used in Europe (960,000 tons/h) is imported from abroad for a value of about 475 million € per year. In total, Africa alone is responsible for the 40% of all charcoal consumed. Moreover, a considerable amount of charcoal does not meet EU specifications. In addition, due to the low technological level, charcoal production is one of the causes of deforestation, thus of land degradation, in those countries. Despite the general growth in EU charcoal consumption, European charcoal production has been decreasing year by year (Figure 13), and due to the lack of innovative sustainable technologies.

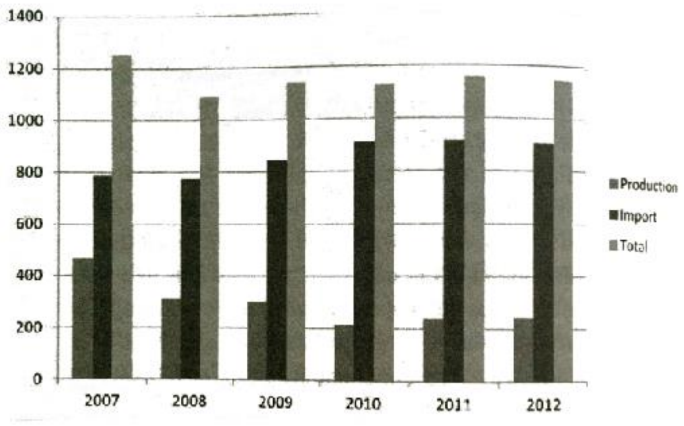

Figure 19. Charcoal production and import in Europe: 2007-2012 (tons x1000) [66]

1.7 Review of charcoal production: process technologies and reactors

Charcoal production technologies' scope is producing charcoal through reactors heating. During the carbonisation process, both gases and liquid are used to support it or to generate heat and it is necessary to heat biomass from ambient to the temperature at which pyrolysis reactions take place, to remove any residual water and to drive pyrolysis reactions [67]. The key factor that allows listing these technologies is the heating system and the charcoal yield that can be achieved. Here below are three different types of pyrolysis reactor system configurations: (1) autothermal reactors, (2) allothermal reactors, and (3) hot gas recirculation.

In the auto-thermal reactor the heat is produced inside the reactor through a partial biomass combustion. The oxidizing agent is oxygen that influences the rate of burning. The heat produced inside drives and supports endothermic reactions in the reactor [68]. The amount of air must be controlled and equally distributed in order to get a charcoal with equal physical-chemical properties [67]. This con can be avoided in advanced continuous systems [30].

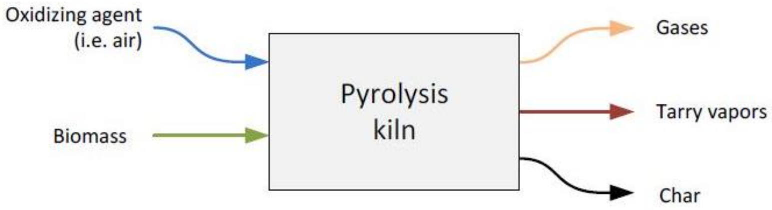

Figure 20. Auto-thermal pyrolysis reactor operating with partial oxidation of biomass [67]

For allothermal reactor, energy comes from an external source or from the combustion of gases or liquids products in the carbonisation process. Hot gases are indirectly in contact with biomass through a heat exchange in the reactor. This system can be used when the heat is produced by the combustion of an external source, i.e. a non-renewable fuel. Disadvantages of this system are the heat loss, heat efficiency and control of the process. However, it has a good feature, which is the fact, that biomass is not in contact with air.

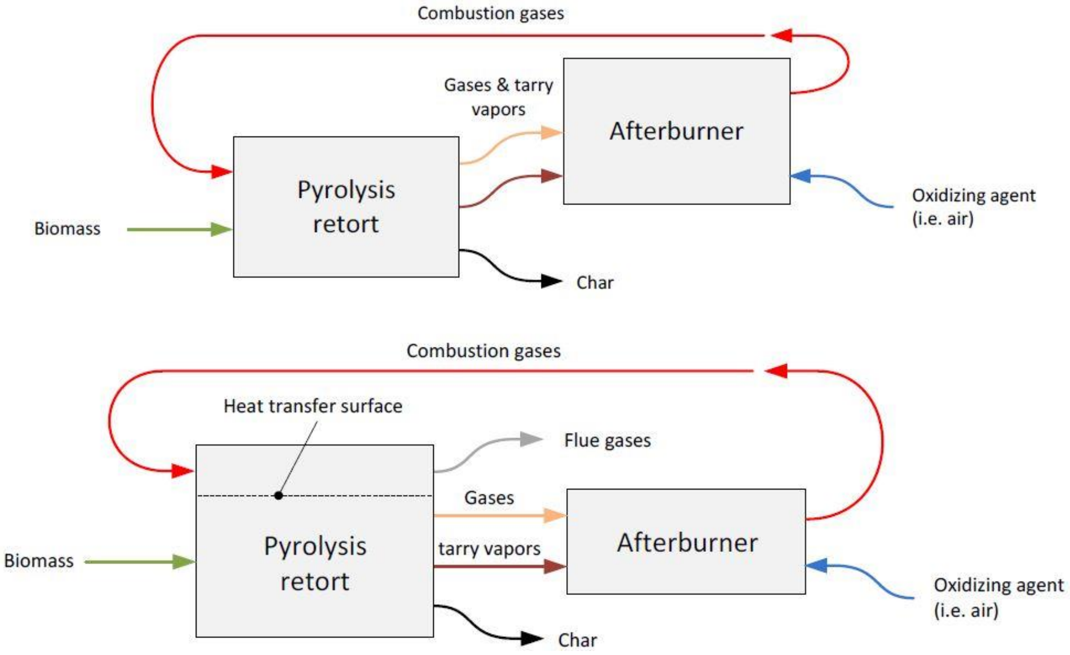

Figure 21. Pyrolysis process with gas and tarry vapor combustion for process heating: hot gas recirculation (above), and allothermal (below) configurations [67]

With hot gas recirculation, pyrolysis vapours are burnt and recirculated into the reactor and the heat coming from the products of combustion contributes to produce energy. Heat for carbonisation process is obtained by burning an external fuel, such as wood, or wood gases, outside the retort and driving heat by wall conduction to the wood contained in the sealed retort.

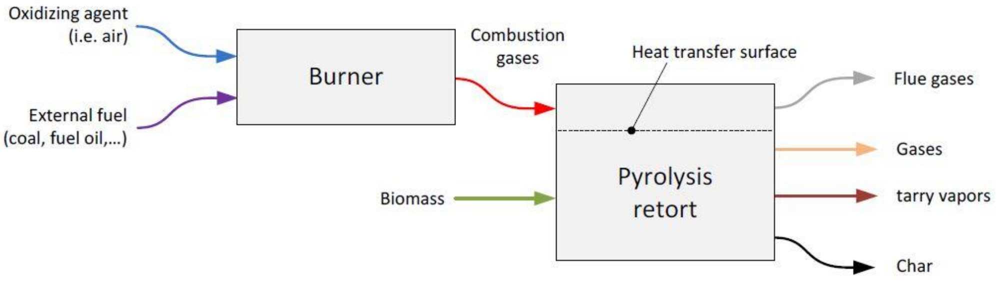

Figure 22. Allothermal pyrolysis reactor heated with external fuel combustion [67]

In conclusion, internal pyrolysis process can be considered the simplest type after the analysis of energy efficiency and costs reduction, in order to increase and improve the feasibility plant [25,26,69].

As mentioned before, charcoal production technologies are characterized by different conversion efficiency, which depends on carbonization process parameters, as well as on the feedstock used. The table below summarizes the range of yields achievable by different technologies available on the market.

Table 9. Charcoal yield of different industrial carbonization processes [30]

Type of Kiln	Production of 1 kg of charcoal from	Kiln efficiency
Traditional Kilns (Earth Pits, Mods)	8- 12 kg wood	8 – 12%
Improved traditional kilns (Brick kilns)	6 – 8 kg wood	12 - 17%
Industrial production Technologies. (Twin retorts, Fluidized bed reactors)	5 – 7 kg wood	14– 20%
New high-yield, low-emission. (Advanced retort systems, advanced fixed bed reactors)	3 – 4 Kg wood	25 - 33%

Emrich proposed a nomenclature to differentiate among all the different pyrolysis reactors [26,69]:

- **Kiln** - kilns are used in traditional biochar making solely to produce biochar.

- **Retorts and converters** – Industrial reactors that are capable of recovering and refining not only the biochar but also products from volatile fractions (liquid condensate and syngas) are referred to retorts or converters.
- **Retort** – The term retort refers to a reactor that has the ability to pyrolyze pile-wood, or logs over 30 cm long and over 18 cm in diameter.
- **Converters** – produce biochar by carbonizing small particles of biomass such as chipped or pelletized wood.

Below is reported a quick review of the most relevant traditional and modern processes for charcoal production benchmarking, in terms of efficiency, system size, and constraints.

1.7.1 Traditional processes

Traditional processes use partial combustion of biomass inside the kiln to supply heat for carbonization. These processes are batch and are extremely low cost, characterized by a very long residence time (some days) but also low global efficiency and high pollutant emissions. In fact, the unique product obtainable from these kilns is charcoal, while hot vapour is not recycled for additional heat generation and for any other scope. Charcoal production efficiencies are very low, in the range of 8 – 14 % wt. but there are some improved kilns which can reach 17 %wt. .

Several different types of systems, from rudimental to improved kilns, have been used: earth pits, mound kilns, metallic kilns, brick kilns, beehive kiln, Missouri kiln.

In these traditional methods, colour of smoke have been used to identify the three different process phase: smoke is white during drying, yellow during pyrolysis and blue once conversion is completed [69,70].

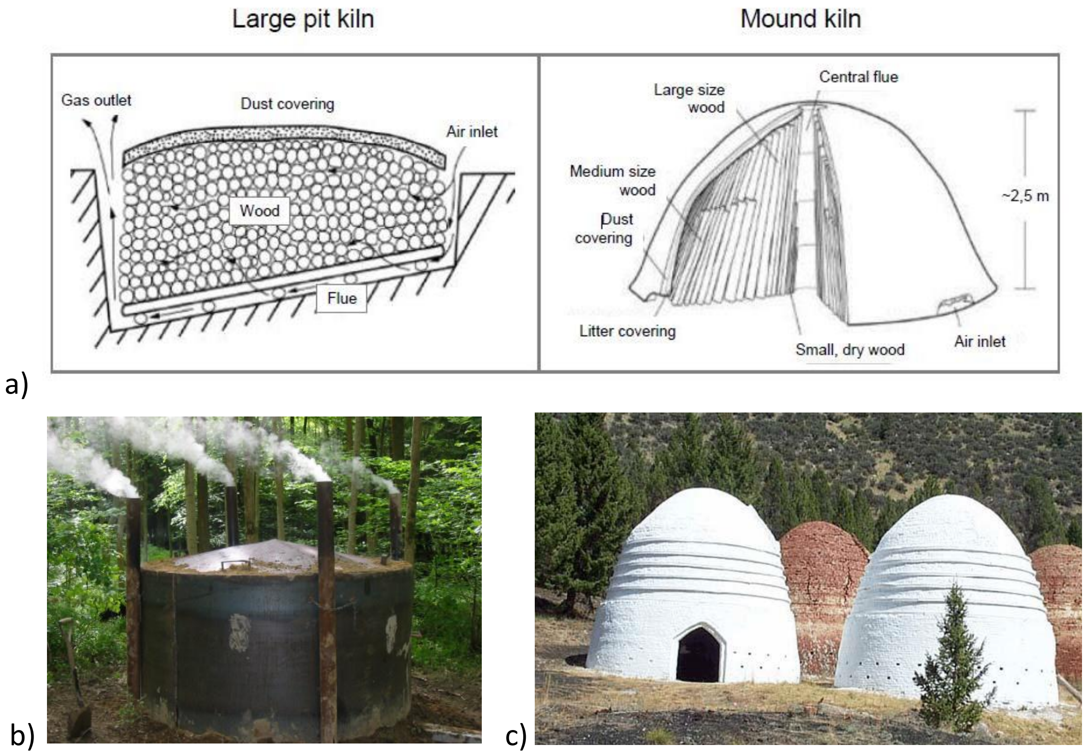

Figure 23. Pictures of charcoal traditional processes: a) earth and mound kilns [71]**; b) metallic kiln; c) bricks kiln** [69]

1.7.2 Retorts and advanced technologies

Most modern industrial charcoal makers use retorts for their process. In a retort, the pyrolysis vapours are separated from the feed material, before being combusted. Theoretically, only the vapours are used to provide the energy sustaining the process, but exceptionally additional fuels can be used, for start-up and in case of feed material that is too wet. Direct contact of the biomass fed with oxygen from air is prevented. This technology ensures that the entire processed biomass is available for the conversion into charcoal (no partial combustion) and for this reason charcoal yields from retort processes can be very high compared with autothermal heating systems. However, the development of retort technologies in the past may have had other reasons than yield optimization alone: separation enables the manufacturer to produce a variety of chemicals, such as acetic acid, wood vinegar, and methanol [72].

Today, the production of these by-products is less viable in view of the competition with other manufacturing processes and retorts economic feasibility has strongly decreased. Some indicative names of existing (or commercially lost) retort processes for the carbonisation of lump wood are: Arkansas or Waggon Retort, Carbo Twin Retort, Badger-Stafford Process (no longer in use), SIFIC process and the related Lambiotte Retort, Degussa Retort (Reichert Retort), VMR (no longer in use) and the O.E.T Calusco Tunnel Retort [73].

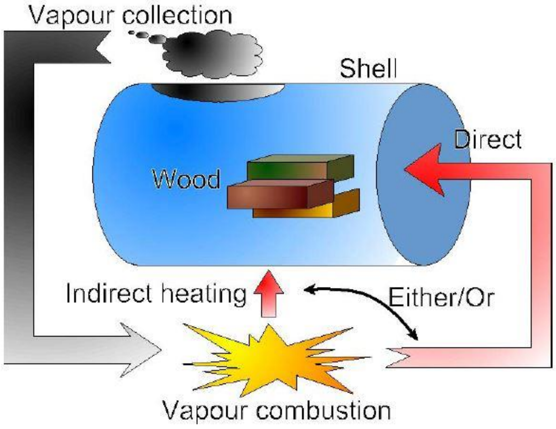

Figure 24. Retort reactor working principle [72]

Carbo Twin Retort Is a semi batch process developed by Carbo Group and consists in a series of vessels, 5 m^3 in size, heated alternatively by means of an external furnace which burns pyrolysis vapour extracted from the process. Carbonization time for one vessel is 12 h while more time is necessary to cool it down before opening. This system is capable to convert logs and producing 900 t/y of charcoal with a yield of around 33% [74].

Lambiotte process is considered one of the most successful technology for charcoal production. It was developed since 1940s and two variants have been adopted: CISR and SIFIC (with by-product recovery). Lambiotte converts small wood logs in a continuous fixed bed reactor of which comprises both conversion and cooling zones. Heat is supplied by burning part of vapour pyrolysis and recirculating hot gas into the reactor. Conversion efficiency is up to 25% with high quality charcoal (82-90% fixed carbon) [75]. The whole system has relevant size and it is available in two capacities 2.000t/y and 6.000 t/y of charcoal produced.

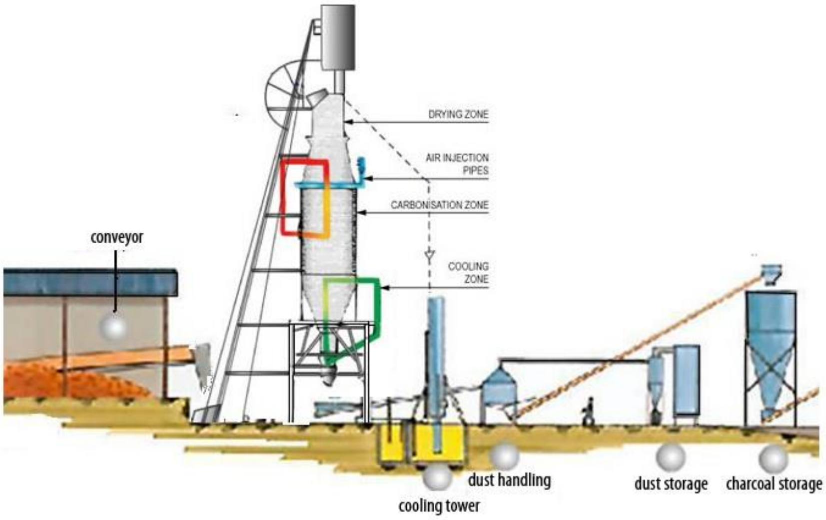

Figure 25. Lambiotte SIFIC carbonization plant [76]

Among the developed carbonization systems, there are plenty of small and medium batch retorts, which some of them are also pressurized reactors. These systems are very simple, sometimes already mounted on a movable skid, for this reason the size is often limited. Some examples of these systems are: Exter retort, Pressvess retort, CharMaker MPP20/40 and, Flash carbonization retort.

Figure 26. Movable reactors: a) Exeter retort and b) Charmaker MPP 20 [77,78]

Continuous converters are currently largely deployed for biochar production. They represent the latest development in carbonization sector addressing in small systems the main features typical of large scale carbonization process. Many literatures are available to compare process data and charcoal yield of different reactors. Fixed bed, rotary drum and screw technologies are utilized for conversion of woodchip and pyrolysis vapour are combusted to the benefit of the process and/or for renewable energy generation [79].

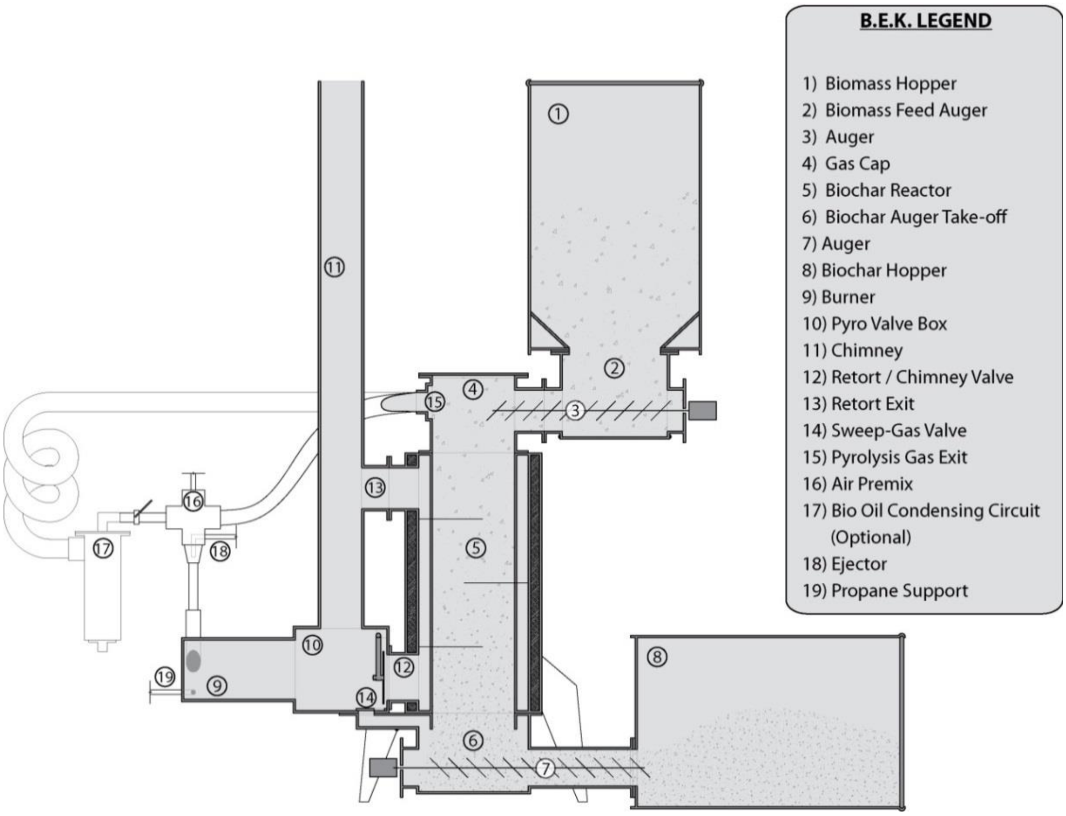

Figure 27. Continuous downdraft reactor for biochar production developed by All Power Labs: BEK (Biochar Experimental Kit) [80]

1.8 Environmental and social aspects

In some specific areas, deforestation and forest degradation, as well as the associated land degradation and soil erosion, are largely caused by wood charcoal production. There is an actual risk of deforestation and a substantial economic unsustainable framework which characterise wood charcoal trading worldwide. Unfortunately, differently from the wood pellets market, strictly regulated and hardly debated, policy makers pay little attention to the ways in which charcoal is produced and sold and whether the wood used for charcoal burning is harvested in a sustainable way.

The business of imported charcoal from poor countries is often associated with marginal social conditions, uncontrolled and illegal harvesting, inefficient production and health risks. In particular, emissions of GHG and VOC from charcoal making associated with non-technological process in poor countries has been estimated in 0.77-1.63 kg C-CO2 (carbon as carbon dioxide equivalents) is emitted per kilogram of charcoal produced [81].

Figure 28. Typical smokes related to traditional charcoal production of charcoal

The common issues characterizing the charcoal production chain in many African countries comprise [82]:

- unregulated/illegal resources
- rampant and systemic corruption
- inefficient conversion technologies
- a perception that it is a poor man’s business
- considered ‘dirty’ and economically unattractive
- free access to wood resources, leading to deforestation and degradation
- the charcoal business is dominated by a few powerful individuals.

The lack of regulation respect contributes to keep the production costs very low. Market retail price of wood used for charcoal production in Africa is almost zero, due to raw wood material is exploited from unsustainably managed wooded areas. Furthermore, this condition brings to a careless, wasteful and inefficient exploitation of the resource, as well as of carbonisation technologies, leading to an impressive disincentive for forest management and tree growing [83]. Investment costs for improved kilns (metal chimneys, etc.) do not pay off if wood remains a free resource.

1.9 Opportunity for small forestry farms

Charcoal making could represent a viable opportunity for forestry companies to diversify the source of income as well as create a new stable business opportunity other than the typical decentralized power generation. Small scale farmers, typical of Southern Europe Countries, are normally not structured to easily deal with issues such as grid connection and authorizations, emission regulation and compliance, management and operation of biomass power generation systems, etc. Moreover, their financial capabilities are often limited, which means that investing in bioenergy plants and/or providing financial guarantees to obtain loan is not an easy task for most of them, thus representing a significant barrier to a wide deployment of these systems. Finally, bioenergy generation can be economically sustainable only in case economic incentives are made available by State or the Region: this fact creates uncertainty in the investor and risks in financing, as any change in the policy framework can directly and negatively impact on whole business. This represents a relevant obstacle to investments in stationary decentralized biomass based systems [84].

In fact, charcoal making was identified as an interesting alternative based on the following assumptions that can be considered as prerequisite conditions for successful biomass based systems in the forestry sector [84]:

- system must be incentive-independent as much as possible;
- renewable power generation – if present – should represent the co-product of a different primary production, i.e. a real additional income;
- plant capital cost must be affordable for small scale farmers, and operation should require technical skills normally available in the forestry sector;

- reliability of the system must be proven and credible, reducing the risks contained in business plans based on “number of hours of operation over several years”;
- system must be environmentally friendly.

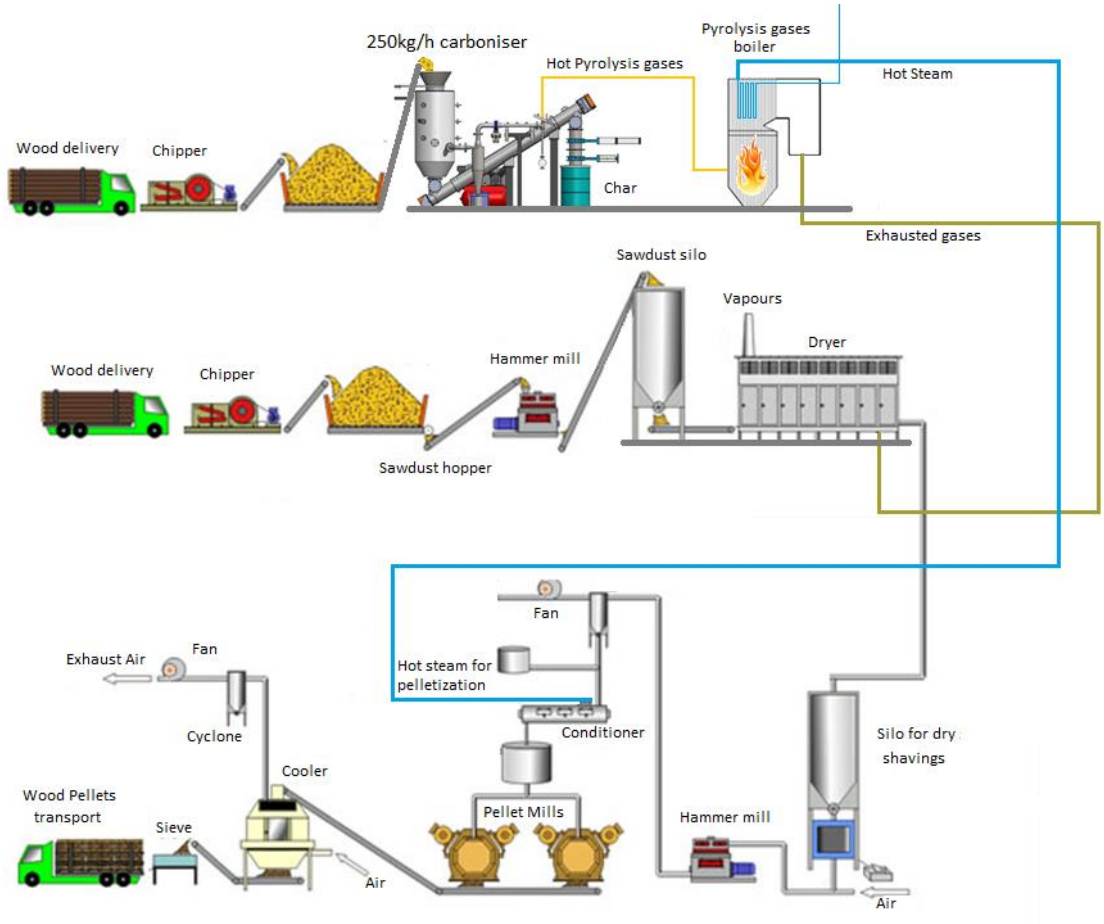

Figure 29. Example of plant scheme of integrated pellet mill and charcoal production

1.10 Aim of the work

This work of thesis has been carried out in the research group of CREAR/RE-CORD of the University of Florence. Aim of this work is to design, build, testing and assess an open top fixed bed downdraft reactor rated 50 kg/h for biomass carbonization, throughout an experimental activity. This work also aims to characterize the entire carbonization process of the pilot unit providing useful information and feedbacks in order evaluate a following upscaling to an industrial scale of 250 kg/h. Deep characterization is carried throughout a mass and energy balance evaluation, as well as an accurate measure of solids, liquid and gas by-products is carried out to compare the result with existing literature experiment in order to set a new benchmark.

In summary, this work evaluates the Re-Cord technology validity from the technical, environmental and economic point of view. The thesis starts from the assumption that the analysed carbonisation reactor depends not only on the quality of the charcoal and the process efficiency, but it is related to a set of external and internal parameters which play a crucial role on the commercialization strategy set up. The global GHG emissions reduction targets set to promote the utilisation of renewable sources, together with the low sustainability of the present charcoal value chain and the strong need for a more efficient monitoring of this market sector, represent an open door for this new sustainable and efficient biomass conversion technology.

2 Carbonization pilot unit

The group CREAR/RE-CORD has been focusing, for at least 10 years on the thermochemical conversion of biomass for energy and chemical production. This work was arranged as a follow-up research started with the regional project BABEL founded by Tuscany Region with the rural developing program PSR 2007-2013 – measure 124. The aim of BABEL project was to study the adoption of wood torrefaction technology and to promote the production and use of torrefied wood in Tuscany region. The project represented for the research group an opportunity to design and build a torrefaction pilot unit, which has been completely modified to build the open top carbonization unit used in in the experimental campaign object of this work.

In order to study the carbonization process and set a scalable pilot unit to be adopted and operated by a small forestry farm, several processes have been evaluated taking in to account: capacity, technological innovation, system complexity, energy consumption, safety, and feedstock & char product characteristics. Batch process represents the most traditional way of carbonization, due its simplicity, low investment cost and a large number of carbonization test results are reported on the literature [69,85]. Despite this traditional process has good qualities such as, possibility to working in pressure, retort configuration, conversion of large particles, higher conversion yields, other critical points cannot be negligible. In particular this process is characterized by a long residence time of biomass in the reactor and for most of the time at variable temperature, meaning a non-optimal control of the process and an untruthful industrial challenge. A unit of a 50 kg/h working in continuous process can be address the challenge of designing an innovative plant and confirm the possibility to make charcoal on small scale with yields comparable to large scale reactors. Results obtained from the characterization of the pilot unit aim to enlarge the few number of continuous carbonization experiments reported in literature. The system chosen is an oxidative auto-thermal process where the thermochemical conversion of biomass takes place in a downdraft fixed-bed reactor operating in open-top configuration.

2.1 Design of the system

Different configurations of the pilot plant have been proposed valuating the possibility of recycling pyrolysis vapour in the reactor for supplying the necessary thermal energy of the process in order to increase the conversion efficiency. To cut the overall cost, the chosen process has been simplified such as the number of components are limited maintaining the functionality of the carbonizer. For instance, the reactor operates below the atmospheric pressure in an open-top configuration avoiding the installation of a controlled feeding system on the top.

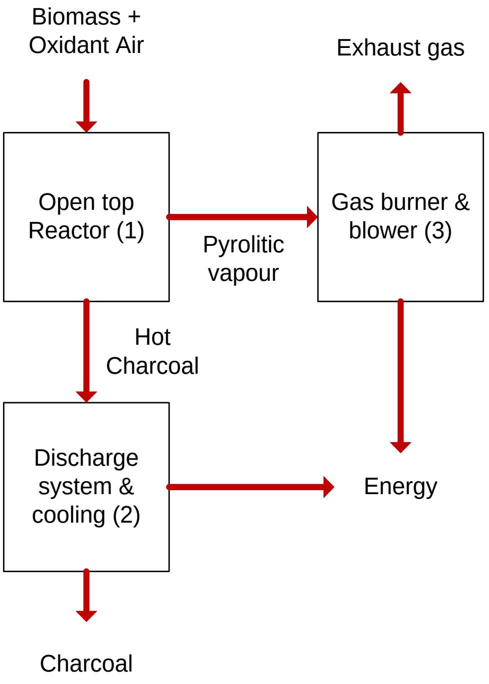

Figure 30. Carbonization pilot unit sketch

The pilot plant is essentially composed by three main sections: (1) loading and conversion of biomass; (2) discharge and cooling system; (3) extraction and burning of the vapour gases.

The first section is characterized by an open-top downdraft reactor, rated 50 kg/h of biomass, where pyrolysis occurs in a controlled oxidative environment at temperature in a range of 450-750°C and ER 0.1-0.2. The heat for pyrolysis is supplied burning a part of pyrogenuos vapours and a part of the biomass.

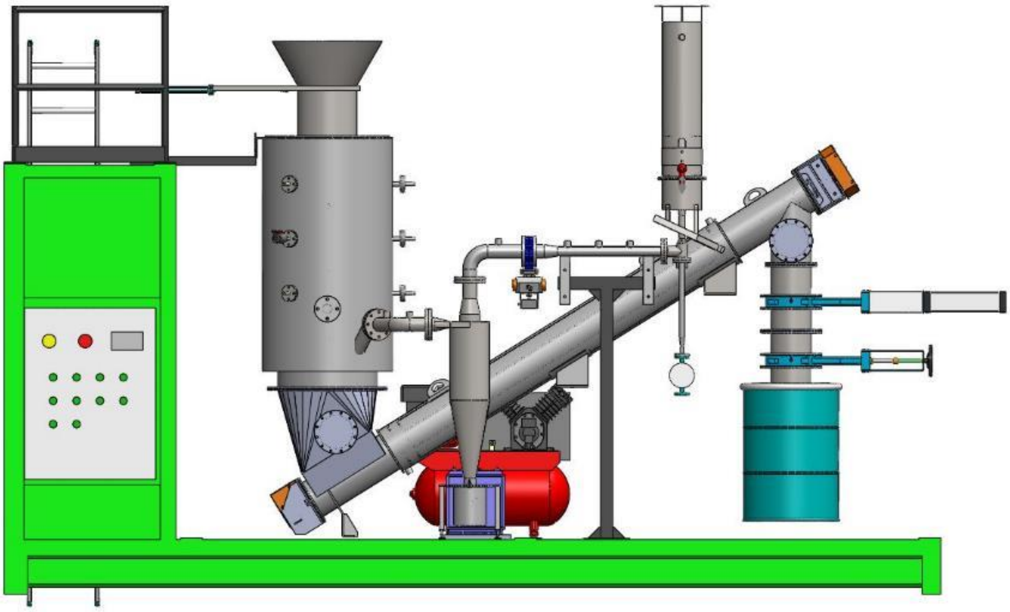

Figure 31. 3D model of the carbonization pilot unit

The discharge and the cooling system (second section) is composed by a cooled-water screw conveyor which must ensure many features: extraction, cooling, reliability, flow-rate control, and air-tightness. After the screw conveyor, charcoal is collected in an airtight removable tank for a lapse-time necessary for cooling down the product up to a safe temperature for handling and storage.

The third section concerns the extraction and burning of the pyrogenous vapours and the recovering of waste heat of the process. An air-driven ejector keeps the gas line pressure below atmospheric ambient, drowning pyrogas from the reactor and consequently sucking air from the top of the reactor to feed the process. To complete the combustion of gas and tars, that represent a sensible pollution emission source, hot pyrogas are burned at stack with possibility to recover heat from the exhaust to benefit adjacent installation and/or for drying biomass input.

At this stage of research, no recovery system has been installed in the pilot unit.

Figure 32. Panoramic view of carbonization pilot unit

2.1.1 The fixed bed downdraft open-top reactor

The reactor has been designed to process an input flow of woodchip or cubes of biomass of 50 kg/h with a moisture content of 15% on a dry basis (typical value for biomass air dried in sheltered environment), exploiting part of the gases produced by devolatilization to feed the process (autothermal) and burning them directly inside the reactor simultaneously to their production. Biomass and oxidant air enter from a top opening and both descend vertically (downdraft) before being extracted from the bottom. By operating in open-top mode, the plant is intrinsically explosion-proof, as it cannot go in overpressure in case of fault.

The fixed-bed reactor is a cylinder canister with internal diameter of 630mm, height 1610 mm, completely made of stainless steel AISI 316, to prevent corrosion due to combined action of acids compounds and reducing environment. A thermal insulation of 10 cm thickness of fibre ceramic and rock wool is installed externally the vertical wall of the reactor.

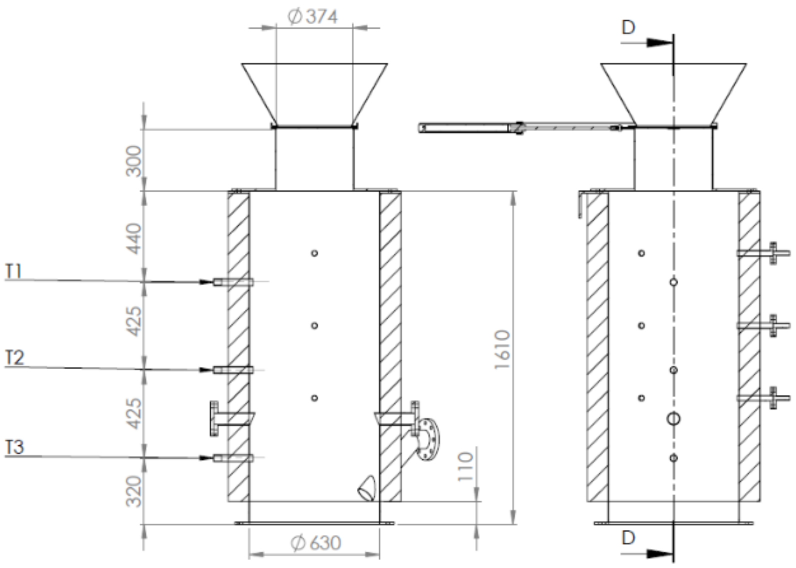

Figure 33. Details of the reactor

On the top there is also installed a non-hermetic knife gate valve, kept open during normal operations, but which closes the upper entrance during shutdown and allows leaking of gas to avid overpressure. Biomass loading and feeding has been done manually pouring the feedstock directly into the reactor, since there hasn't been installed any automatic system on the pilot unit at this stage. During normal operations biomass level should be maintained as possibly constant, in the buffer duct mounted between gate valve and reactor.

Nine secondary air inlets arranged along the reactor at three different heights are included in the reactor to experiment different working condition. All the tests considered in this work have been carried out with additional openings closed. Process ignition is ensured by manually operation through two opposite openings placed on the bottom. Three thermocouple type K (T1, T2, T3) have been installed along the reactor in order to measure and control process temperature profile.

The residence time of particle in the reactor has been set as a minimum of 2 h to obtain a slow heating rate and consequently improving carbonization [26,28].

Figure 34. Reactor details: side view with thermocouple and top view

Superficial gas velocity (SV) expected, varies along the reactor from 0.02 m/s at top and 0.12 m/s before extraction. This is in accordance with literature, which a low SV causes relatively slow pyrolysis conditions at around 600°C, and produces high yields of charcoal 20-30%, large quantities of unburned tars, and a gas with high hydrocarbon content and high tar (volatile) content [86].

Gas extraction pipe is 3 inches tilted at 45° to prevent entrainment of solid particles and fines of converted char bed from the bottom of the reactor to downstream gas line and components. The reactor is directly flanged and mounted on the inlet hopper of the discharge screw conveyor.

2.1.2 Discharge and cooling system

A screw conveyor is installed under the reactor allowing to control extraction of hot charcoal and consequently the residence time and the biomass flow capacity of the carbonization process. It has been designed to discharge up to 120 kg/h of charcoal mass flow with a maximum particle size of 8-10 cm and it is also capable of dust handling, in fact char does not present particular difficulties for the auger because char powder performs such as a lubricant.

In order to reduce height of the entire unit, the screw is tilted of 32° without any limiting in discharge capacity. It is made of stainless steel AISI 304 completely air-tight to prevent risks of explosions and leaking of char dust. A hopper of 0.1 m^3, with at least 70° slopes, supports the above reactor and channels hot charcoal for the time necessary to start cooling. The screw conveyor is around 3 m length and has an internal diameter of 250 mm. The electrical motor is controlled by an inverter in order to continuously vary the rotational speed, as well the mass flow rate. To ensure lower mass flow rate is it possible to interrupt the discharge and set an “on-off” interval time by means of the PLC.

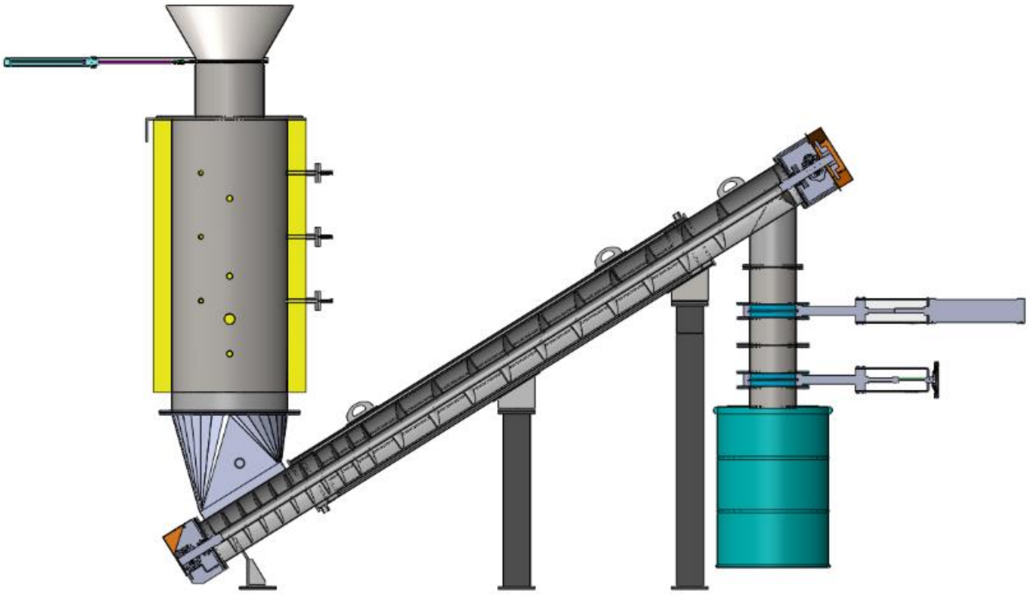

Figure 35. Section view of the char discharge system and reactor

Discharge of the hot products generates problems of handling and storage due to the risk of self-ignition of the same, then it is considered safe to expose the coal in atmospheric environment only at temperatures below 65°C [69]. The hot charcoal is then stored in special tanks air-tight waiting for the natural cooling process. Given the long-time dedicated to this operation the plant requires more tanks (0.2 m^3 barrel) replaced manually during the process. Hermetic condition is ensured by a knife gate valve installed downstream, which is closed during barrel replacement.

Figure 36. Char collector barrels

To accelerate cooling of hot charcoal to the benefit of operations and limiting following risks of self-ignition during storage [87], the external wall of the conveyor is jacketed (for a length of 2,5 m) with an outer line in which flows cooled water.

Several temperature sensors are installed on discharge section of the unit, to monitoring and to prevent any overheating and consequently damages to the one of the most delicate part of the carbonizer. Two thermocouple type K are placed at the inlet (T8) and outlet (T9) of the screw conveyor to evaluate temperature drop of charcoal. Temperature of discharged charcoal in the barrel is manually measured every regular time intervals (T10).

2.1.3 Gas line: extraction and burning

The third section concerns the extraction and burning of the pyrogenous vapours and the recovering of waste heat of the process. Hot vapours are extracted from the bottom of the reactor by an air blown ejector capable of working with good reliability at high temperature (up to 600°C) and with condensable vapour (tars). It is important to note that the piping system must be kept at temperatures above 380°C to avoid tars condensation and the consequent possible clogging of the line, for this reason the pipe is thermally insulated. Between reactor and ejector, a cyclone-filter removes solids and particles.

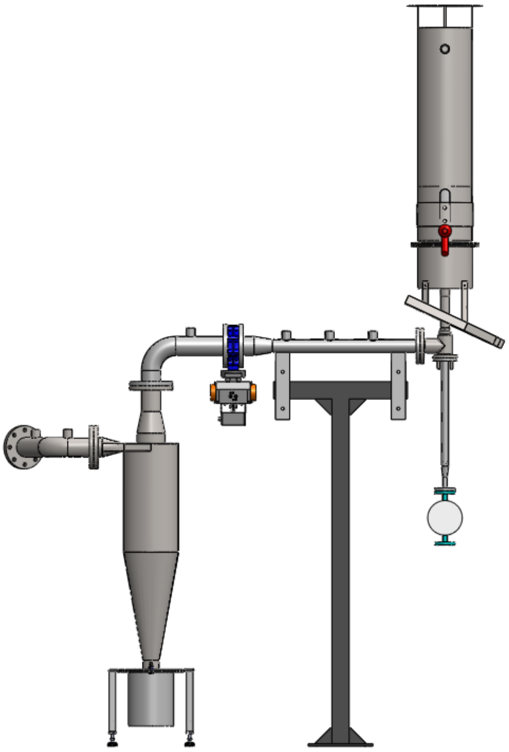

Figure 37. Pilot unit gas line 3D model

The ejector has been designed to control the air-ratio in the process and extract approx. 60-70 kg/h of vapour at full operation from the reactor, and consequently to feed in oxygen inside, creating a sub-pressure that draw the air inside the reactor. The ejector is regulated by a butterfly valve which ensures the required vacuum pressure and therefore the expected gas mass flow along the pipeline. A reciprocating compressor of 5,5 kW (7,5 Hp) feeds the ejector and others equipment.

As mentioned, a burner linked with a heat recovery exchanger is installed downstream the ejector to complete the combustion of gas and tars that represent a sensible pollution emission source. A pilot burner of 6 kWt is used in this experimental campaign to ensure the complete combustion of pyrolysis vapour at torch.

The ejector is made in AISI 316 capable of working at temperature up to 600°C and it is driven by compressed air in the range of 2 - 4 bar g in order to create necessary low pressure and drawing the gas. Once the driven flow pressure is set, the regulation valve is adjusted to set the pressure drop through the gas line and to suck the desired process gas flow. Maximum mass flow rate sucked by ejector is approx. 113 kg/h considering the pressure drop on the line with valve completely open.

During the commissioning tests, the gas line was firstly supplied with air at ambient temperature causing local condensation of tar and subsequent clogging of the ejector itself. To prevent cold spot and enhance the durability of the tests, it has been installed a heater to supply air up to 500°C.

More details on the ejector and its gas flow control are reported in the following paragraph.

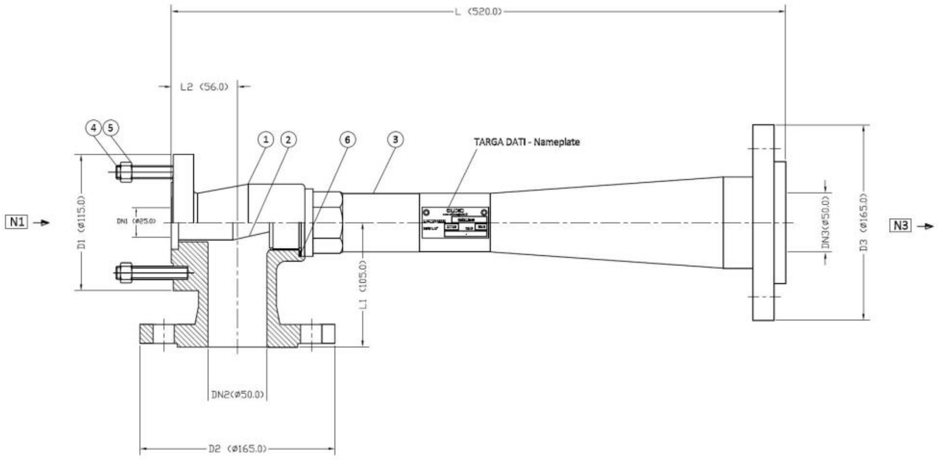

Figure 38. Technical drawing of the high temperature air driven ejector

Combustion of pyrolysis vapour takes place in a in a cylinder stack, of 250 mm diameter and 1300 mm length, installed at the ejector discharge port. The hot gas flowing at high speed ratio (> 20 m/s) hits a bluff body to increase its turbulence in proximity of the pilot burner. Oxidant air necessary to the incineration is primarily supplied directly in the ejector due to the motive air (approx. ER=0,05) and the rest is naturally drawn throughout an opening placed at the bottom at the stack. Relative position of pilot burner and bluff body can be adjusted depending on process conditions and gas quality. A thermocouple is placed in the stack to measure combustion temperature and to display quality of combustion. An additional opening port exists to collect exhaust gas before being discharged it in the atmosphere.

Figure 39. Details of stack and gas regulation valve

2.1.4 Piping & instrumentation diagram

The pilot unit is equipped with a PLC, which allows to control the process and to visualize data obtained from sensors installed on the unit. Regarding temperature measurement, eight thermocouple type K were used on the plant: three for the internal temperature of the bed reactor, two for the hot gas in the pipeline, two in the screw, and one at the torch for the combustion of the pyrogenous vapours. Two pressure transducers are installed on the gas line to measure relative pressure after the reactor and another before the ejector. A manometer coupled with pressure regulator is installed to control the air-flow to the ejector. A schematic of the carbonizer is reported in Figure 40.

Two measure points for gas characterization are displayed in the scheme: GA is for hot tar sampling and gas analysing, EM is for exhaust gas measurement.

In Annex A is reported a detailed P&iD of CarobON pilot unit developed by Re-Cord. The system is covered by a patent for the Italian market: "*Impianto per la produzione di carbone vegetale*" IT FI2015A000109 (2017).

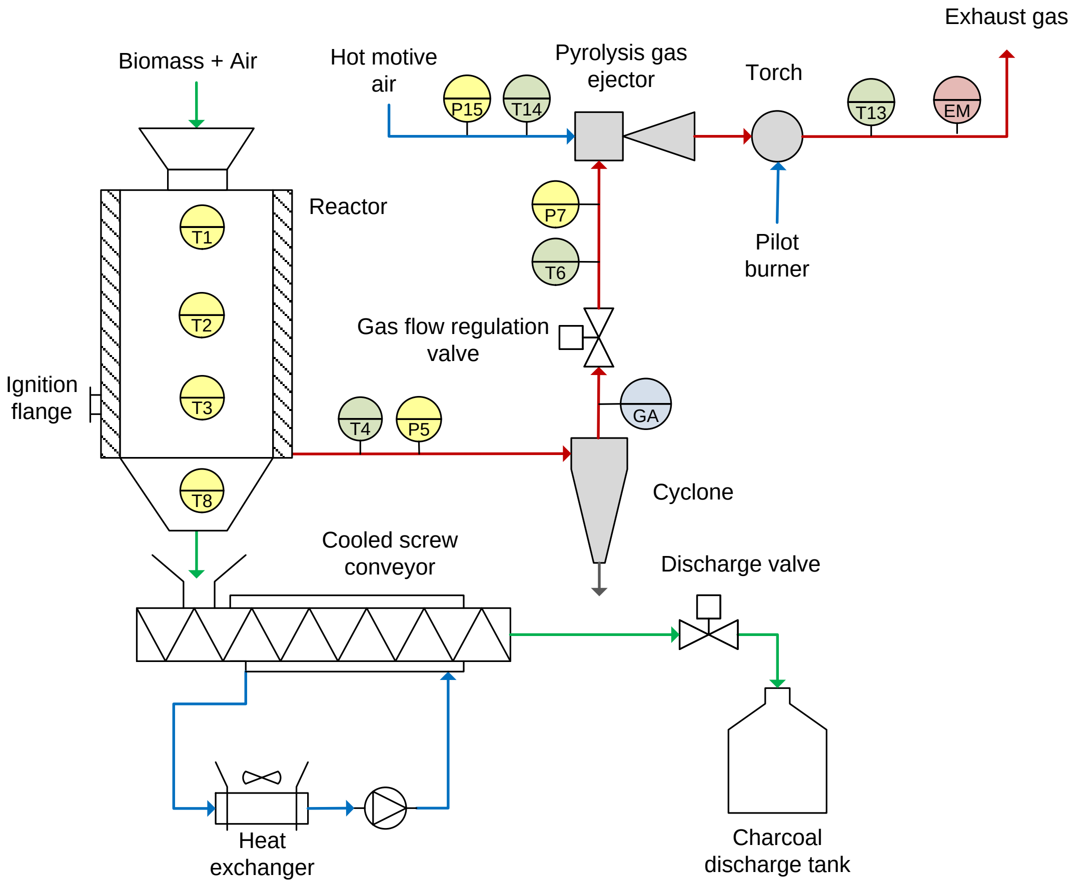

Figure 40. P&ID of the CarbON unit

2.2 Design principle

2.2.1 Preliminary mass and energy balance

Carbonization pilot unit reactor was initially designed after a long study of available literature trying to optimize the size and the process configuration in order to set up and develop a robust asset aiming to research the continuous process and furtherly scaling up an industrial system. Through Babel Project and other works [88], Re-Cord developed and designed a reactor capable of convert 50 kg/h of woodchip in continuous operation. To avoid any type of wasteful and inefficient process modelling, reactor design was based on basic calculation and hypothesis; after the experimental campaign, it was verified that the assumptions were very close to the actual results. To calculate the heat for pyrolysis, it was assumed: to heat woodchip with moisture content of 15% wt., from ambient to 500°C. Based on literature review on existing plant we assumed also a carbonization efficiency of 24% wt. db.. Heat of pyrolysis was conservatively assumed to be negligible and it was set an iterative calculus to estimate the quantity of biomass and pyrolysis vapour to burn in order to generate the heat necessary to take the rest of the biomass in pyrolysis condition, and taking in to account also stoichiometric air input and dissipating heat.

The theoretical ER calculated was 0.1, with air flow input of 25 kg/h and an estimated gas flow rate of approx. 65 kg/h. Results of the preliminary mass and energy balance, considering the reactor and potential energy recovery are reported in Figure 41.

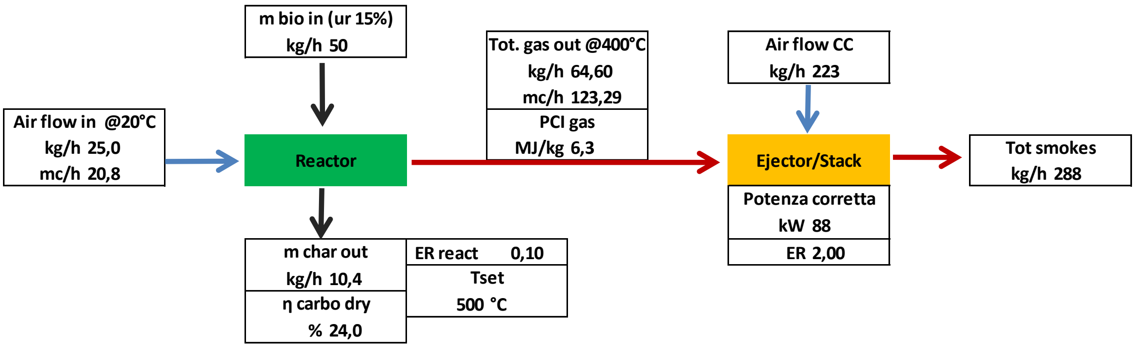

Figure 41. Preliminary mass and energy balance

2.2.2 Gas line and ejector design

Gas flow speed in the pipes has been chosen as a compromise between pressure drop through the line and dragging to limiting tar and particles accumulation. Considering gas at 400°C the speed at full operation are respectively: 6.5 m/s for 3 inches and 15 m/s for 2 inches pipes. Pressure drop along the reactor has been considered at maximum 15 mbar, according Dasappa results [89] on a similar reactor operating in gasification condition. Pressure drop of the line and cyclone are 1.5 mbar e 8 mbar [88].

A customized ejector has been specifically manufactured for this application taking in to account desired process data and some margin. It is composed by three parts: nozzle, main-body and diffuser; and it is easy to be disassemble and cleaning to remove any blockage.

Working principle and flow directions are reported in the following scheme:

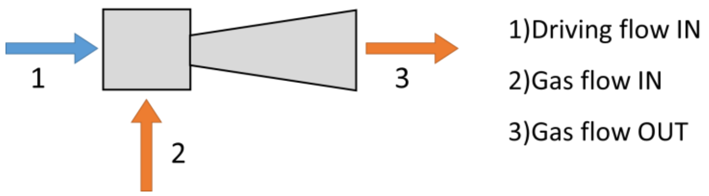

Figure 42. Working principle scheme and legend of air driven ejector

Mass balance equations which rule the ejector are:

$$\begin{cases} \dot{m}_1 + \dot{m}_2 = \dot{m}_3 \\ \dot{m}_1 = f(T_1, P_1, nozzle, fluid_1) \\ \dot{m}_2 = f(T_2, P_2, \dot{m}_2, fluid_2) = f(T_1, P_1, T_2, P_2, fluid_1, fluid_2, nozzle) \end{cases} \tag{3}$$

Despite the small difference between air density and pyrolysis vapour density, we have been assumed to suck air from the process, without any remarkable difference in results. Following formulas consider fluids such as an ideal gas. It has been also considered that outlet pressure is atmospheric.

Mass flow rate through the nozzle [kg/h] (air nozzles at supercrit. press. ratio) is:

$$\dot{m}_1 = 3600\,\varphi \frac{\pi D^2}{4} P_1 \sqrt{\frac{2}{RT}\frac{\gamma}{\gamma+1}\left(\frac{2}{\gamma+1}\right)^{\frac{2}{\gamma-1}}} \tag{4}$$

with respectively:

D = nozzle throat diameter [m] = 3.6 mm

φ = nozzle coefficient = 0,99

γ = adiabatic exponent (cp/cv) - (constant with temperature)

T = absolute fluid temperature [K]

R = constant gas, 287 J/kg K

$\dot{m}_1$= driving fluid flow [kg/h]

P1 = driving fluid pressure (abs.) [Pa a]

Intake air mass flow rate [kg/h] is:

$$\dot{m}_2 = \dot{m}_1 K \sqrt{\frac{293}{273+T_2}} \sqrt{\frac{273+T_1}{293}} \tag{5}$$

with: *K = experimental coef. provided by manufacturer (is function of P1 and P2)*

Gas outlet speed from diffuser [m/s]:

$$V_{out} = \frac{\dot{m}_1 \frac{C_1}{MW_1} \frac{1.013}{P_1} + \dot{m}_2 \frac{C_2}{MW_2} \frac{273+T_2}{293} \frac{1.013}{P_2}}{3600\,A} \tag{6}$$

with:

A = end cross section of diffuser [m^2]

P1 and P2 = absolute pressure [bar a]

T2 = intake fluid temperature [°C]

C = fluid molar density [l/mol] = 22,4 l/mol

MW = fluid molar weight [g/mol] = 29 g//mol air

For safety reason is important to verify and avoid any risk of back-flare from the stack into the gas line through the ejector. In this case, ejector already consists in an active flame arrestor (Venturi type) [90] and the gas speed must be higher than maximum flame speed of the fuel component existing in the fuel gas.

The **maximum gas speed in the ejector throat**.

$$V_{max} = V_{out} \frac{D}{d} \tag{7}$$

D = end diffuser diameter [m] = 0.052 m

d = ejector throat diameter [m] = 0.024 m

According to Perry [91] the maximum flames velocity for Hydrogen mixed with air at 57% (gas mixture non ignited) I 2.83 m/s which is reasonably higher with margin than gas velocity recorded during the tests that will follow (i.e. test 11: > 25 m/s). This verify allows to ignite the pilot burner for all the entire test duration even during the start-up of pilot unit.

Here below is reported in Table 10 a summary of some ejector data relative to driving air ambient temperature and including experimental K factor experimental coefficients provided by manufacturer. Internal diameter of nozzle ejector is 3.6 mm.

Table 10. Summary table of ejector data including K-factor provided by manufacturer

DRIVING PRESS. (bar a)	DRIVING TEMP. (°C)	DRIVING AIR FLOW (kg/h)	VACUUM PRESSURE (bar a)	K_ejector	GAS TEMP. (°C)	GAS FLOW (kg/h)	OUTLET SPEED (m/s)
3	20	25,70	0,988	4,184	400	70,9	23,6
			0,963	2,8896		49,0	18,7
			0,938	1,3982		23,7	12,6
			0,921	0		0,0	6,7
4	20	34,26	0,988	4,237	400	95,8	29,5
			0,963	3,4955		79,0	26,0
			0,938	2,7188		61,5	22,1
			0,913	1,65958		37,5	16,4
			0,888	0,6356		14,4	10,5
			0,876	0		0,0	6,7
5	20	42,83	0,988	3,6945	400	104,4	31,6
			0,963	3,5808		101,2	31,4
			0,938	3,1545		89,1	29,1
			0,913	2,5009		70,7	24,9
			0,888	1,8188		51,4	20,3
			0,863	1,0799		30,5	15,0
			0,838	0,3126		8,8	9,2
			0,83	0		0,0	6,7

To control accurately the gas mass flow rate during the test it has been created a Matlab function where it is possible to set data input temperatures, pressures and desired gas flow rate, obtaining the pressure P2 to set manually on the gas line through opening valve regulation, as well as the calculated velocities. Ejector K coefficients were interpolated in Matalb allowing to obtain a continuous function valid for whole working condition of the ejector (Figure 43).

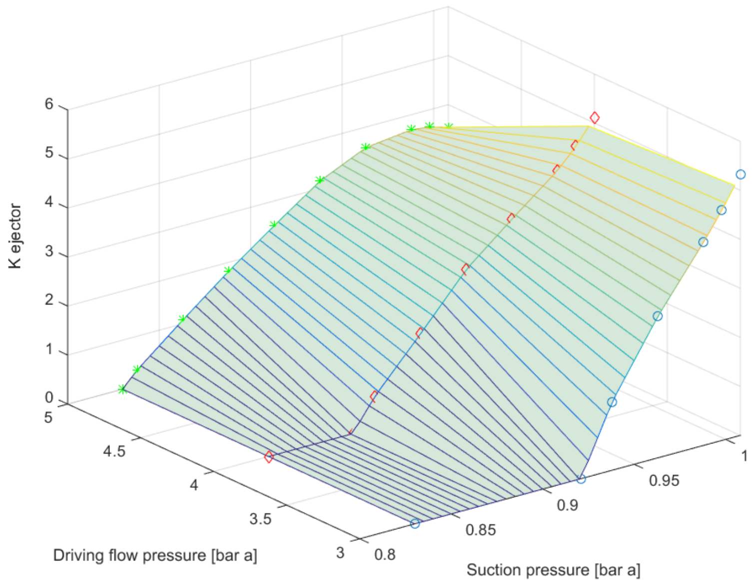

Figure 43. Matlab chart of K ejector coefficients

2.3 Validation tests

After the construction of the pilot unit it was carried out an extensive test campaign to validate functioning and design of the pilot unit and primarily evaluating the performance in view of a dedicate experimental test which aimed to measure and characterize the entire process. These validation tests might be also considered a commissioning tests to proof the efficacy of carbonization and verify the mechanical reliability of the designed system. Useful data has been collected to acquire experience to scale-up and design a new innovative continuous carbonizer to an industrial scale based on the 50 kg/h pilot unit.

The entire test campaign, which has been carried out during this work of thesis, comprises 13 tests for an overall duration of 65 h (ejector working), testing two different types and species of woodchip (approx. 2500 kg of biomass has been used) and obtaining interesting and encouraging results.

Figure 44. Carbonization unit during functional test operations

In this paragraph are explained the most representative validation tests (4 and 6) to report preliminary observation including reactor behaviour, reliability, issues and positive feedbacks on the technology. The scope of this paragraph is only to introduce the experimental test. A better and complete description regarding adopted methodology, procedures and achieved results are reported in Chapter 3, as well as a full and detailed experimental activity of two final tests (11 and 12) with several analysis and characterizations available in comparison with existing literature experiments.

Results of tests 4 and 6, here described, were presented by Re-Cord group at European Biomass Conference & Exhibition in Vienna in 2015 [92]. Both tests were performed using the same methodology and showed two different results.

Woodchip used within the test was mainly hardwood chestnut coming from Florence area and produced by a drum chipper[3], rich in small thin particles and dust and with nominal size of 1-2 cm. Moisture content at the time of test was 18,7 %wt. ar., bulk density (ar.) was 225 kg/m3. and fixed carbon content was 25,2 %wt. db.

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[3] Woodchip for tests 4 and 6 is the same of test 12. Basically only moisture content changed between the tests.

An online gas analyser (NDIR/electrochemical gas analyser) was used to monitor dry gas composition before incineration of: CO, CO2, CH4+, O2 and H2. Before entering the instrument, the gas was forced to pass through 3 traps (impinger bottles) to remove water vapour, tars and particulate.

In order to reduce the heating time during the start-up, the reactor was loaded with charcoal up to the lateral flange and then filled with woodchip. The char bed was ignited manually through both lateral flanges with ejector working. During these tests, the pilot burner was switched on when oxygen concentration in the gas was under 2% vol., although any risk of back flare existed due to the intrinsic security of the ejector itself. Biomass was manually loaded at regular interval to maintain at the top the bed height and the gas flow rate it was set to 65 kg/h to simulate the designed condition. Both tests lasted untill any failure happened to the reactor.

At the end of the test, to obtain a qualitative evaluation of carbonization efficacy char samples were randomly collected from the barrel, mixed together and sent to laboratory.

Table 11. Summary of test data of validation tests 4 and 6

Test data	**Unit**	**Test 4**	**Test 6**
Feedstock			
Moisture	*% wb. ar.*	*18,7*	
Ash	*%wt. db.*	*0,7*	
Volatile Matter	*%wt. db.*	*74,1*	
Fixed carbon (calc.)	*%wt. db.*	*25,2*	
Mean size	*cm*	*1-2*	
LHV	*MJ/kg (db.)*	*17,7*	
effective duration (ejector working)	*hh:mm*	*04:34*	*05:38*
average capacity (at full operation)	*kg/h*	*31,4*	*41*
pilot burner ignition after	*hh:mm*	*0:45*	*1:15*
Average main temperatures			
T2 reactor	*°C*	*533*	*589*
T3 reactor	*°C*	*617*	*617*
T4 gas	*°C*	*409*	*403*

Some considerations were addressed together for both tests because the behaviour was basically repetitive despite some issues due to biomass bridging in the reactor. Pressure drop along the reactor was 1 mbar. Gas temperature coming out from the reactor was stable during the test in the range of 450 – 500°C and also an effective regulation of the gas extracted from the reactor was proved.

Continuous adjustment of the regulation valve opening was necessary to compensate the gas flow loss caused by partly clogging of the line. Condensation of water and tars was largely visible at torch until the ignition of the pilot burner as well as a reaching of 300°C on gas line (T4).

Although the averages measured temperatures of two tests were similar and close each other (T3 = 617°C for both), reactor temperature profiles were different due to instability with obvious differences in carbonization results. This instability was caused mainly by biomass bridging issues in the reactor where temperature decreased in proximity of the bridge with the effect that bed was not properly stratified and homogeneous after removing the bridge. This issue limited primarily the quality of char produced and also the capacity of the reactor itself.

Generally, the pilot unit showed good and promising results in view of the experimental campaign which followed. Here below are reported some details of the two tests with temperature, gas and char results.

2.3.1 Test 4

Test 4 lasted 4 h and 34 min and was affected by bridging for the entire length. In particular was evident that T3 was unstable only for 45 min after the pilot burner ignition to become stable at 650-700°C. T2 instead, didn’t never reach stability and it went down to below 200°C most probably for a large bridging occurred between 12:00 and 12:50. In this period of time T1 increased meaning that water vapour went back to the reactor top opening due to lack of biomass in the upper zone and also low extraction gas flow rate. After manually removing the bridge and readjusting the flow rate (at 12:43) the T2 increased proving the effective regulation of the unit. This it was also confirmed by the reduction of T1.

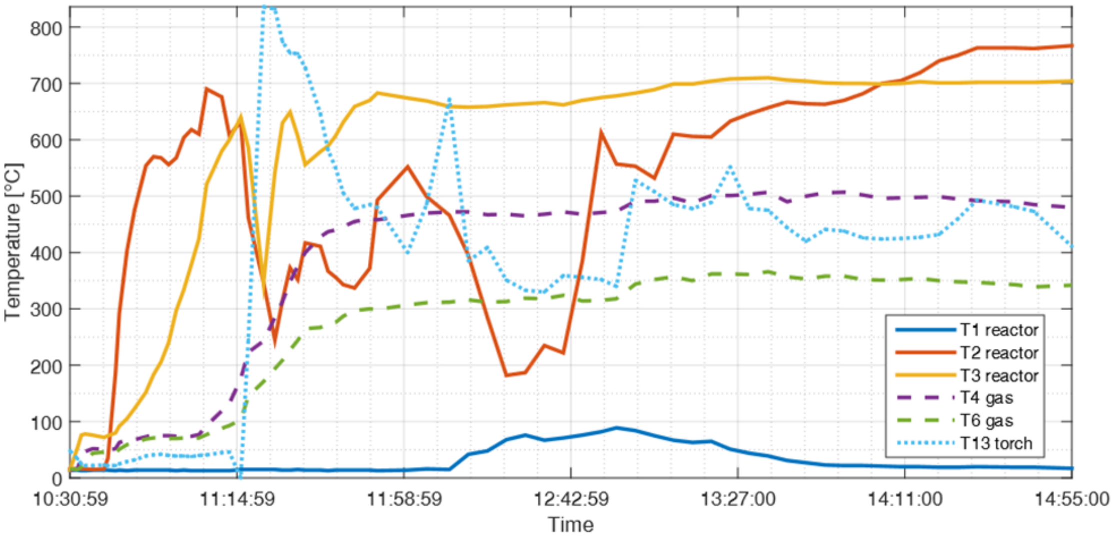

Figure 45. Test 4: reactor temperature profile

Average biomass capacity was 31 kg/h, confirming that bringing influenced this parameter and also low char conversion was expected in this test. After the ignition of the pilot burner at stack, T13 reached its peak above 800°C because of condensate organics were burning.

In the Figure 46 below are reported the pressure measured on gas line and gas composition.

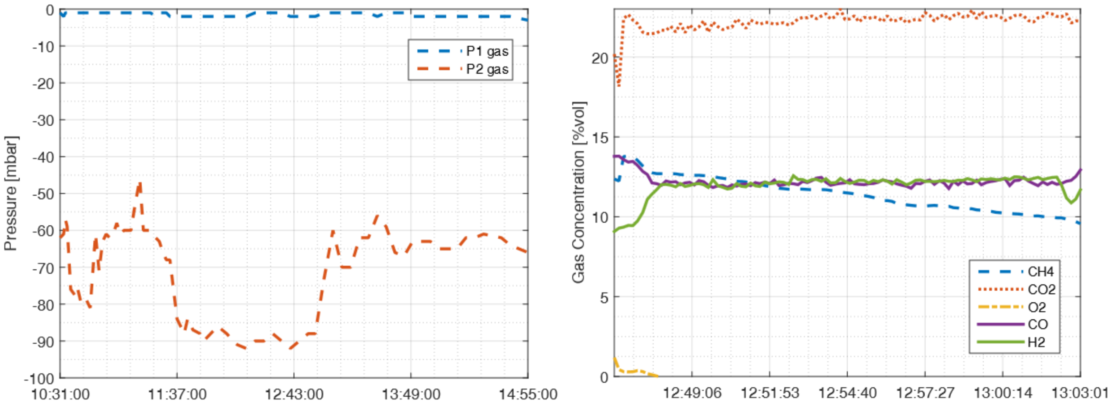

Figure 46. Test 4: gas line pressure and gas line analysis

Dry gas composition was measured for 15 min (12:48 – 13:03) after bridging removal. It was extremely stable and complied with literature. CO2 was the most predominant specie as expected (22%vol.), as well as CO and H2 (12%vol.). CH4 was presumed to be high due to measure affected by organics and for this reason it was necessary to replace traps filter during the test. In Table 12 are listed the average dry gas composition of test 4.

Table 12. Test 4: average composition of dry gas

Test 4: Average composition of dry gas (%vol)	
CH4+	*11,4*
CO2	*22,3*
O2	*0,0*
CO	*12,2*
H2	*12,1*
N2 (calc.)	*42,0*

2.3.2 Test 6

Test 6 proved the reactor stability in a long run and achieved important results in terms of quality of charcoal produced. Effective duration of test was 5 h and 34 min, longer than test 4 and it lasted until reactor temperatures collapsed due to a bridging. After pilot burner ignition (11:20) T2 presented some variability due to minor bridging which didn't have influence on bed stratification. Between 13:00 and 14:45 reactor was stable at high temperatures with T2 and T3 in range of 650-750°C and the gas flow rate was set at 80-85 kg/h.

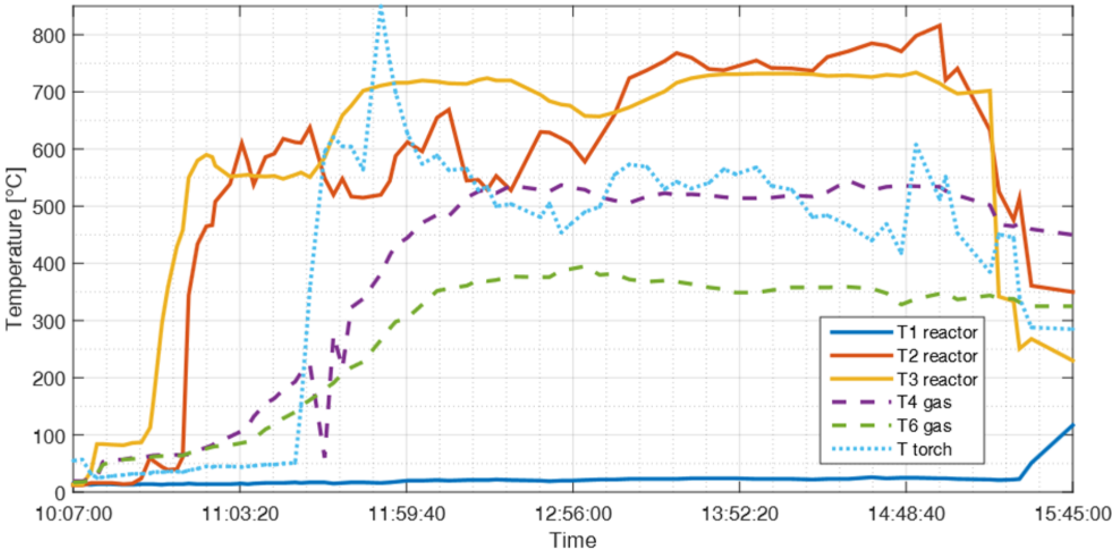

Figure 47. Test 6: reactor temperature profile

Despite the temperature were higher in comparison to optimal carbonization condition, the reactor was under control and continuously regulated to maintain its stability. In fact, average biomass capacity of this test was 41 kg/h confirming that it was possible to reach the design parameter of 50 kg/h target with some minor improvement on the pilot unit. At 15:00, a final bridging happened in the hopper between reactor and screw conveyor and after some attempts to remove it the test was interrupted.

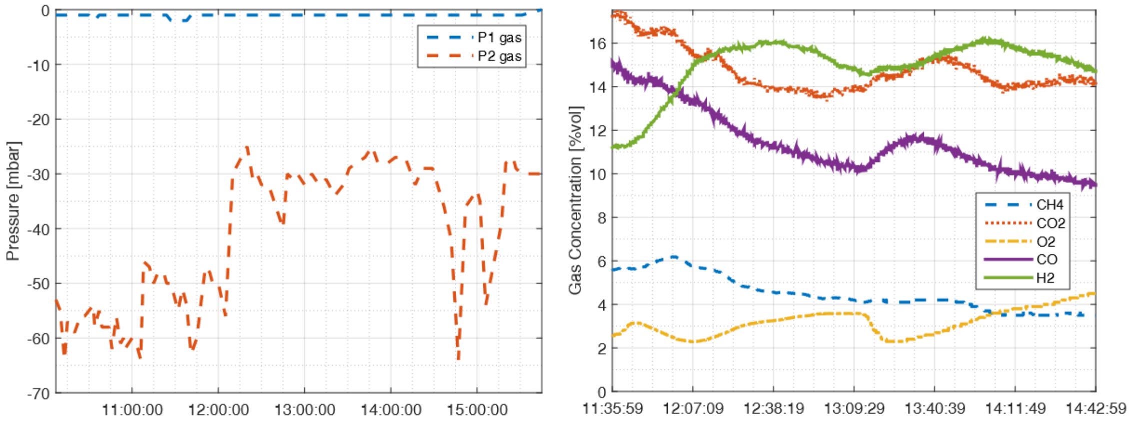

Figure 48- Test 6: gas line pressure and gas line analysis

Dry gas composition (Figure 48 and Table 13) was recorded for more than 2 h and the measurement was affected by non-air sealing in the conditioning line which influenced the stability. High concentration of H2 was recorded (av. 15%vol.) as well as CO2. High temperature on reactor had an influence on cracking reaction reducing the amount of heavy compounds and CH4+ with increment of H2.

Table 13. Test 6: average composition of dry gas

Test 6: ***Average composition of dry gas (%vol)***	
CH4+	*4.39*
CO2	*14,81*
O2	*3,14*
CO	*11,29*
H2	*15,11*
N2 (calc.)	*51,26*

2.3.3 Preliminary observations and further improvements

Lab analysis on char samples collected after the test showed two different results as expected. The main difference was in Fixed carbon content that was 72,6 %wt, db. for Test 4 and 92,6 %wt.db. for test 6.

Fixed carbon content of test 4 was influenced by bridging occurred in the middle of test and in fact the char content didn't comply with EN 1860 Norma for BBQ charcoal which requires at least 75%wt.db. of FC., but instead it was suitable for biochar application. The high value of FC (92,6 %wt.db.) resulted in test 6 demonstrated that it was possible to convert with efficacy woodchip, proving the effective working of the designed reactor, as well as the obtained charcoal could be suitable in many sectors application such as metallurgy and activated carbon production. In Table 14 are reported proximate analysis and calorific value of char samples for the two validation tests.

Table 14. Carbonization test 4 and 6 results

Char analysis results	**Unit**	**Test 4**	**Test 6**
Moisture	*% wb. ar.*	*4,0*	*4,3*
Ash	*%wt. db.*	*26,0*	*6,5*
Volatile Matter	*%wt. db.*	*1,4*	*0,9*
Fixed carbon (calc.)	*%wt. db.*	*72,6*	*92,6*
HHV	*MJ/kg (ad.)*	*28,1*	*30,3*

Small size carbonized woodchip doesn't satisfy charcoal norms (EN 1860) and for this reason for further experiment was necessary to test a larger woodchip size.

Figure 49. Char collected after test 6 and char sample

In picture Figure 49 it is shown a bridging occurred at the top of the reactor. Basically, woodchip used had a large amount of fines and dust which didn't flow properly down trough the reactor. A metallic pole was used within the test campaign to press down the bed and limiting bridges formation.

Figure 50. Bridging effect at the top of the reactor

Since is difficult to measure accurately bed temperature into the reactor and taking in to account radial distribution, thermocouples were installed horizontally to measure centre zone in the reactor. In these tests, it was evident that some of the bridging causes were also thermocouple position.

Other possible sources of biomass bed instability were caused by: sucking hot gas from one lateral single opening (opposite to thermocouples) causing potential possible preferential channels through the bed; and rotation and shape of the screw which recirculates converted woodchip in the hopper.

In Figure 51 is reported the internal view of the reactor during discharge the day after the test. In the picture is evident that the left side, in proximity of thermocouples, collapsed while the right side was static. One probable reason could be that during the cooling of the reactor part of vapour condensate on woodchip acting as adhesive.

Figure 51. Biomass bed instability inside the reactor

To overcome and reduce bridging on following tests, thermocouples were moved on the side of the reactor avoiding any sort of resistance to the bed flow. Bottom hopper which connects reactor and screw conveyor was modified, increasing inclination from 60° to min 75° to avoid any risk of bottom bridging formation.

Figure 52. Agglomerate of tar at ejector and tar condensation at torch

Tar and vapour condensation was extremely evident during the warm up of the process, thus until the gas reached at least 300°C on pipe line. During this transient time, it was presumed that part of the tar condensate on some point in gas line causing partial clogging and blockage of the line. Inspection confirmed that torch worked properly after pilot burner ignition and all the tars were burnt above the pilot burner as shown in Figure 53.

Figure 53. Internal view of the ejector and stack during inspection after the test

The most critical part was the ejector where in proximity of the nozzle were large amount of tars agglomerate were found. Nozzle fed with ambient temperature represented a cold point where tar condensate on nozzle surface for all the duration of test until the blockage. To improve the system, it was decided to design a pressurized air heater to avoid condensation at ejector. Despite the new feature was available only for test 12, the start-up and ignition procedure was changed limiting tar condensation and sending preheated gas to ejector.

The new start-up procedure consisted in ignition of the char bed, filled up to lateral flanges, with reactor empty and ejector off. Woodchip was gradually added until the reactor was filled up to the top opening and ejector was finally enabled only when reactor temperature profile was optimal for carbonization (T2/T3 500°C). The new procedure warmed up the downdraft reactor in updraft configuration such as some small gasifiers [15].

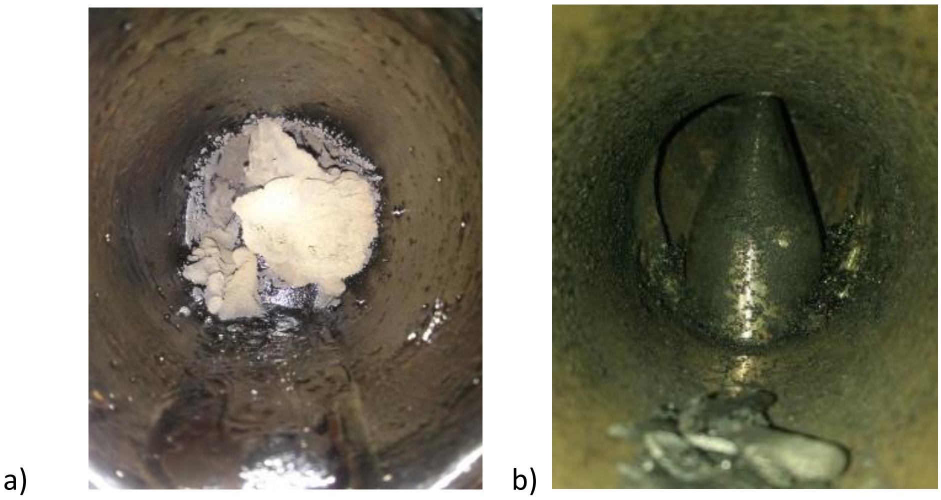

Figure 54. Tar condensation effect at ejector nozzle with motive air at: a) T ambient, b) 400°C with heater

With the new air heating system of 5 kW it was possible to set and maintain the temperature up to 500°C. In Figure 54 is shown tar condensation effect after approx. 12 hours ejector working with ambient air with blockage of gas line (figure a) and the nozzle completely tar free after working 7 hours with 400°C air in test 12.

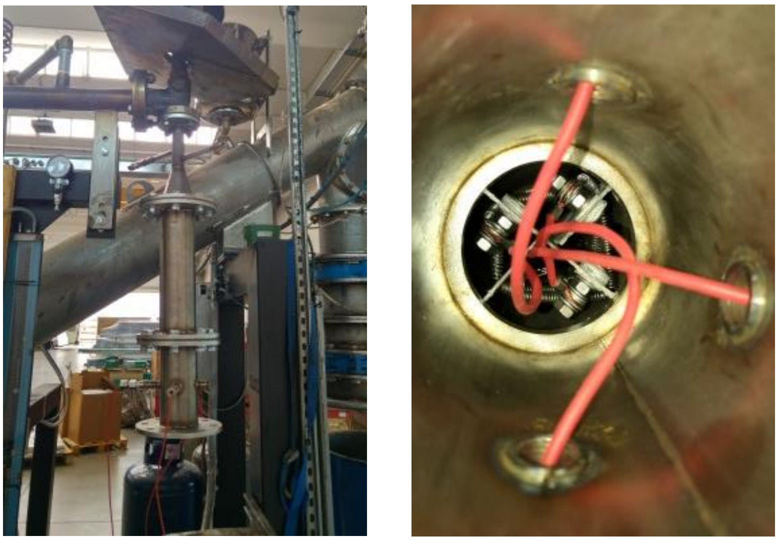

Figure 55. Pressurized driving air heater with internal view

During the experimental campaign, some other failures and blockages on the gas line occurred at cyclone inlet especially caused by part of the bed was sucked with vapours from the reactor. The first reason is because small carbonized woodchip is very light and at high flow rate above 70 kg/h part of the bed was dragged from reactor. In fact, no issues were found operating with larger woodchip. Figure 56 shows part of the char bed that was found on the pipe between reactor and cyclone.

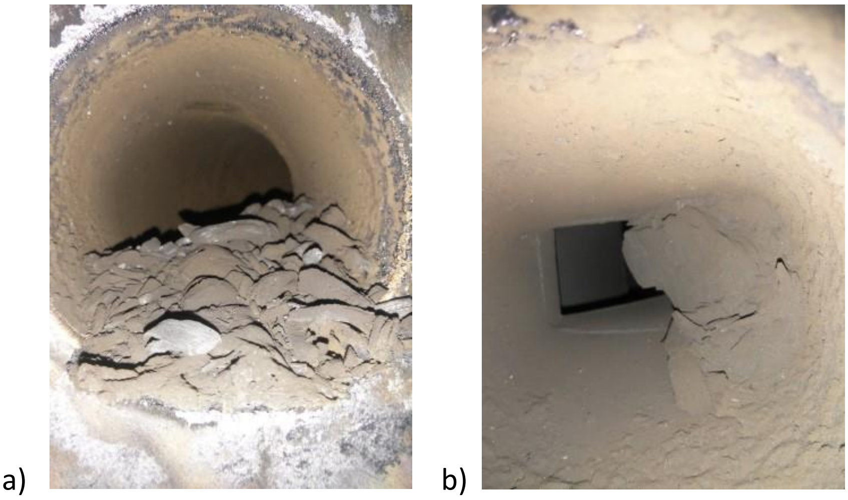

Figure 56. Gas line technical issues: a) sucked char bed in pipe before cyclone; b) partial clogging of cyclone inlet

To limit the drag effect with small woodchip and to obtain a better radial temperature distribution it was designed a new discharge connection between cyclone and reactor. The new gas line system (Figure 57) will be assembled and tested after this thesis work.

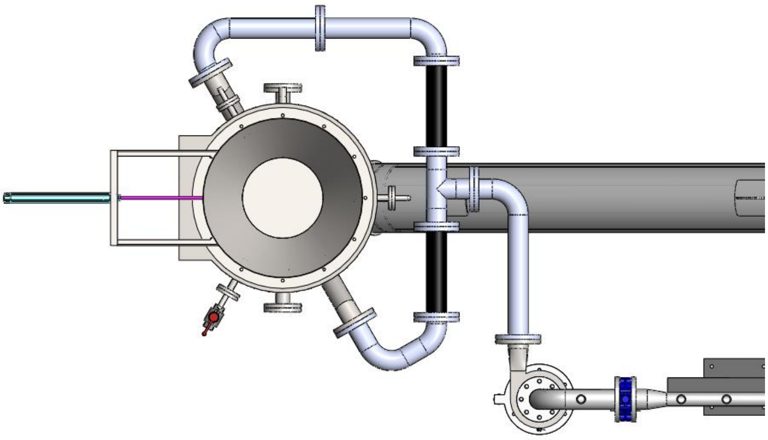

Figure 57. New future gas line configuration on CarbOn pilot unit

Some deformations of the reactor wall were found at bottom in the proximity of lateral flanges after 50 hours of tests, caused most probably by the high temperature reached during the char ignition.

Figure 58. Reactor inspection and internal view after test 11

3 Experimental activity

This chapter describes the two final experimental tests where entire process characterization has been carried out in order to evaluate performance of the continuous downdraft open top technology by means of two different types of woodchips. The two tests analysed derived from the entire experimental campaign and pilot unit development, allowing to pilot unit to perform and last with reliability operating in design condition.

The aim of the experimental activity is also of to compare carbonization results with few existing literature experiments and to support upscaling of the proposed process and technology to a larger demo scale unit. Calculated mass and energy balance is reported in chapter 4.

In test 11 was used large woodchip, suitable for BBQ production, and it was performed a full characterization of process input/output and conversion efficiency evaluation. Test 12 was done by means of small woodchip (the same type of the validation tests before described) and in addiction of characterization of test 11, hot vapours and emission analysis were also available.

3.1 Materials and methods

3.1.1 Experimental setup

The CarbOn pilot plant is a continuous biomass carbonization system based on open top, downdraft technology, operating in oxidative pyrolysis. An exhaustive and detailed explanation of the system is described in Chapter 2. The pilot is essentially composed by three sections, detailed in Figure 59: (1) loading and conversion of biomass; (2) charcoal discharge and cooling system; (3) extraction and burning of the pyrolysis vapors. The plant, made in stainless steel (AISI 304 and 316) and supported on a self-standing 6x2.5m structure, is rated for 50 kg/h of biomass with up to 20 %wt. moisture content.

Figure 59.Experimental setup of test 12

Section 1 comprises the gate valve, kept wide-open in normal operation, and the reactor body. The gate valve, non-hermetic, is placed on top of the reactor and ensures the entry of biomass and oxidant (air). The reactor is externally insulated and consists of a cylindrical volume with an internal diameter of 630 mm and a length of 1500 mm. Here, biomass is converted in a controlled oxidative environment in the temperature range of 500-750°C with a solid residence time of approx. 3 h in the reactor and 2 h in the cooled discharge. By operating in open-top mode, the plant is intrinsically explosion-proof, as it cannot go in overpressure in case of fault.

Section 2 comprises a screw conveyor and air-tight tanks for the collection of charcoal. The screw conveyor is water cooled, allowing a safe discharge of the solid in the air-tight collection tank.

Section 3 comprises a cyclone for dust abatement, an air-blown ejector and a torch. Hot vapors are extracted from the bottom of the reactor by the ejector, capable of working with good reliability up to 600°C, and with condensable vapors. It is important to note that the piping system must be kept at temperatures above 380°C to avoid tars condensation and the consequent possible clogging of the line.

3.1.2 Test procedure

Experimental test was carried out in a single daily run, thus reactor was ignited in the morning and switched off in the afternoon continuing to discharge and collect charcoal samples. When it was not possible to continue in the evening, charcoal was sampled the day after until the reactor was completely empty.

Before ignition, reactor was loaded with imported commercial charcoal up to lateral flanges height. Lump charcoal was made of small logs and pieces of different size and shape in comparison with woodchip used in the test in order to recognize when carbonized biomass within the test was discharged in the barrel. Top gate valve remained open for all the duration of the test, as well as pilot burner at stack and driving air heater (if available).

Ignition of charcoal bed took place with ejector off and empty reactor, simulating an updraft configuration for the time of ignition in order to minimize tar condensation on gas line. Woodchip was loaded through the top while T2 and T3 were controlled avoiding cooling down the reactor. Once, temperatures T2/T3 reached the desired process temperature (approx. 500°C), ejector and discharge conveyor were enabled, thereafter gas flow regulation valve was set to desired pressure drop on the gas line to suck the design gas flow ratio. During the test an operator maintained constant the level of biomass in the reactor to minimize effect of temperature variation [93] and also to avoid bridging formation.

Process was mainly controlled by regulating gas valve opening and screw conveyor speed in order to maintain design process parameters and desired thermal profile.

Discharged char was monitored to identify depletion of commercial charcoal and forthcoming carbonized woodchip. Produced charcoal was collected in barrels of 200 litre and sampled with a canister of 14 litre approximately every 15 min at the discharge port. Each barrel and collected sample were weighted to estimate the test mass balance. Reactor was switched off, after at least 4 h at full operation and char sampling lasted for the time necessary to empty the reactor.

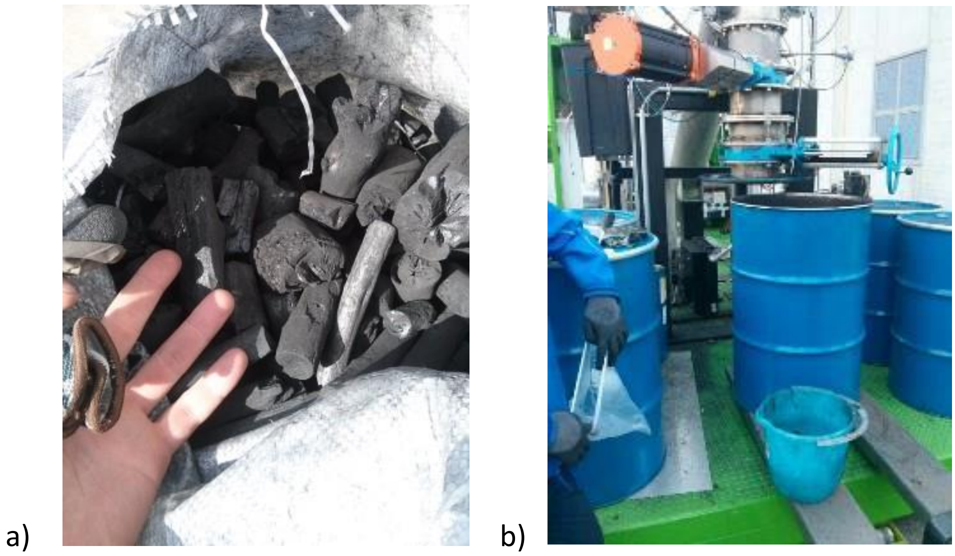

Figure 60. Commercial lumped charcoal use for reactor ignition (fig. a), char sampling operation (fig.b)

3.1.3 Analytical methods and laboratory analysis

Chemical and physical analyses were performed at Re-Cord analytical laboratory according European Norms or internal standards. Each determination was carried out at least in triplicate; the average of the triplicate was retained as the measured value (x_{avg}), and the uncertainty on the measurement (C x_{avg}) was calculated as half of the difference between the maximum and minimum among the triplicates, according to the following equation:

$$\Delta x_{avg} = \frac{\max(x_i) - \min(x_i)}{2} \tag{8}$$

where i=1…n indicates replicates of the measurement and x stands for measured value. Analytical determinations were performed on a "as received" basis (ar), i.e. with the moisture content determined by equilibrium conditions with the storage environment.

3.1.4 Feedstock analysis

Two different lignocellulosic biomasses were tested on the pilot unit to verify the influence of the size on carbonization efficiency. Both woodchips were a mixture of hardwood species.

First biomass sample, chipped in large size, was composed by acacia, alder, ash and elm and was supplied by a forestry farm industry based in northeast Italy (Pinosa srl). The second woodchip sample, characterized by small size, was mainly chestnut and was provided by a local forestry farm based in central Italy (Fratelli Travaglini sdf).

Throughout the experimental campaign, woodchips were stored in a container, and sampled according to CEN/TS 14778-1:2005. Prior to the test the material was left aground to dry out below 20 %wt moisture content. Both woodchips were characterized in order to define size and chemical composition.

3.1.5 Proximate analysis

Moisture was determined in a Leco TGA 701 instrument according to EN 14774-2:2009 by heating at 105°C and holding until the sample achieved a constant weight.

Ashes were determined for woodchip and for charcoal with the same instrument according to EN 14775:2009 and EN 1860-2:2005, by heating the sample under constant air flow up respectively to 550°C and 710°C, and held until the sample achieved a constant weight.

Volatile matter was instead determined according to EN 15148 by heating the sample at 900°C under constant nitrogen flow. The percentage of volatile matter is calculated from the loss in mass of the test portion after deducting the loss in mass due to moisture.

3.1.6 Ultimate analysis

The content in carbon, hydrogen, nitrogen (CHN) was determined through a Leco TrueSpec according to EN 15104:2011. A sample of about 0.080 g was weighed with a precision of 0.1 mg in a tin foil cup (Leco). The tin foil cup was twisted to seal and then placed in the carousel of the instrument. In the method, carbon, hydrogen and nitrogen are simultaneously determined as gaseous products (carbon dioxide, water vapour, and nitrogen). Oxygen (dry basis) is estimated by difference as per the following equation:

O %wt dry = 100 – C % wt dry - H % wt dry - N % wt dry - Ash % wt dry.

3.1.7 Determination of the calorific value

Higher heating value was measured according to UN 14918:2009 by means of a Leco AC5800 isoperbol calorimeter. A sample of about 1 g was weighed with a precision of 0.1 mg in a crucible, then the crucible and a nickel ignition wire were placed into the calorimeter. The equipment was closed and pressurized to 29 bar with high purity oxygen (99.999%), then settled into the bucket which was previously filled with a fixed volume of distilled water. After a suitable period required to reach thermal equilibrium, the ignition was automatically started and temperature was measured by means of an electronic thermometer with an accuracy of 0.0001 °C The higher heating value automatically calculated by the instrument is then corrected accounting for the residual length of the nickel wire.

3.1.8 Determination of particle size distribution and bulk density

Woodchip was characterized in terms of particle and size distribution according to two different technical standards: EN 15149 and EN 14961. Both norms require to sieve the sample and divide it in different fractions. Two different methodology are applied for solid biofuels: EN 15149 calculates by means of a formula of the median value of a particle size [d50], instead EN 14961 defines a range where the granulometry is classified.

Bulk density of both samples of woodchip and char were measured according to EN 15103:2009.

3.1.9 BET surface area

Char surface area (BET surface) was calculated according to reference standard ISO 9277 by means of Quantachrome Nova 2200 E BET.

Samples were dried in oven at 160°C for 24h, then degassed in vacuo at 160°C for 4h by means of the Quantachrome Nova 2200E internal degasser. Isotherm graphs were obtained by 20 absorption points and 20 desorption points in the 0.005 - 0.99 range of P/P0. Char surface areas were calculated from many of the 20 absorption points measured in a range 0.005 - 0.3 of P/P0: the choice of the most suitable points was made by Micropore BET Assistant software.

3.1.10 PAHs content

The PAHs (Polycyclic aromatic hydrocarbons) extraction from char was performed following DIN CEN/TS 16181. Briefly, about 10 gr of sample were extracted with Toluene (Sigma Aldrich, ACS reagent HPLC grade) by a Soxhlet apparatus, the solvent part was then concentrated and injected in a HPLC apparatus equipped with a diode array detector and previously calibrated with 16 EPA PAHs standards by a 5-points calibration curve.

3.1.11 Online gas analysis

Online measurement of dry gas composition was carried out by means of an NDIR/electrochemical gas analyzer model MCA 100 SYN P, made in Italy by ETG Risorse. The apparatus is equipped with an optical bench (NDIR) for measurement of CO, CO2 and CH4 concentration, and two distinct electrochemical cells for the quantification of O2 and H2. Instrument specifications are reported in Table 15.

Since infrared absorption spectra of hydrocarbon compounds heavier than CH4 could overlap with CH4 spectra, before entering the instrument the producer gas was forced to pass through 2 impinger bottles and one online filter for particulate: the first impinger was filled with CaCl2 to collect particulate, the second impinger was filled with activated carbon to stop heavier organic compounds, and the particulate filter was used to prevent activated carbon dust, entrained by the gas stream, to enter the NDIR.

Table 15. Gas analyzer specification

Method	Gas	Resolution	Range	Accuracy	Precision	Response time (T10→90)
NDIR	CH_4+	1 ppm	0-40%	±2% rel.	3.0% rel.	<30 s
	CO	10 ppm	0-10% 10-40%	±0.02% abs. o ±3% rel. ±5% rel.	0.01% abs. or 0.8% rel.	<30 s
	CO_2	100 ppm	0-16% 16-50%	±0.3% abs. o ±3% rel. ±5% rel.	0.03% abs. or 5% rel.	<30 s
Electrochemical	H_2	1 ppm	0-40%	±2% rel.	3.0% rel.	<30 s

Note: -Response time refers to the time taken for the instrument output to rise from 10% of the previous value to 90% of the new value;
- CH_4+ measure includes C_2H_4, C_2H_6 and higher

Figure 61. Gas analyzer devices and tar sampling bench

3.1.12 Tar sampling

Tar sampling was carried out according to the guidelines provided by technical specification for gasification UNI CEN/TS 15439:2008 by means of a sampling bench specifically built for the purpose. The sampling scheme was modified in the same configuration of Daouk (Cirad, France) [44] in order to operate with higher tar concentration and to compare Re-Cord and Cirad experiments.

The tar sampling line is composed of: trace heated filter and line, a series of 250 ml glass impingers, some of them empty and the others partially filled with isopropyl alcohol, a thermostatic bath (-15/20°C) and a flow conditioning and metering section, comprised of a membrane pump and flowmeters.

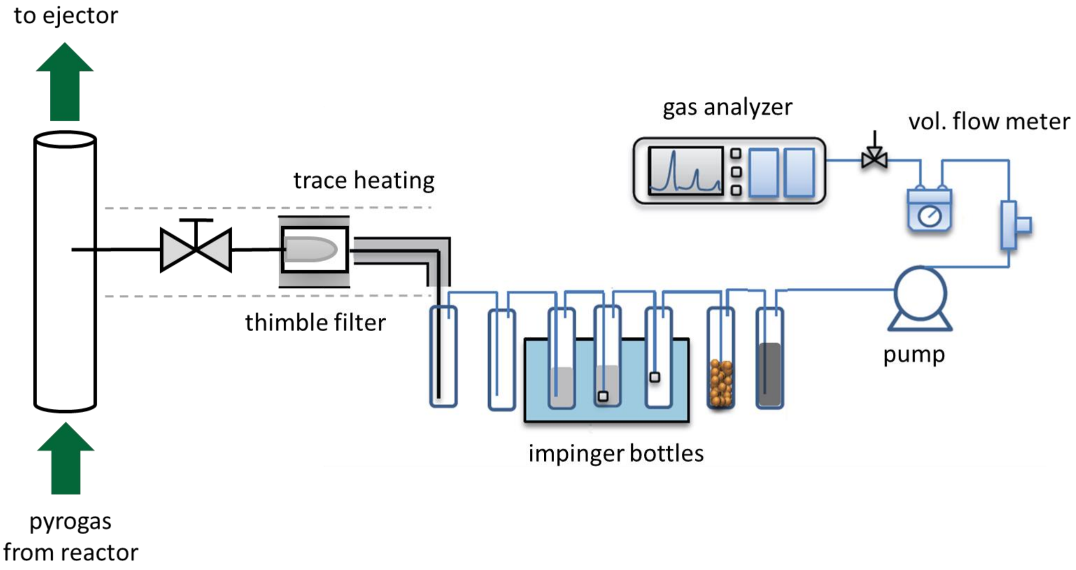

Figure 62. Tar sampling line scheme configuration

The pyrolysis gas is withdrawn (non-isokinetic) at constant flowrate from the plant and is filtered by means of a thimble filter in fiberglass capable of working up to 500°C with filtration grade of 0,8 µm. Filter and gas line are kept at of 350°C to avoid condensation before the bottles. Then the gas passes through seven impinger bottles, which three are plunged into the cold bath (four are at ambient temperature). The isopropyl alcohol in the impingers acts as solvent for tar and contaminants entrained in the producer gas, which are removed from the gas stream and collected in the liquid. Impingers are positioned in these arrangements: (1) empty metallic bottle (Tamb), (2) empty bottle (Tamb), (3) bottle filled with 100ml isopropyl alcohol (-20°C), (4) bottle filled with frit and 100ml isopropyl alcohol (-20°C), (5) empty bottle with frit (-20°C). Two additional bottles are used as conditioning to prevent damages to downstream instruments: (6) bottle with desiccant ($CaCl_2$), (7) bottle with activated carbon.

Once a sufficient amount of producer gas has been withdrawn (generally between 300 and 600 litres), the gas line is closed, the piping is rinsed with isopropyl alcohol and the liquid collected along with the liquid inside the impingers. The bottles with condensate (1-5) are then sent to laboratory to be analysed.

Five temperature measurement points are installed on the bench: thermostatic filter, traced gas line, bath cold, inlet and outlet pyrolysis gas.

Here below are reported two pictures of the tar sampling installation.

Figure 63. Tar sampling installation details: thermostatic line and filter, impingers bottles configuration

3.1.13Exhaust gas analysis

The analysis of exhaust gas concentration was implemented through a gas analyzer model Green Line 8000, made in Italy by Eurotron Instruments, which measures CO, O2, and NO concentrations. Resolution and accuracy of electrochemical sensors are respectively 0.1 vol.% and ±0.1 vol.% (O2 sensor), 1 ppm and ±4% (CO sensor) and 1 ppm and ±5 ppm (NO sensor).

Exhaust gas is withdrawn from a port installed on the stack before being discharged in atmosphere. Hot gas is cooled down by copper tube and then is filter passing through a conditioning line to remove water and contaminants before entering the instrument. Measurement is taken manually by the operator at regular times.

Figure 64. Exhaust gas sampling point at stack

Table 16. Exhaust gas analyzer specification

Parameter	Method	Range	Resolution	Response time max	Accuracy
O2	Electrochem.	0-25%	0.1%	20 s	±0.1% vol.
CO	Electrochem.	0-20000 ppm	1 ppm	40 s	±10 ppm (<300 ppm) ±4% mis (<2000 ppm) ±10% rgd (>2000 ppm)
CO%	Electrochem.	0-10%	0.01%	50 s	±0.01% (< 0.2%) ±5% rdg (> 0.2%)
NO	Electrochem.	0-4000 ppm	1 ppm	40 s	±5 ppm (<100 ppm) ±4% mis (up to 3000ppm)

In Table 16 are reported gas analyzer specifications. When CO concentration is higher than 20000 ppm the instrument switches in “dilution” mode and can measure CO concentrations up to 10% with lower accuracy.

In order to compare emission with existing Italian TLV (D.Lgs.152:2006), the measured concentration of pollutant was corrected referring to referred to a dry gas with O2 level of 11% at temperature of 0°C and pressure 101,3. The formula that was adopted to refer CO and NO concentration is the following.

$$[X]_R = [X]_M \frac{20{,}9 - [\%O_2]_R}{20{,}9 - [\%O_2]_M} \tag{9}$$

Where [X] is the gas specie concentration, R is the reference, M the measured, $[\%O_2]_R$ the reference O_2 concentration in vol% and $[\%O_2]_M$ is the measured O2 concentration in vol%.

3.1.14 Chemical composition of liquid from tar sampling by GC/MS-GC/FID

For the identification and quantification of compounds of the liquid collected throughout the tar sampling, a gas-chromatograph GC-2020 (Shimadzu) equipped with a mass spectrometer GCMS-QP2010 GC 2010 Plus (Shimadzu) , both equipped with a FID detector and a ZB 5HT Inferno (Zebron) column (60 m length, internal diameter 0.250 mm, film diameter 0.20 µm) were used. In particular, the GC MS apparatus was used to discover the qualitative composition of the sample comparing the spectrum with a NIST 11 library, GC FID was used instead for the quantitative analysis of the selected compounds after a 3-4 points calibration with pure molecular standards and using o-terphenyl as internal standard

The analysis was performed with a column flow of 2.02 ml min^{-1} with an initial temperature of 40°C (holding time 10 min) increased to 200°C (heating rate 8 min, holding time 10 min) and then increased to 280°C (heating rate 10 min, holding time 30 min).

3.1.15 Plant performance data

Key performance data of the pilot unit have been calculated from the properties of biomass and charcoal produced in the test carried out during test 11 and 12. The carbonization process has been characterized in terms of four different parameters: charcoal yield (eq. 1), fixed carbon yield (eq. 2), char carbon yield (eq. 3), net energy conversion efficiency (q. 4), according to the following formulations:

$$Cy = m_{char}/m_{bio} \tag{10}$$

$$fCy = Cy \cdot [(\%fC) / (100 - \%feed\ ash)] \tag{11}$$

$$CCy = Cy \cdot (\%C_{char}/\%C_{bio}) \tag{12}$$

$$\varepsilon = (m_{char,ar} \cdot LHV_{char,ar})/(m_{bio,ar} \cdot LHV_{bio,ar}) \tag{13}$$

Charcoal yield (*Cy*, eq. 1), is a measure of efficiency of the pyrolysis process, where mchar and mbio are the dry mass of charcoal and biomass respectively. The **fixed-carbon yield** (*fCy*, eq. 2), proposed by Antal and co-workers [94], measures the effective conversion of the ash-free organic matter in the feedstock to a relatively pure, ash-free carbon, where % feed ash is the percentage ash content of the feed. **Char carbon yield** (*CCy*, eq. 3), proposed by Antal and co-workers [28], is a measure of the elemental carbon of feed that is retained in the charcoal, and is particularly significant for carbon sequestration purposes. For eq. 3, $\%C_{char}$ and $\%C_{bio}$ are the elemental carbon content of dry charcoal and biomass respectively. Finally, the **net energy conversion efficiency** (ε, eq. 4) represents the fraction of biomass chemical energy retained by charcoal, and $m_{char,ar}$ and $m_{bio,ar}$ are respectively the as-received mass of charcoal and biomass, and LHV is the lower heating value.

3.1.16 Travelling time calculation

To attribute the effective process temperature at which the char samples have been converted along the reactor, it has been adopted a simple model, which calculates the travelling time for each section of the pilot unit by means of some input data. The model, besides, evaluates the amount of the loaded biomass corresponding to the discharged char samples, to measure the efficiency of carbonization occurred in the test and, in addition, the thermal history profile of char sample along reactor.

Travelling time calculator considers a series of input data listed as follow:

1. Reactor section volumes and temperatures
2. Char samples characterization
3. Feedstock characterization
4. Sampling data

The evaluation is based on these hypotheses:

1. Plant is divided into n sections
2. Total travelling time is the sum of travelling time of each section
3. Bulk density of solid, for each section, is constant and it is the mean value between input and output
4. No mixing of solid, or rather, constant axial speed in cross sectional area
5. Fill ratio of screw conveyor is assumed by experience
6. Measured temperature is uniform in each section
7. Interval time of char sampling is fixed
8. Char mass of each sample is constant within the considered discharge interval time, and it is calculated splitting overall mass char flow in the number of samples.

Screw conveyor is considered such as cylinder, non-completely full and with an internal net volume depending to a fill ratio assumed by experience. Biomass input mass flow is considered as the average of the entire test.

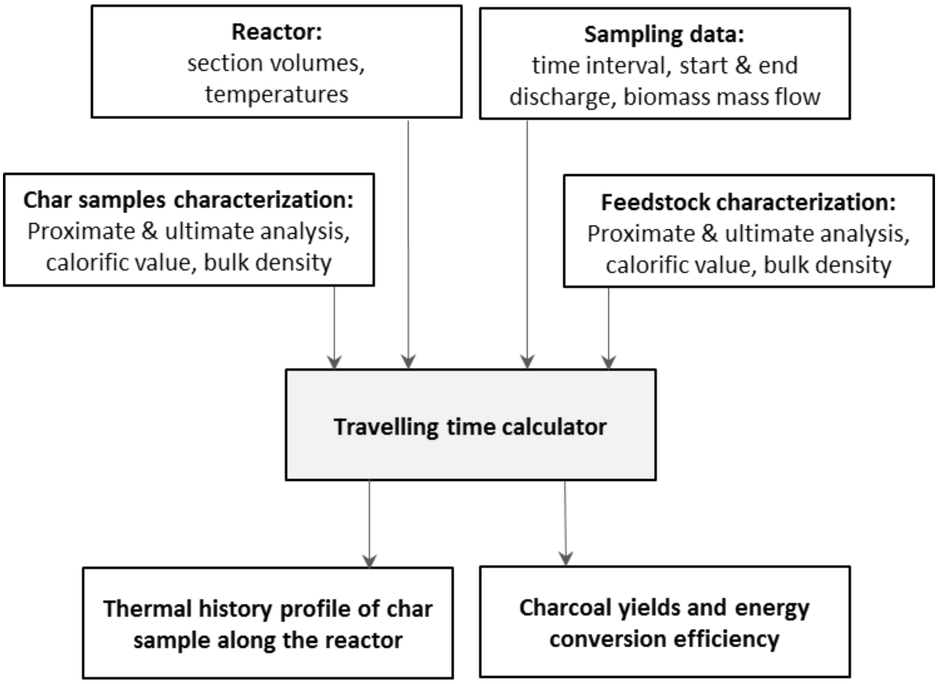

Figure 65. Travelling time calculator schema

Equation used to calculate the travelling time in a section *i* of the reactor is reported below:

$$T_{t_i} = \frac{4}{\dot{m}_c + \dot{m}_b} \cdot \frac{V_i}{BD_i + BD_{i-1}} \tag{14}$$

Where:

V_i = section volume (m^3)

$\dot{m}_c$ = char output mass flow (kg/h)

$\dot{m}_b$ = biomass input mass flow (kg/h)

BD_i = average bulk density in the section i (kg/m3)

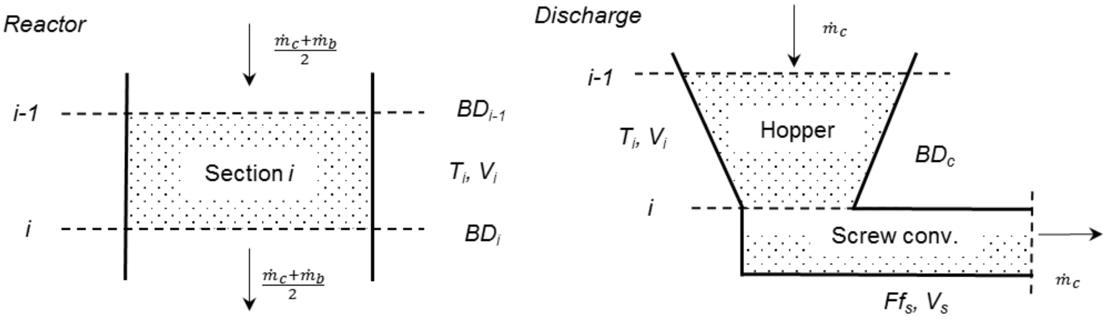

Figure 66. Geometrical exemplification of reactor and discharge sections

In the discharge section (hopper and screw conveyor) the formula can be simplified as:

$$T_{t_i} = \frac{1}{\dot{m}_c} \cdot \frac{V_i}{BD_c} \tag{15}$$

and virtual volume considered of the screw is:

$$V_i = V_s \cdot Ff_s \tag{16}$$

Where:

BD_i= average bulk density in the section i (kg/m3)

Ffs = screw fill factor

Vs = internal volume of screw (m3)

The pilot unit has been divided in six sections, as shown in Figure 65: (1) Inlet – T1; (2) T1 – T2; (3) T2 – T3; (4) T3 – Hopper inlet; (5) Hopper – Screw inlet; (6) Screw inlet – Outlet.

An exemplificative flow chart representing a summary of the method adopted is reported in Figure 68. It important to note that to the correct application of the method the mass flow rate must be constant in the interval of time considered.

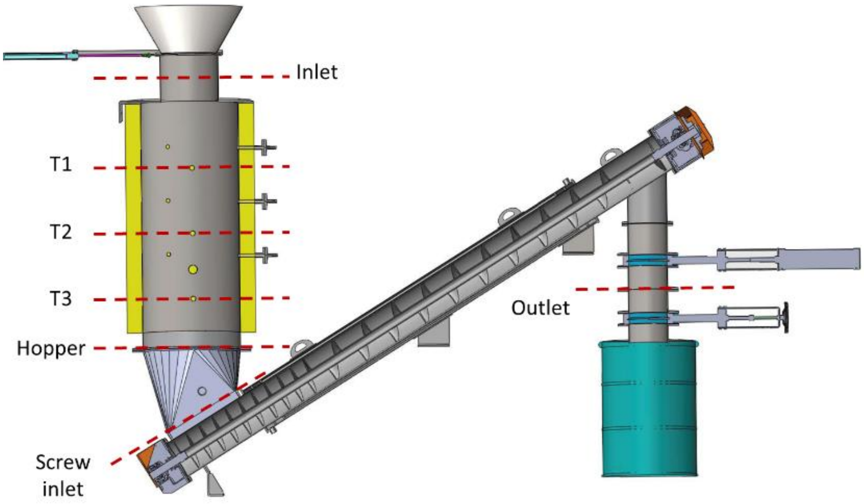

Figure 67. Pilot unit sections considered for travel time calculation

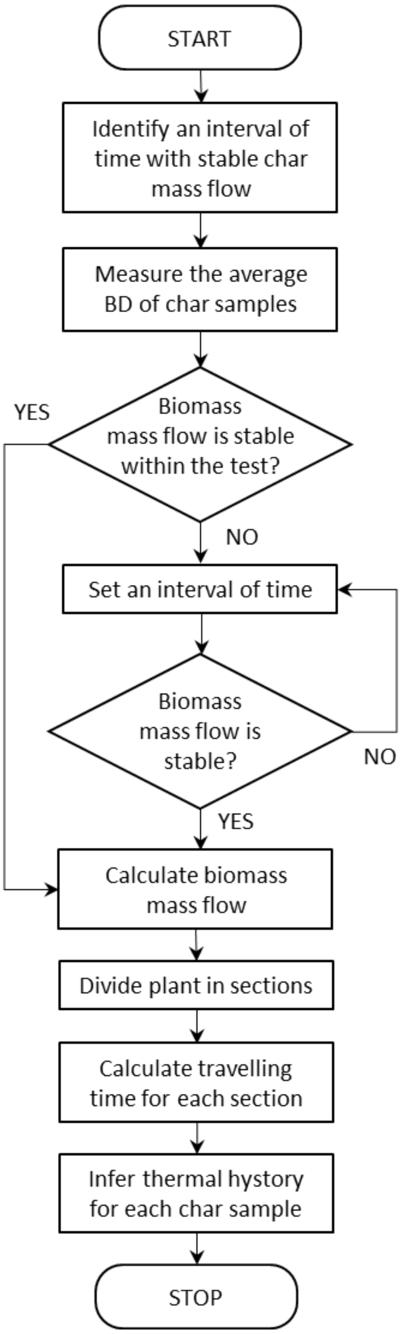

Figure 68. Travelling time flow chart methodology

3.2 Experimental results

3.2.1 Feedstock analysis

Lignocellulosic woodchip used in test 11 was hardwood made up of different species: acacia robinia, alder, ash, elm. Woodchip was produced by means of a screw chipper Laimet-HP21, to retain most part of the initial size and to avoid crumbling and wreckage after carbonization. Although a larger size of woodchip would have been tested, this type has represented the larger traceable size on the Italian market, however represented a reasonable compromise at this stage. Particle size measurement shows median value of particle size of 28 mm and P-63 class. Moisture content at loading time was 11%wt.db and fixed carbon was 18,5%wt. db.

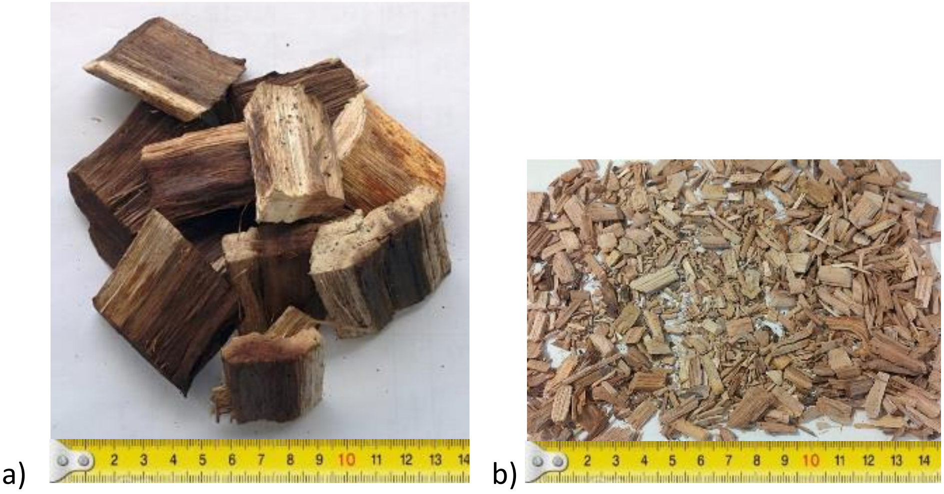

Figure 69. Woodchip samples: a) Test 11, b) Test 12

Woodchip of test 12 was hardwood composed of chestnut specie, produced with a regular rotary drum chipper and resulting in small size of a median value of 7,1 mm (P-31,5 class) typical of a common woodchip as shown in Figure 68. Moisture content prior to the test was 13,2 %wt.ar. Fixed carbon and volatile matter were respectively 25,5%wt.db. and 74,2%wt.db.

A complete analysis and comparison for both woodchips is reported in Table 17.

Table 17. Feedstock characterization

	Test 11	Test 12	Ref. Norma
Biomass Physical Characteristics			
type	hardwood	hardwood	-
species (mixture of:)	acacia, alder, ash, elm	chestnut	-
median value of a particle size [d50] (mm)	28	7,1	EN 15149-1:2010
P-class	P63	P31,5	EN 14961-1:2011
bulk density (ar, kg/m3)	228	213	EN 15103:2009
bulk density (calc. dry, kg/m3)	203	186	EN 15103:2009
Proximate analysis			
moisture at loading time (ar, wt.%)	11,0	13,2	EN 14774-2:2009
volatile matter (db, wt.%)	80,8	74,2	EN 15148:2009
ash (db, wt.%)	0,7	0,7	EN 14775:2009
fixed carbon (db, wt.%)	18,5	25,1	-
Ultimate analysis			
C (db, wt.%)	48,51	49,74	EN 15104:2011
H (db, wt.%)	7,13	5,28	EN 15104:2011
N (db, wt.%)	0,33	0,19	EN 15104:2011
O (db, wt.%)	43,29	44,45	EN 15104:2011
Calorific value			
LHV (db, MJ/kg)	18,73	18,44	EN 14918:2009

3.2.2 Test 11 – large woodchip

Process characterization of large woodchip carbonization was performed in test 11, which lasted 4 h and 30 min, in order to gather information and data about process necessary to estimate mass and energy balance of a system capable to produce high quality charcoal suitable also for BBQ market.

Reactor was ignited from lateral flange at 9:15 and ejector was enabled at 9:54 with reactor completely full. Gas flow rate was regulated at the beginning at 105 kg/h to reduce transient time and consequent clogging of the line. At 10:25, T2 and T3 reached suitable carbonization temperatures, and burner and screw conveyor were enabled. As shown in temperature plots (Figure 70), reactor temperatures stability was obtained at 11:00 and it lasted for more than 3 hours until 14:30. In this period averages of main important parameter were: T2=640°C, T3=607°C, T4=537°C and gas flow was 88 kg/h, (higher than design parameter). Temperature curves profile were smoothed compared with validation tests 4 and 6 because thermocouples were moved from the centre to the wall avoiding any obstacle to biomass flow. Minimal bridging effect were found within the entire test, confirming that large woodchip is less affected by blockage despite a temporary bridging occurred at 12:00.

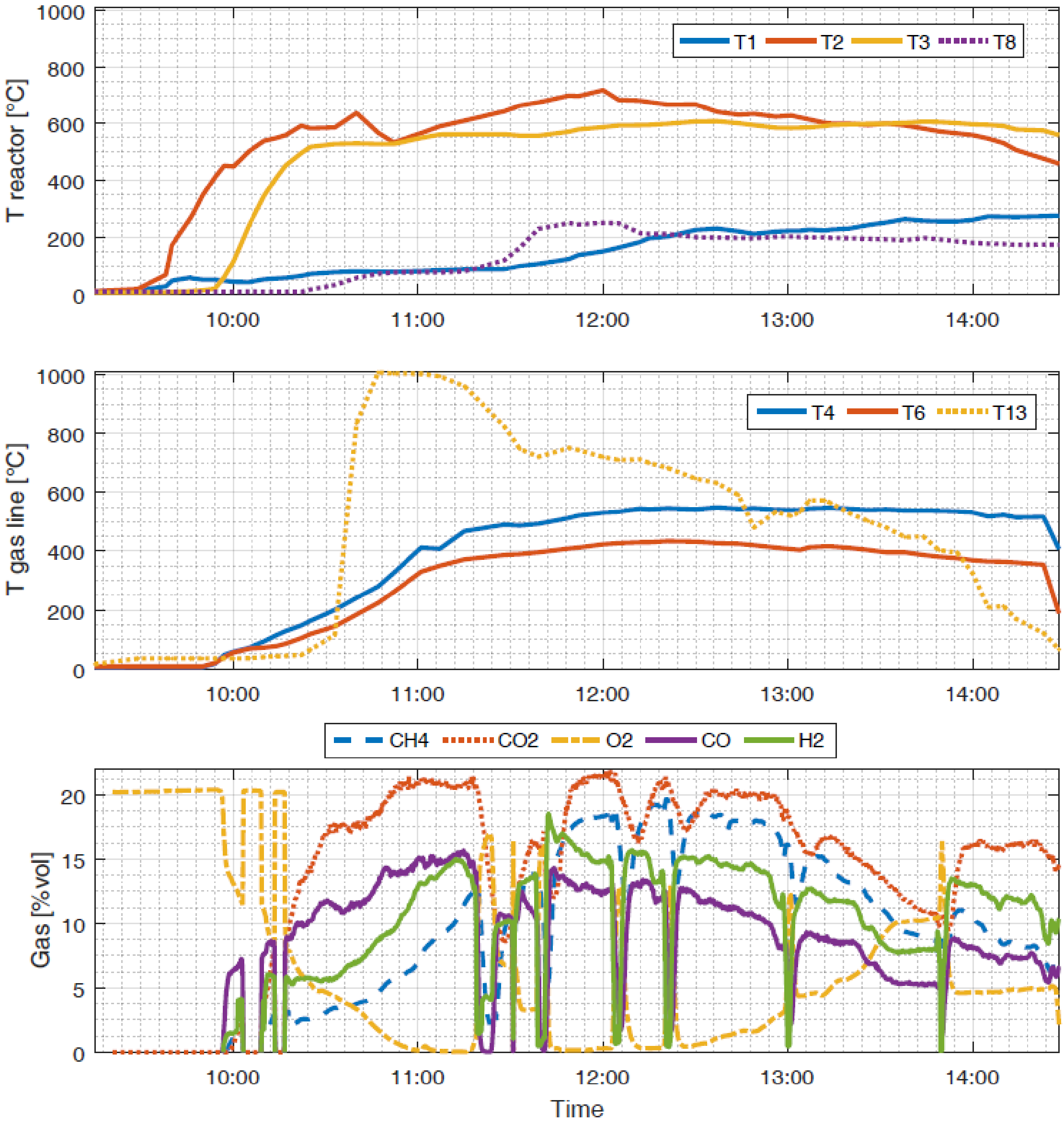

Figure 70. Temperature and gas composition of test 11

Biomass bed pressure drop was approx. -0,5 mbar with effect that some smoke went up along through the reactor and came out from the top opening; for this reason the gas flow rate was maintained high to minimize that effect. T1 increased during the test due to thermal conduction from bottom along the metal wall.

Since no air heating system was not available, the test suffered of partially clogging of the gas line, that it is evident from parameter trends after 12:00. T13 after the first peak, due to accumulated tar burning, continued to decrease as well as T2. In particular, partial clogging is evident from P7 (Figure 71) which collapsed after 12:00 despite V6 was totally opened one hour later trying to maintain the adequate gas flow rate. Average gas flow rate between 11:00 and 14:30 was 88 kg/h higher 35% than design parameter.

Permanent gas composition was monitored throughout the entire test and plot and it is reported in Figure 70. Some interruptions were necessary to change organics traps but it wasn't enough to limit interference of heavy molecular compounds on CH4 measurement. After 12:20, O2 concentration increased because of sealing issue related to low pressure in gas line.

Taking into account the observation period between 11:50 and 12:00 before clogging and sealing issues, gas compositions were stable except for high CH4 value and the averages were (Table 18): CO2 = 21,14%; CO = 12,73%; and H2 = 15,29% mostly influenced by CH4 and higher than expected also in comparison with a gasifier.

Table 18. Gas analysis of test 11

Gas	*Avg. composition [%vol]*	*Instability [%vol]*
*CH4+**	18,06	1,3
CO2	21,14	1,8
O2	0,20	27,0
CO	12,73	1,9
H2	15,29	3,0

Note: -measure of CH4 is affected by tars;
- observation period 11:50 – 12:00

In Figure 71are reported valve opening and pressure plot and relative calculated gas flow rate and superficial velocity and in Figure 72 gas velocity at ejector in throat and out of diffuser. Superficial velocity was between 0,1 e 0,2.

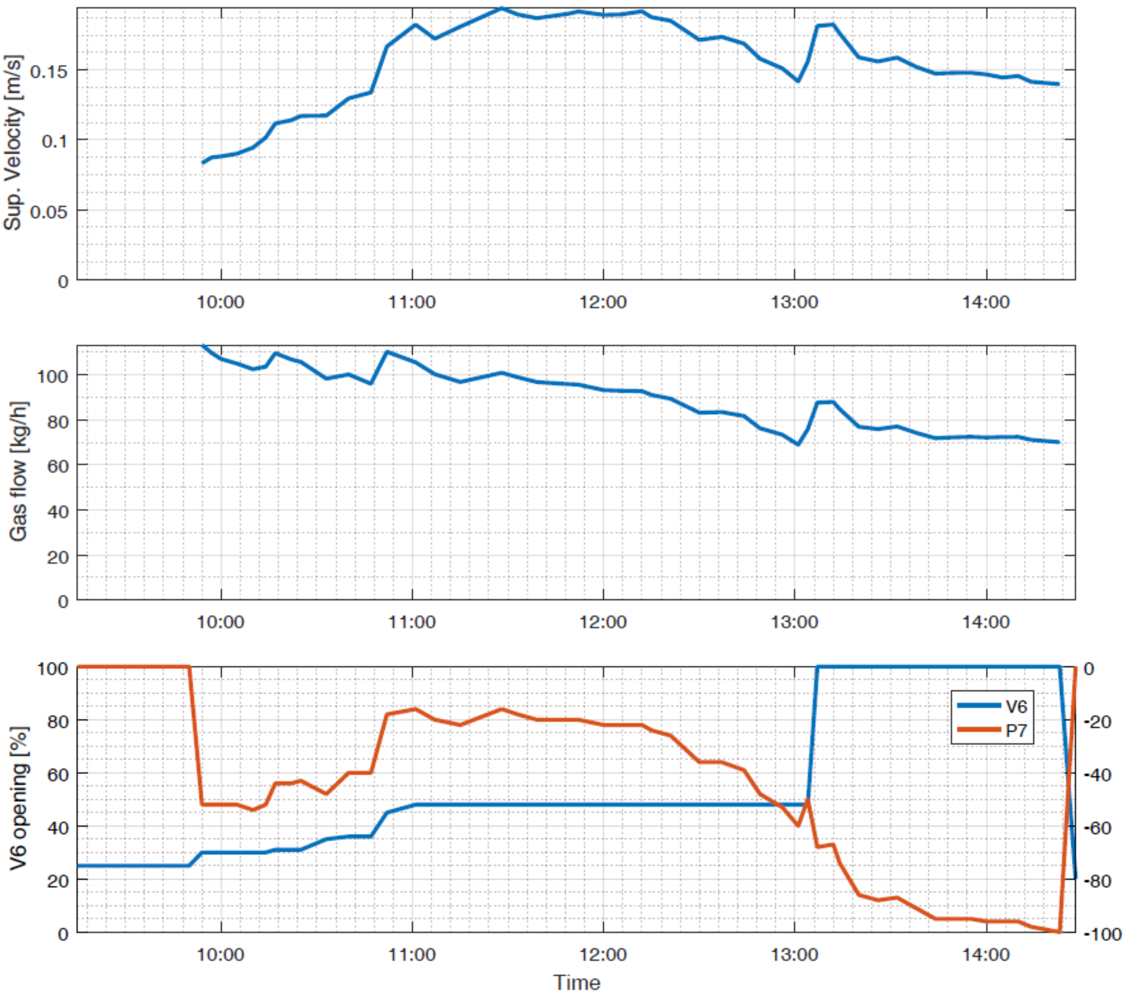

Figure 71. Test 11: Superficial velocity, mass gas flow rate, valve regulation and sucking pressure in mbar

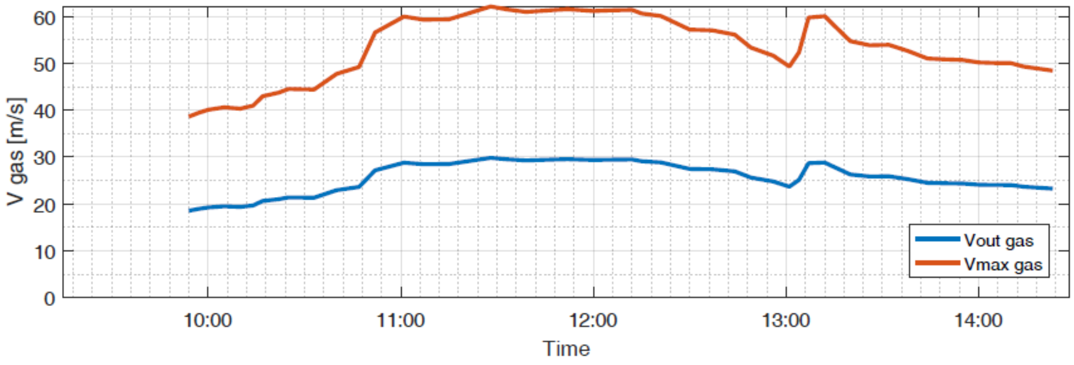

Figure 72. Gas velocity at ejector during test 11: out of diffuser and maximum in throat

Average biomass input was respectively 46,4 kg/h wet and 41,3 kg/h dry. Char and unconverted woodchip were discharged in 8 barrels until the reactor was completely empty. In Figure 73 are reported single batch weights and cumulative curve of biomass loading and char discharging. Is important to underline that both cumulative curves are constant except for the initial part where reactor (for loading) and screw conveyor (for discharge) were empty.

Twelve char samples, identified as woodchip converted within the test, were collected approx. every 15 min at the discharge port between 14:58 and 17:24, and their calculated biomass loading correspond to 9:31 and 13:28. Discharge was interrupted the day of test between samples 9 and 10 and it was restarted the day after, adopting a different procedure. For this reason, an error was introduced in calculated biomass inlet time. Average char output was 16,5 kg/h wet (16,1 kg/h dry) between 15:00 and 17:00 (barrels 4 and 5).

Calculated total biomass travelling time was in average 5 h 14 min which comprises the following interval times related to each plant's section: reactor 2 h 58 min, hopper 1 h 25 min, screw conveyor 51 min.

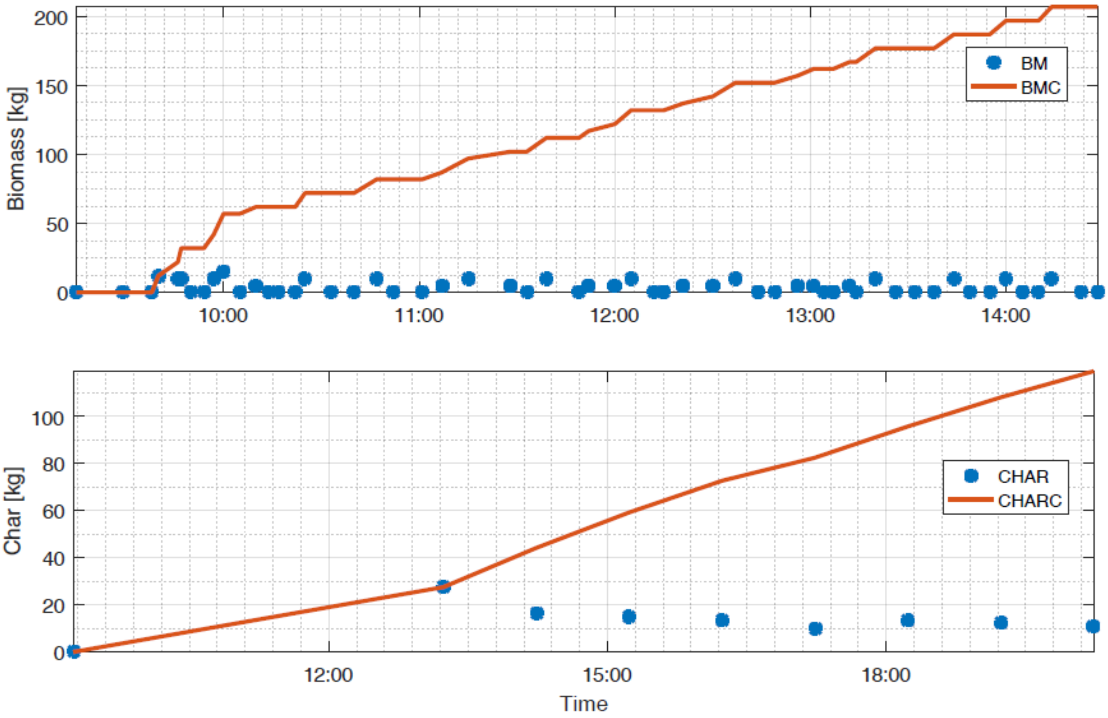

Figure 73. Biomass and char flow rate of test 11: cumulative curve and single batch measure

In Table 19 and Figure 74 are reported laboratory results and pictures of char samples. After a visual analysis, charcoal samples from 1 to 5 were mostly chipped biomass derived char, but with some lump charcoal pieces which represented the starting charcoal used to ignite the reactor. This demonstrates that there was a mixing inside the plant, most probably taking place in the hopper. Samples 1 and 2 were very dusty compared to the other samples, on contrary samples 3-9 had low dust. Samples 10 -12, they were a mixture of uncarbonized biomass and charcoal.

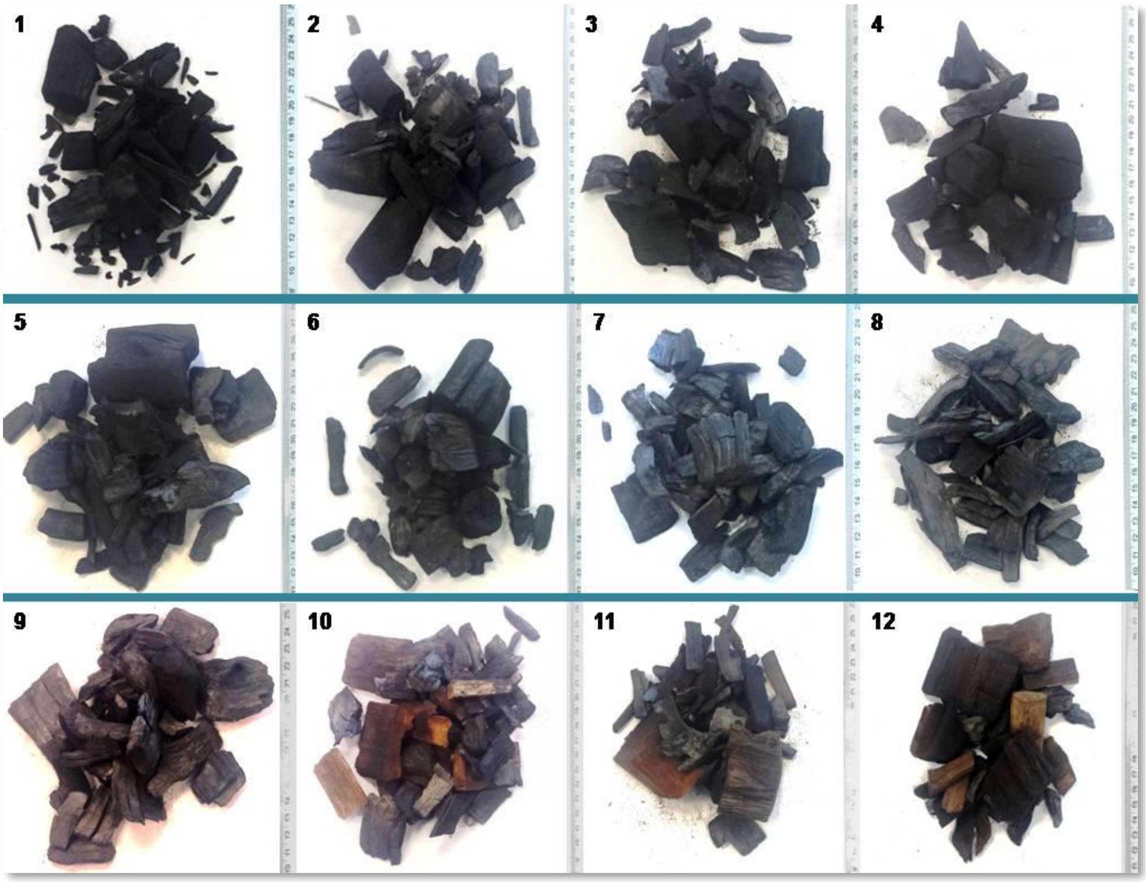

Figure 74. Char samples (1-12) of test 11

Fixed carbon content was high in the range of 86,3 - 90,5, more than 85 %wt db for samples 1 - 9 confirming that charcoal manufactured is high quality suitable for many industrial applications. Samples 10 – 12 presented low fixed carbon contented less than 45%wt db. Discharge samples were characterized of small size particles, and granulometry available for some samples was between 66 -78%wt of pieces larger than 16mm. Bulk density was variable within all samples. First samples had higher values around 200 kg/m3, due to powder and some lump charcoal pieces. Samples 5-10 had lower bulk density, in particular 7-9 samples were very light, approx.115 kg/m3. Samples 11 and 12 were 201 kg/m3, confirming that no conversation occurred.

Table 19. Test 11 char samples characterization (1-12)

Sample n.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**Ref. Norma**
biomass inlet time (hh:mm)	9:31	9:47	10:07	10:19	10:36	10:53	11:35	11:45	11:57	13:01	13:07	13:28	-
char sampling time (hh:mm)	14:58	15:14	15:34	15:46	16:03	16:20	16:32	16:42	16:54	17:08	17:14	17:24	-
barrel (n°)	3	4	4	4	4	5	5	5	5	5	6	6	-
Biomass Physical Characteristics													
granulometry (%wt > 16mm)	n.a.	76	66	n.a.	n.a.	78	n.a.	n.a.	67	n.a.	n.a.	n.a.	EN 14961-1:2011
bulk density (ar, kg/m^3)	201,8	209,0	195,0	180,9	156,1	160,0	116,8	115,5	112,3	138,4	201,0	201,0	EN 15103:2009
Proximate analysis													
moisture (ar, wt.%)	1,6	1,8	1,8	2,3	2,3	2,6	2,6	2,6	3,5	3,9	4,2	4,9	EN 14774-2:2009
volatile matter (db, wt.%)	8,9	8,4	9,5	10,8	12,1	6,5	8,4	6,2	8,5	57,2	60,7	72,2	EN 15148:2009
ash (db, wt.%)	3,8	3,2	3,6	2,9	3,0	3,5	3,3	3,3	3,0	1,7	1,1	1,1	EN 14775:2009
fixed carbon (db, wt.%)	87,3	88,4	86,9	86,3	85,0	90,0	88,2	90,5	88,5	41,0	38,2	26,7	-
Ultimate analysis													
C (db, wt.%)	87,9	89,1	87,5	87,7	88,0	90,5	88,4	91,2	89,2	66,3	61,8	56,8	EN 15104:2011
H (db, wt.%)	1,9	1,8	2,2	2,3	2,0	1,8	2,0	1,6	1,9	4,8	5,7	6,4	EN 15104:2011
N (db, wt.%)	1,0	0,9	1,0	0,9	0,9	0,9	0,8	0,7	0,7	0,6	0,5	0,5	EN 15104:2011
O (db, wt.%)	5,3	4,9	5,6	6,3	6,2	3,2	5,5	3,1	5,2	26,5	30,9	35,2	EN 15104:2011
Others													
LHV (db, MJ/kg)	32,6	32,4	32,0	32,1	32,2	32,4	31,3	32,3	31,3	21,6	20,9	20,3	EN 14918:2009
Surface area - granules (m^2/g)	n.a.	n.a.	140,7	n.a.	94,7	n.a.	158,0	n.a.	n.a.	n.a.	n.a.	n.a.	ISO 9277
Surface area - powder (m^2/g)	125,0	n.a.	93,5	n.a.	106,6	n.a.	214,5	n.a.	n.a.	n.a.	n.a.	n.a.	

Regarding bulk density and size of char manufactured, it is necessary to consider to briquet it to fulfil comply with EN 1860-2.

Surface area characterization was carried out on both powder and granules of some samples (3,5,7) in order to evaluate their difference. Granules, except for samples 3, had in general less surface area than powder. A correlation between bulk density and surface area is demonstrated, thus high surface means high devolatilization and low bulk density. Sample 7, had a very high BET surface 214,5 and 158,0 m2/g respectively for powder and granules.

Thermal history of the sample was inferred from the data collected during operation and correlated to char quality parameters during data post-processing. In Figure 75 is reported thermal history profile of char samples 1-9.

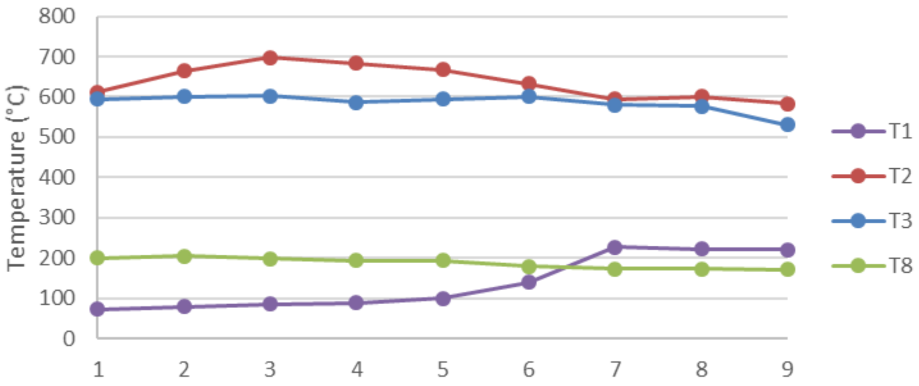

Figure 75. Test 11 Char samples thermal history along travelling though reactor

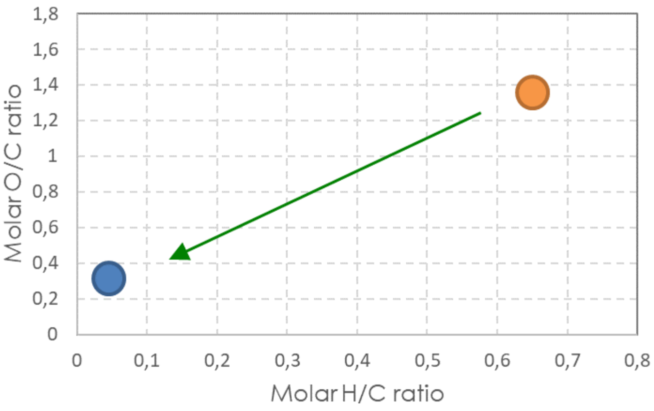

Figure 76. Van Krevelen diagram of biomass and char samples of char – Test 11

Mass balance considered only barrels 4 and 5 (samples 2-10) according to thermal history profile referring to reactor at full operation and it lasted 3 h and 14 min. Efficiencies for each barrel 4 and 5 were calculated, as well as the average yields representative of the test. Barrel 4 (samples 2-5) had a dry charcoal yield of 24,6%wt db and presented higher efficiency compared to barrel 5 which was 23,7%wt db. Average charcoal yields were: 22,0%wt wb and 24,0%wt db. In Table 20 are reported all the carbonization efficiencies of test 11

Table 20. Carbonization efficiencies of test 11

	Cy (wb)	*Cy (db)*	*FCy (db)*	*CCy (db)*	*ε(wb)*
Barrel 4 (samples: 2 - 5)	22,4±0,7%	24,6±0,7%	21,4±2,2%	43,9±1,6%	43,1±2,2%
Barrel 5 (samples: 6 - 10)	21,8±0,7%	23,7±0,7%	19,0±2,2%	38,9±1,6%	38,3±2,2%
Average yields (samples: 2-10)	**22,0±0,7%**	**24,0±0,7%**	**20,0±2,2%**	**42,8±1,6%**	**40,2±2,2%**

3.2.3 Test 12 – small woodchip

The entire process was extensively characterized in test 12 measuring performance of the unit by means small woodchip as feedstock and describing the key findings of this experimental work. Main temperatures and pressures along the reactor (temperature profile) and gas line, as well as gas composition of pyrolysis gas and exhausted were registered. Tar sampling was performed, providing interesting results in comparison with existing literature. The product was characterized in respect to elemental and proximate analyses, BET surface, particle size distribution, also in the perspective of its use a biochar or further processing into activated charcoal.

Test 12 was the longest and most reliable test of the entire experimental campaign, enduring for 8 hours between ignition and shutdown, and 7 h and 13 min with ejector working. Since driving air heater was installed, any sort of clogging occurred. External air temperature the day of test was 30°C.

Bed ignition started at 9:45 with burner and ejector running to allow warm up of torch and ejector. Regulation valve (V6) remained closed until temperature T2 reached 500°C, then screw conveyor was enabled as well as gas flow rate was set at 65 kg/h. Differing from other tests, are evident reactor temperature trends. T3 and T1 were stable at around 500°C and 35°C, respectively. T2, after the ignition, decreased slowly to 40°C, which means that fleaming pyrolysis occurred between T2 and T3 and reached its optimal stability at 15:00 (almost 5 hours later than ignition). Temporary bridgings happened until 14:00 with no significant effect. At steady state, reactor was operating with a desired carbonization profile with peak temperature of 500°C at bottom. In Figure 77 are reported temperature profiles along reactor and gas line, as well as permanent gas composition of PG in 1 h observation period at steady state during tar sampling.

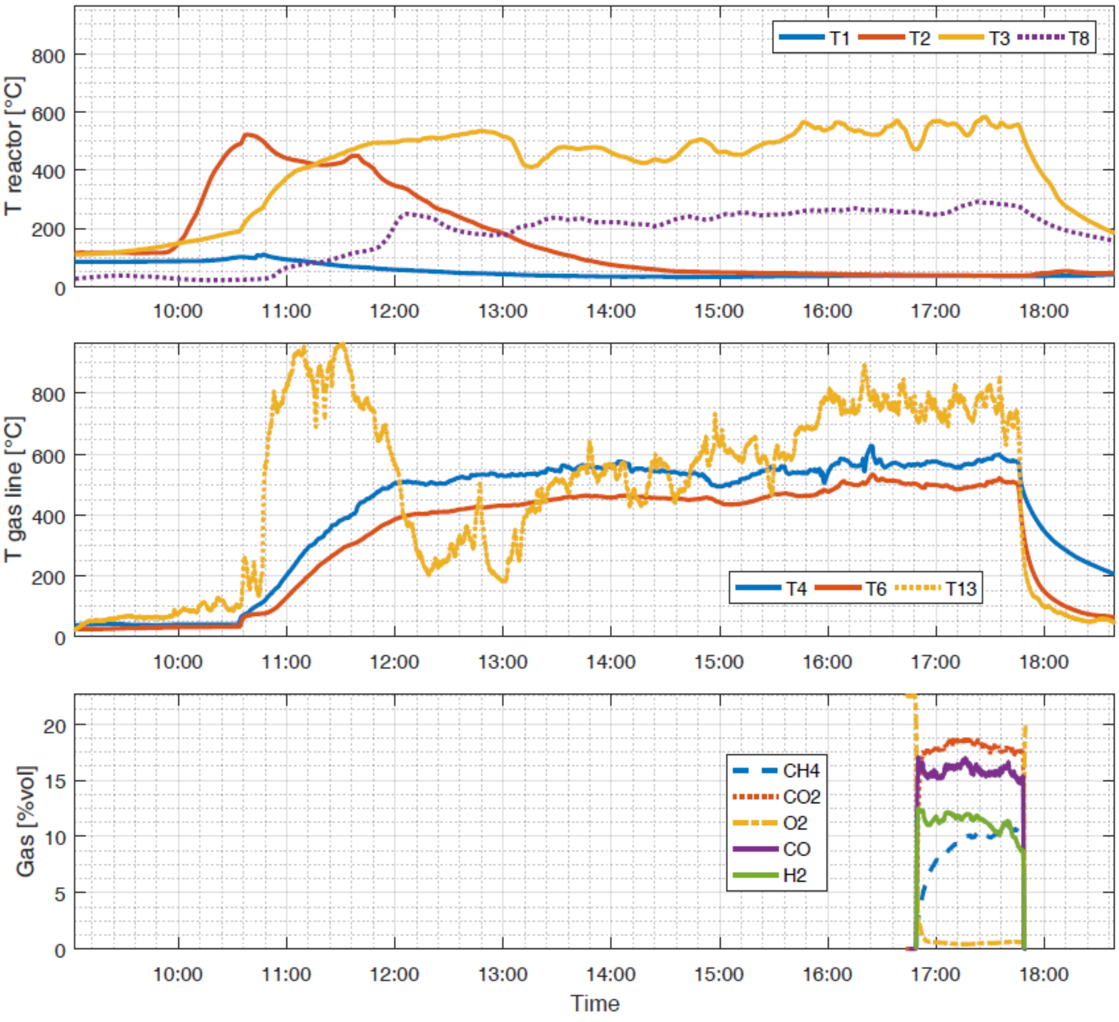

Figure 77. Temperature and gas composition of test 11

Looking at temperature profiles it is possible to point out three distinct phases: (I) between 10:00 and 12:00, bed was ignited and system was heating up reactor and gas line; (II) between 12:00 and 15:00, reactor stabilization was occurring; (III) from 15:00 to 17:45, reactor temperature profile was stable at full operation.

In second transient phase, it is possible to highlight that torch's temperature (T13) increased from 400°C up to 750°C until process wasn't stable, meaning that pyrolysis vapour was burning correctly at stack. Gas line temperatures were stable at: T4= 550°C and T6=480°C, as expected.

Volume concentration of permanent gases in pyrolysis vapour were measured before incineration between 16:52 and 17:48; dry pyrolysis vapour was composed in average of: CO2 18%; CO 16%; H2 12%; CH4+ 9% (including C2H4, C2H6 and higher). Dry gas composition is reported in Table 21.

Table 21. Dry gas analysis test 12

Gas	*Avg. composition [%vol]*	*Instability [%vol]*
CO2	17,95	2,3
CO	15,80	2,9
H2	11,19	7,1
CH4+	9,27	15,8
O2	0,56	24,0
N2 (calc.)	*45,23*	-

Note: - observation period 16:52 – 17:48

Ejector motive air heater was set at 400°C and any blockage or clogging occurred within the test to the benefit of gas flow stability. At full operation, average gas flow rate was 66,5 kg/h and main average temperatures were: T2 41°C; T3 526°C; T4 556°C; T6 484°C; T13 713°C. Reactor pressure drop was 0,5 mbar, while minimal valve regulation was made to maintain design flow. Calculated superficial velocity was also stable between 0,15 and 0,2 m/s. In Figure 78 are reported plots of SV, mass gas flow rate, pressure and valve opening. In Figure 79 is reported gas velocity at ejector.

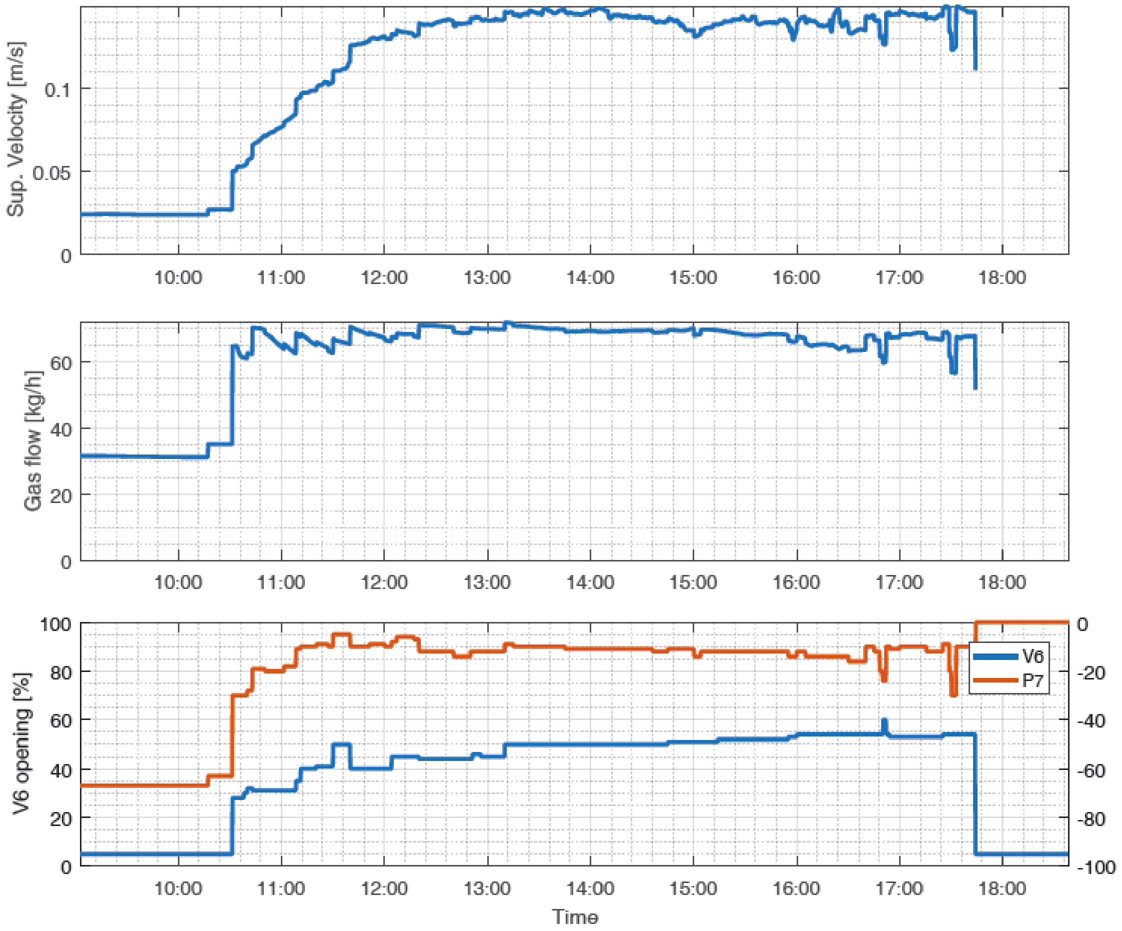

Figure 78. Test 12: Superficial velocity, mass gas flow rate, valve regulation and sucking pressure in mbar

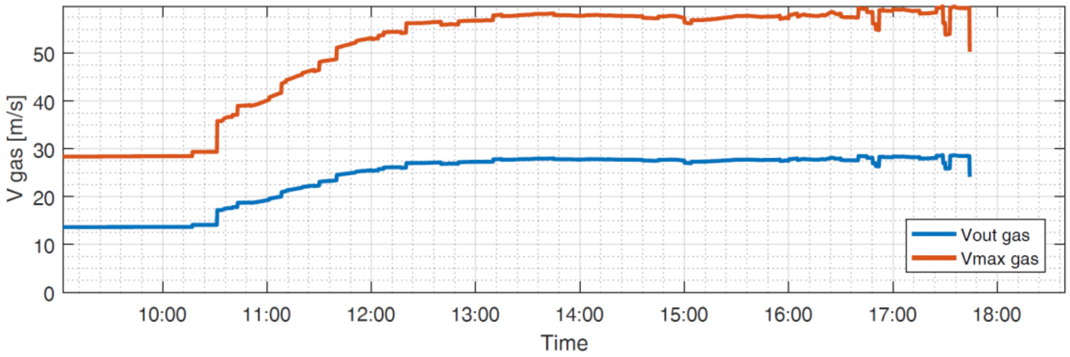

Figure 79. Gas velocity at ejector during test 12: out of diffuser and maximum in throat

Average biomass input was respectively 42 kg/h wet and 36,5 kg/h dry between 11:07 and 17:37. Char and unconverted woodchip were discharged in 8 barrels until the reactor was completely empty. In Figure 80 are reported single batch weights and cumulative curve of biomass loading and char discharging. Is important to underline that both cumulative curves are constant except for the initial part where reactor (for loading) and screw conveyor (for discharge) were empty.

A total of 43 samples were collected every 15 min until reactor was empty. Char sampling discharge was concluded the day after the test after a night stop. For this reason, wording of samples was identified by two number: first number is the day and second is the progressive sample. To simplify post processing data and travelling time calculation, sampling time was virtually carried out and continued after the test.

Fourteen char samples (from 1.15 to 2.28) were identified as woodchip converted within the test. They were collected at discharge port between 16:45 and 20:00, and their calculated biomass loading time correspond to interval 10:52 and 14:07. Average char output was 8,5 kg/h wet (8,2 kg/h dry) from 16:45 to ore 20:15

Calculated total biomass travelling time was in average 5 h 52 min which comprises the following interval times related to each plant's section: reactor 3 h 16 min, hopper 1 h 37 min, screw conveyor 59 min.

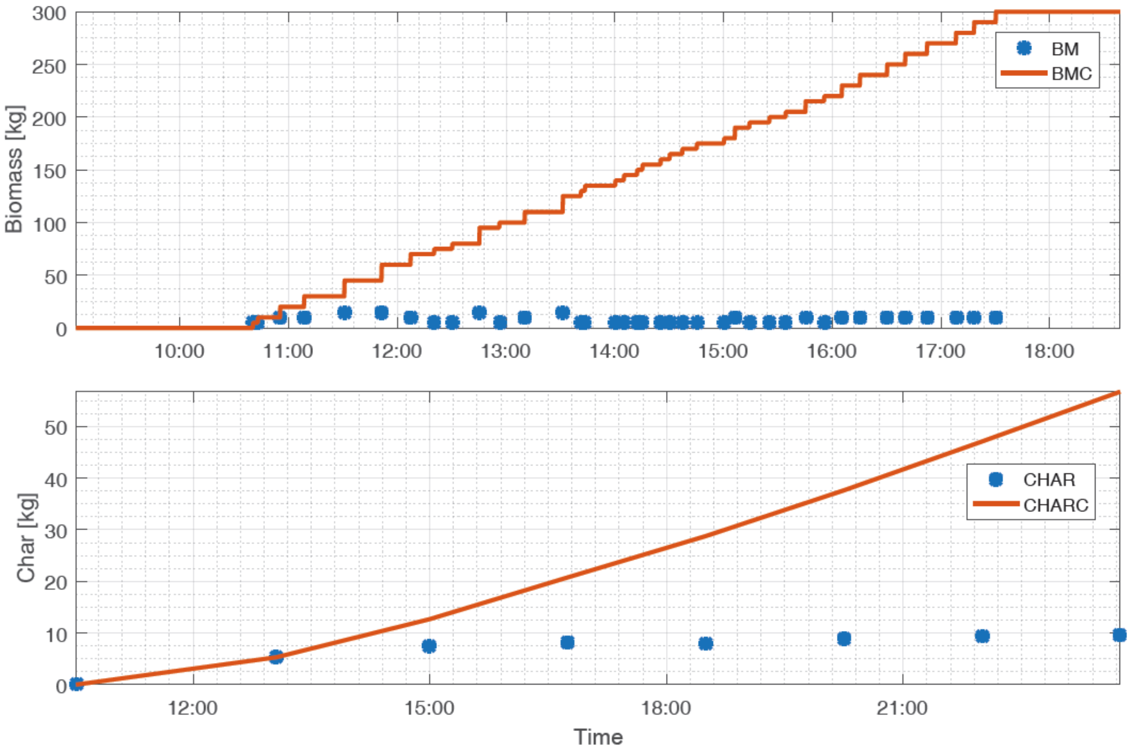

Figure 80. Biomass and char flow rate of test 12: cumulative curve and single batch measure

In Table 22 and Figure 81 are reported laboratory results and pictures of char samples.

After a visual analysis, all char samples from 1.15 to 2.26 were mostly chipped biomass derived char (only one large piece of commercial lump charcoal was present in sample 1.15), confirming that discharged charcoal was manufactured within the test. Last two samples 2.27 and 2.28 were composed by a mixture of uncarbonized biomass and charcoal. Despite particles shrinkage was evident, they largely retained size of initial woodchip with low dust production.

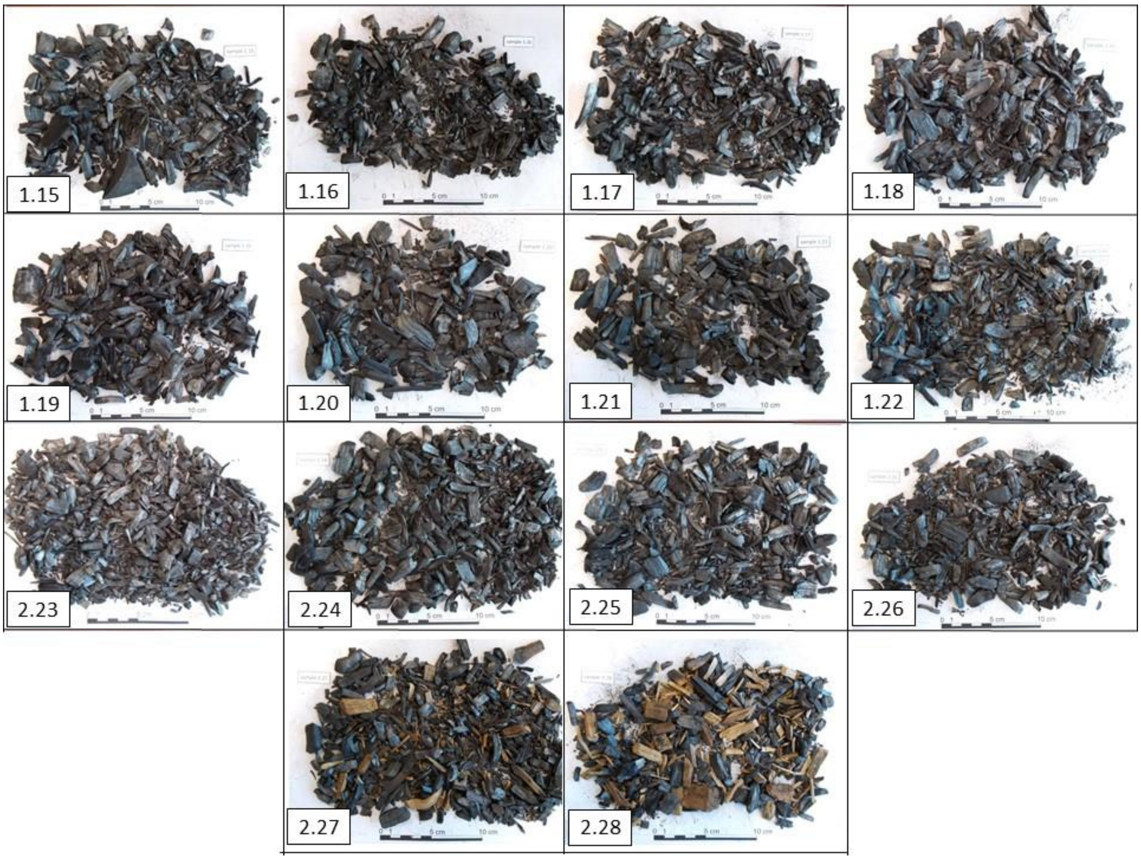

Figure 81. Char samples (1.15-2.28) of test 12

Fixed carbon content was high in the range of 79,7 – 89,1%wt db for samples 1.15 – 2.26 confirming that charcoal manufactured is high quality suitable for many industrial applications. Last two samples, 2.27 and 2.28, had low fixed carbon of 61,7 and 50,6 %wt db. Particle size of discharged charcoal was characterized according EN 15149 and granulometries had median values [d50] between 7,0 and 10,7 mm. Bulk density was almost stable and low for well carbonized samples (1.15-2.26) in the range of 114 – 137 kg/m3. Samples 2.27 and 2.28 were 163 and 191 kg/m3, confirming that limited conversation occurred.

Figure 82. Char sampling during test 12

Surface area characterization was carried out on seven samples (15, 16, 17, 19, 21, 23, 25) ant it was in the range of 196 and 98 m3/g, suitable for following activation.

Thermal history of the sample was inferred from the data collected during operation and correlated to char quality parameters during data post-processing as shown in Figure 83, 84 and 85. Some trends and correlations were noted.

Until T2 was higher than 100°C, samples 15-17 displayed a correlation with high Bet surface and fixed carbon content, especially for the first one that it was evident. In opposition, fixed carbon content and Bet surface were lower for sample 21, although no significative information of temperature was available due to single point measurements were not significant of the entire reactor section.

The same consideration might be made for last samples 27-28 which were not properly converted and they had low fixed carbon and high bulk density.

Table 22. Test 12 char samples characterization (1.15 - 2.28)

Sample n.	**1.15**	**1.16**	**1.17**	**1.18**	**1.19**	**1.20**	**1.21**	**1.22**	**1.23**	**2.24**	**2.25**	**2.26**	**2.27**	**2.28**	**Ref. Norma**
biomass inlet time (hh:mm)	10:52	11:07	11:22	11:37	11:52	12:07	12:22	12:37	12:52	13:07	13:22	13:37	13:52	14:07	-
char sampling time (hh:mm)	16:45	17:00	17:15	17:30	17:45	18:00	18:15	18:30	18:45	19:00	19:15	19:30	19:45	20:00	-
barrel (n°)	4	4	4	4	4	4	4	5	5	5	5	5	5	5	-
Biomass Physical Characteristics															
median value of a particle size [d50] (mm)	8,9	7,9	8,9	10,7	8,2	10,0	10,7	8,3	7,0	7,4	8,4	7,3	8,0	8,9	EN 15149-1:2010
bulk density (ar, kg/m^3)	130	128	125	114	130	137	134	125	146	134	125	134	163	191	EN 15103:2009
Proximate analysis															
moisture (ar, wt.%)	3,2	3,3	3,4	3,9	3,3	3,7	3,9	3,7	3,2	2,6	2,6	2,5	3,0	0,2	EN 14774-2:2009
volatile matter (db, wt.%)	8,7	9,1	10,2	11,0	11,6	17,2	19,2	11,8	12,7	13,7	12,7	16,3	35,8	48,1	EN 15148:2009
ash (db, wt.%)	2,2	1,8	1,9	1,7	2,5	2,5	1,2	2,3	3,9	2,9	2,5	2,2	2,4	1,3	EN 14775:2009
fixed carbon (db, wt.%)	89,1	89,1	87,9	87,3	85,9	80,4	79,7	85,9	83,4	83,4	84,9	81,5	61,7	50,6	-
Ultimate analysis															
C (db, wt.%)	90,8	91,1	90,8	89,8	89,9	83,8	85,3	87,3	86,8	86,5	86,7	85,1	73,1	62,2	EN 15104:2011
H (db, wt.%)	1,7	1,7	1,8	1,8	2,0	2,5	2,5	2,1	2,1	2,2	2,2	2,4	3,5	4,3	EN 15104:2011
N (db, wt.%)	0,5	0,5	0,4	0,4	0,4	0,4	0,4	0,5	0,5	0,4	0,5	0,4	0,3	0,2	EN 15104:2011
O (db, wt.%)	4,8	4,9	5,0	6,2	5,2	10,8	10,6	7,8	6,7	8,0	8,2	9,9	20,7	32,0	EN 15104:2011
Others															
LHV (db, MJ/kg)	31,9	32,1	32,1	31,5	32,0	29,5	30,1	30,8	30,8	30,5	30,6	30,1	25,3	20,6	EN 14918:2009
Surface area - granules (m^2/g)	196	163	141	n.a.	124	n.a.	98	n.a.	138	n.a.	138	n.a.	n.a.	n.a.	ISO 9277

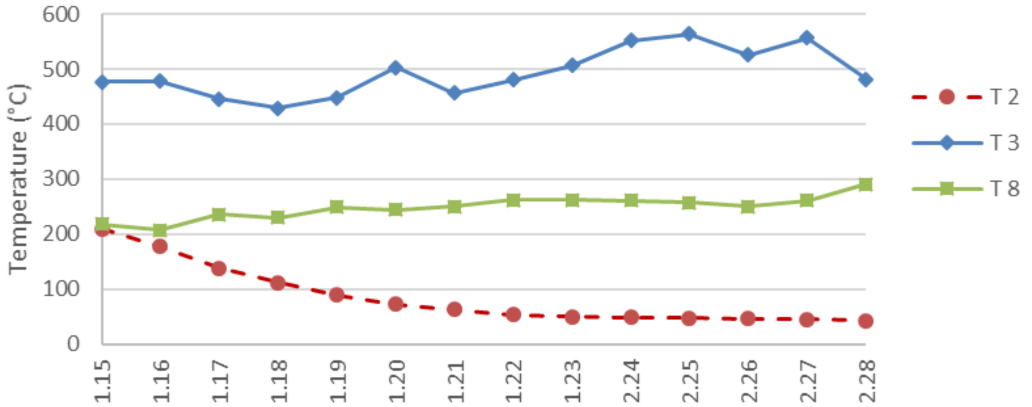

Figure 83. Test 12 Char samples thermal history along travelling though reactor

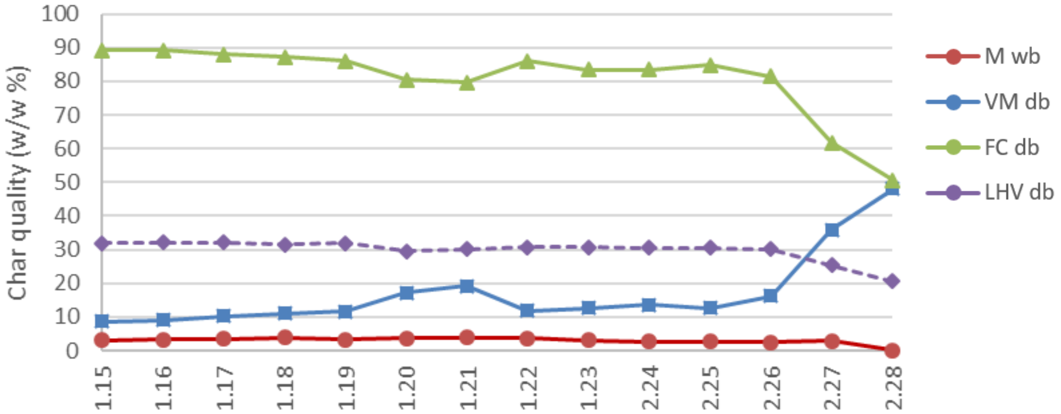

Figure 84. Test 12 char samples proximate analysis

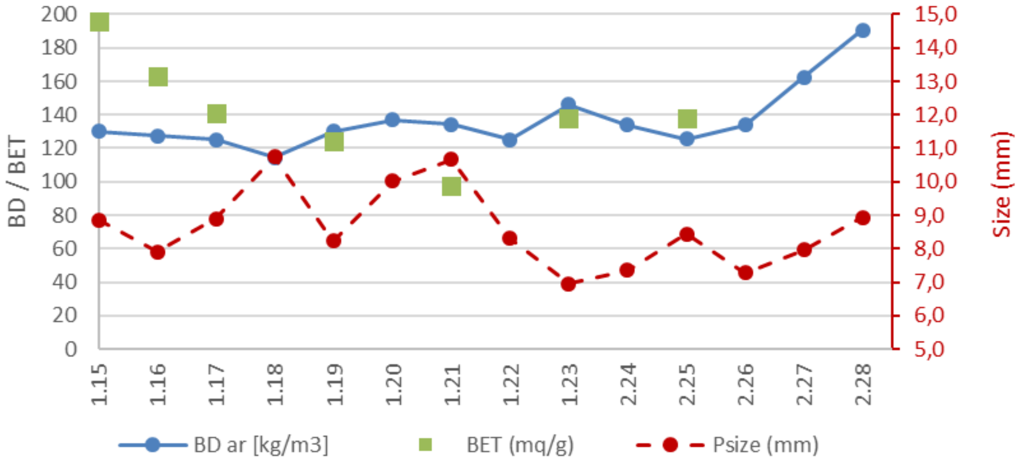

Figure 85. Bulk density, BET surface area and particle size of char samples test 12

Mass and energy balance was performed considering only barrels 4 and 5 (samples 1.15-2.28) according to thermal history profile referring to reactor at full operation and its lasted 3 h and 15 min. Efficiencies for each barrel 4 and 5 were calculated, as well as the average yields representative of the test. In the reported test, charcoal mass yield (Cy) in excess of 22 %wt db was achieved, with a fixed carbon content higher than 85 %wt db as shown before. The fixed carbon yield (fCy) was 19 %wt, the char carbon yield (CCy) 39 %wt and the net energy conversion efficiency to char (ε) was equal to 42%.

In Table 23 are reported all the carbonization efficiencies of test 12 by means of small woodchip.

Table 23. Char efficiencies of test 12

	Cy (wb)	*Cy (db)*	*FCy (db)*	*CCy (db)*	*ε(wb)*
Average yields (samples: 1.15-2.28 – barrels 4 and 5)	20,1±0,7%	22,4±0,7%	18,2±2,2%	38,3±1,6%	41,2±2,2%

Several measurements were carried out on exhaust gas before being discharged into the atmosphere. Pollutant concentration was previously recalculated referring to a dry gas with O2 conc. of 11% at temp. of 0°C and pressure 101,3 kPa.

TLV taken as reference to preliminary evaluate how stack was efficiently working within the test, was the Italian D.Lgs.152 which specified limits of: CO = 350 mg/Nm3 and NO_2 = 500 mg/Nm3. Gas analysis highlighted high CO emission until reactor and stack temperatures were not stable. In this period (between 13:00 and 16:00), CO concentration was in the range of 4.000-15.000 ppm with stack temperature below 700°C. Correlation between CO and temperature at stack was evident also at steady state, with incineration temperature around 800°C. Here CO concentration was very low (<100 ppm) except for a peak of 2750 ppm at 17:40 where torch was not performing properly.

In Figure 86 is reported the graph relative to CO concentration emission and stack temperature for the entire observation period with detail of stability.

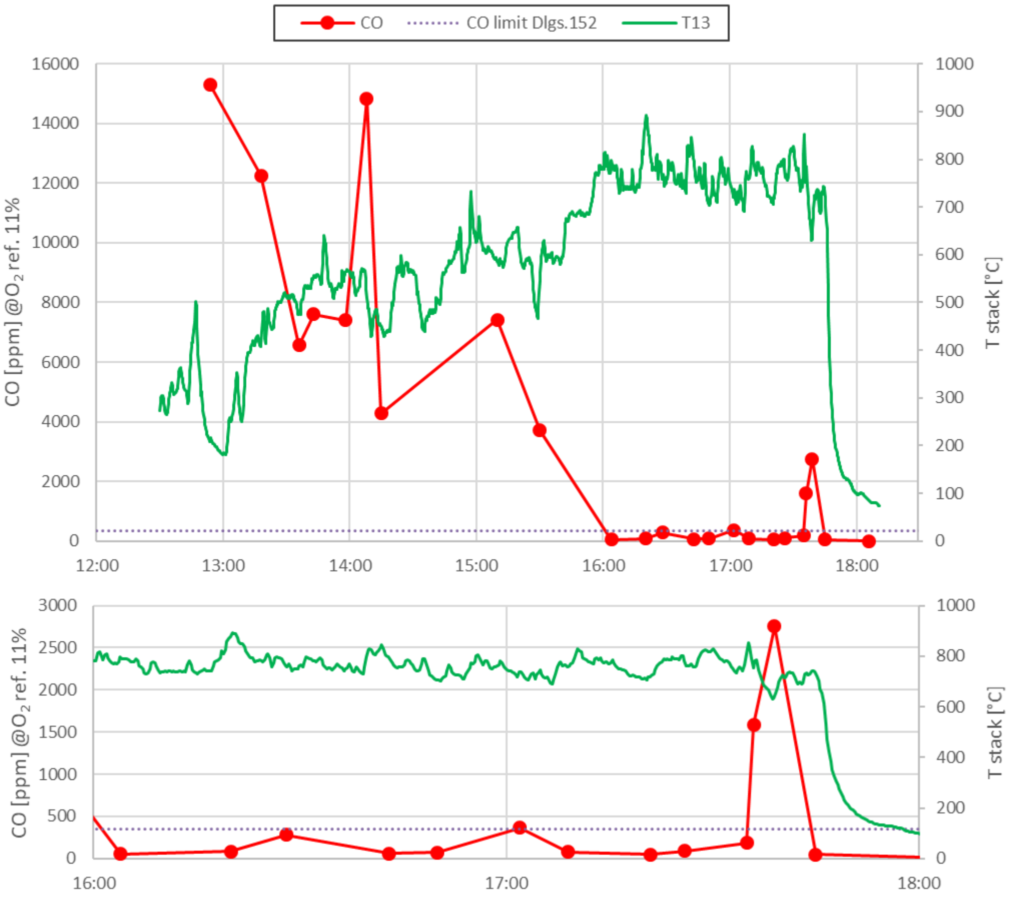

Figure 86. CO emission after post-combustion at stack during test 12

NO concentration was in average very low and almost constant throughout the entire test. According Italian D.Lgs.152, the TLV for NO_x is 500 mg/Nm3. Maximum NO concentration measured was 35±10 mg/Nm3 and this peak was reached when torch was performing at high temperature.

Tar sampling was conducted in accordance internal method adopted by Daouk (Cirad) [44] based on gasification technical standard UNI CEN/TS 15439:2008. Sampling was performed for almost 1 h (between 16:43 and 17:42) with reactor working at steady state condition. Filter and tubing were maintained at 350°C, cold bath was in average -14°C (due to very high ambient temperature, 35°C) and first bottle temperature was 250°C. The total volume of gas sampled was 0,270 m3 with an average flowrate of 4,5 l/min thorough the test.

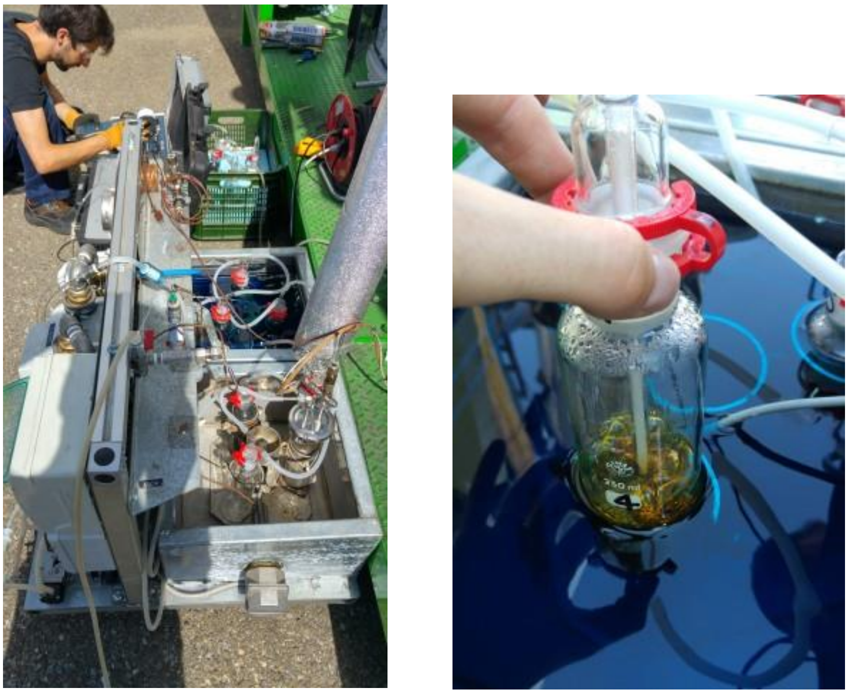

Figure 87. Tar sampling operation of test 12

Visual inspection of impinger bottles train displayed a large quantity of organic compounds were collected due to brown – orange dark colour of liquid (alcohol + condensate). After test, all pipes were preliminary washed out “on-field” with a measured volume of isopropanol to collect all tars condensed outside the bottles.

First bottle was mostly empty, apart a small amount of solid and hard condensate stuck to the bottom. This condensate was composed by heavy molecular compounds characterized by low boiling point. Second bottle (empty before the test) was liquid phase due to water content and dissolved organic. Third and fourth bottles most probably retained most of tar and water content due to the cold bath. Bottle number three had a higher level of liquid and lighter brown than the fourth owing additional isopropanol was used for cleaning silicon tubes. Last bottle (5) was empty and no evident trace of residue was displayed. In Figure 88 are reported images of tar sampling bottles after the test and an internal view of first metallic bottle.

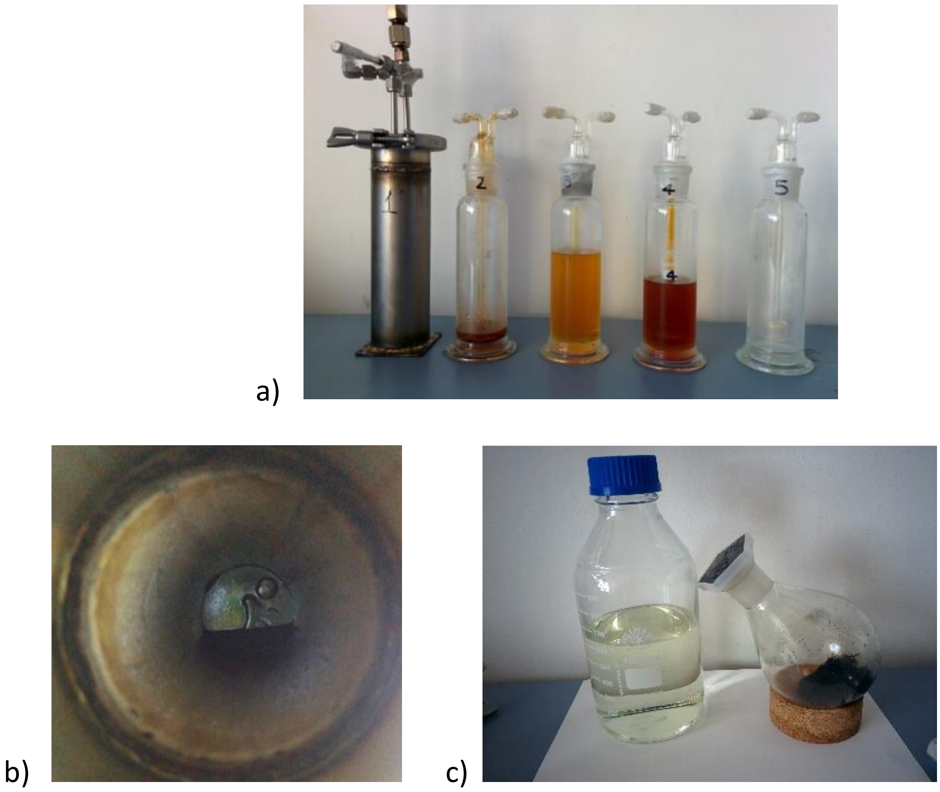

Figure 88. Train impinger bottles (fig. a); internal view of first metallic bottle (fig. b); and heavy bottom and lighter condensate after rotavapor separation (fig. c)

Despite sampling port wasn't isokinetic, fiberglass thimble filter was weighted after the test to estimate a dust load on gas. Difference in weight of filter, before and after test, was 0,3354 g corresponding to 1,24 g/Nm^3 of dust & particles concentration in raw gas. Filter holder was visually inspected to assess if some condensation happened in advance on its internal surface. No sort of advance condensation wasn't recognized confirming excellent performance of the hot thermostatic line.

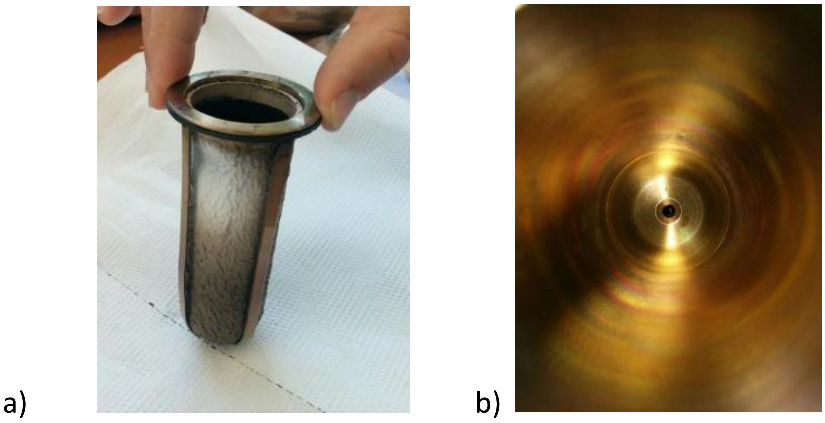

Figure 89. Fiberglass thimble filter (fig.a) and internal view of filter holder (fig.b) after test 12

Results of GC/FID analyses was carried out on the solutions collected with the tar sampling bench. For the determination of tar content in pyrolysis vapour gas, the laboratory sample handling procedure comprised the following steps:

- weight and volume measured of the whole sample;
- withdraw 10 ml for the determination of the water content via KF titration;
- withdraw 1 ml for the GC/MS analysis (GC-detectable tar);
- place the sample in rotavapor to remove the solvent and record the weight of the residue (gravimetric tar).

Mainly due to their molecular weight and structure, not every individual tar specie can be separated and detected with chromatographic methods.

By means GC-MS were identified 47% of organic compounds existing in the condensate. A significant lower production of tars in comparison with inert pyrolysis was confirmed, as well as a higher formation of process water (78,2%wt.), such as found by Daouk (74,7% %wt.).

Significative secondary tar formation, such as Phenols and Aromatics (Benzene, Toluene, Styrene, Indene, …), was observed from list of identified organic compounds, which remarked that cracking on primary tars occurred. Main species produced were: Acetic acid (2,37%wt), Furans (1,68%wt), Benzene (1,45%wt), Levoglucosan (1,19%wt), Methanol (0,70%), whose values were calculated referring to mass fraction condensate dry biomass input (excluding water biomass) and were also compared to Daouk results.

In Figure 91 and in Table 24 are reported full characterization of identified organics of Re-Cord test 12 in comparison with Daouk's experiment result.

The Equivalent Ratio (ER) of the test was 0,15.

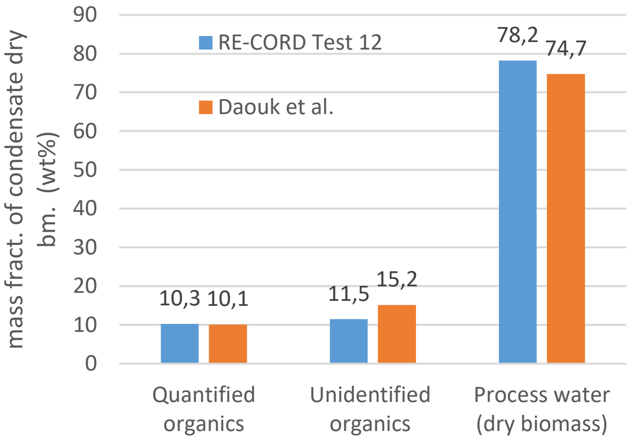

Figure 90. Quantified mass fraction of condensate

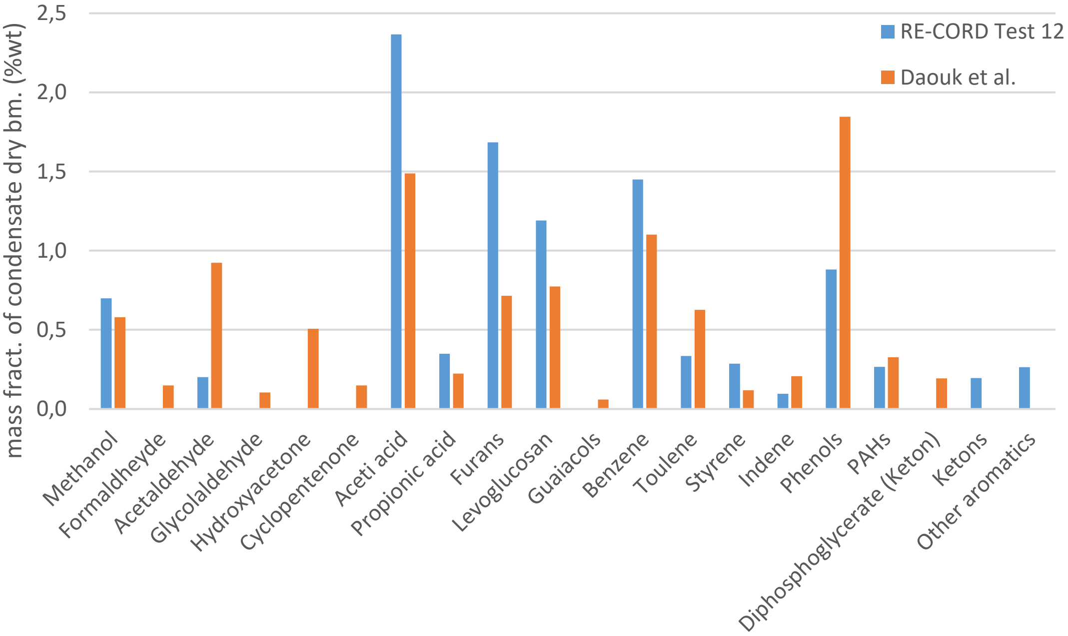

Figure 91. Tar sampling result comparison: Re-Cord Test 12 vs Daouk et al.

It is important to highlighted that this result was achieved by means of a pre-industrial prototype reactor rated to 50 kg/h, fully confirming Daouk's result which adopted a lab scale of ten time less capacity. In fact, the average biomass capacity during the tar sampling was 36,5 kg/h db, while for the laboratory reactor was 3,34 kg/h db. In Table 25 is reported a comparison of two process parameters.

Table 24. Identified organics species in condensate by Re-Cord compared to Daouk

Specie	Re-Cord (%wt.)	Daouk et al. (%wt.)	T boil (°C)
Methanol	0,70	0,58	*64,70*
Formaldheyde	n.d.[1]	0,15	*-19,10*
Acetaldehyde	0,20	0,92	*20,40*
Glycolaldehyde	n.d.[1]	0,10	*115,00*
Hydroxyacetone	n.d.[1]	0,51	*n.d.*
Cyclopentenone	n.d.[1]	0,15	*n.d.*
Acetic acid	2,37	1,49	*117,90*
Propionic acid	0,35	0,22	*141,17*
Furans	1,68	0,71	*31,35*
Levoglucosan	1,19	0,77	*n.d.*
Guaiacols	0,00	0,06	*205,00*
Benzene	1,45	1,10	*80,09*
Toulene	0,33	0,63	*110,63*
Styrene	0,29	0,12	*145,16*
Indene	0,10	0,21	*182,62*
Phenols	0,88	1,85	*117,90*
PAHs	0,27	0,33	*342,03*
Diphosphoglycerate (Keton)	n.d.[1]	0,19	*n.d.*
Ketons	0,19	n.d.	*n.d.*
Other aromatics	0,26	n.d.	*n.d.*
Unidentified organics	11,49	15,16	*n.d.*
Process water (dry biomass)	78,25	74,75	*100,00*
Total	**100,00**	**100,00**	
Quantified organics	10,27	10,10	

Note: water biomass excluded

n.d.[1]: no standard / no found

Table 25. Comparison of Re-Cord and Daouk experiments

Parameter	**Re-Cord**	**Daouk E., (2015)**
Biomass capacity (kg/h db)	36,5	3,34
Biomass type	Chestnut	Maritime pine
Process Equivalence Ratio (ER)	0,15	0,13
Quantified organics (w/w% of total organics)	47 %	40 %

Since biomass carbonization in downdraft reactor it is not far in principle to gasification in the same reactor type, a benchmarking of tar concentration in dry gas with four types of small scale gasifiers was done. All concentrations were impressively higher than gasification and this means the difficult in designing of a reliable industrial carbonization system which is capable to handle such high amount of tars. While water and GC tar concentrations were in the range of 2-10 ten times higher, gravimetric tar was extremely higher, in the range of 35-1500 times.

Table 26. CarbON tar sampling results in comparison with 4 small scale downdraft gasifiers

Plant type	**CarboOn** (mg/m3)	Gasifier A (mg/m3)	Gasifier B (mg/m3)	Gasifier C (mg/m3)	Gasifier D.1 (mg/m3)	Gasifier D.2 (mg/m3)
gravimetric tar conc. in dry gas	**24.444**	484	733	503	118	16
GC tar conc. in dry gas	**9.859**	452	304	194	746	936
GC benzene conc. in dry gas	**3.085**	n.a.	n.a.	n.a.	1.711	3.798
water conc. in dry gas	**284.000**	n.a.	50.950	27.207	22.328	93.557
Note: tar sampling method for gasifiers according EN 15439						

Figure 92. PAHs extraction with Soxhlet

PAHs extraction from CHAR samples (US EPA) was carried out on char samples 15 and 21 and compared with three samples of test 13 (not described in this work). The quantitative analysis showed the presence of the main following species: Naphthalene, Phenanthrene, Anthracene, Pyrene, and others. In Figure 93 is reported result of PAHs extraction for samples 15 and 21 of test 12 and other three samples of test 13.

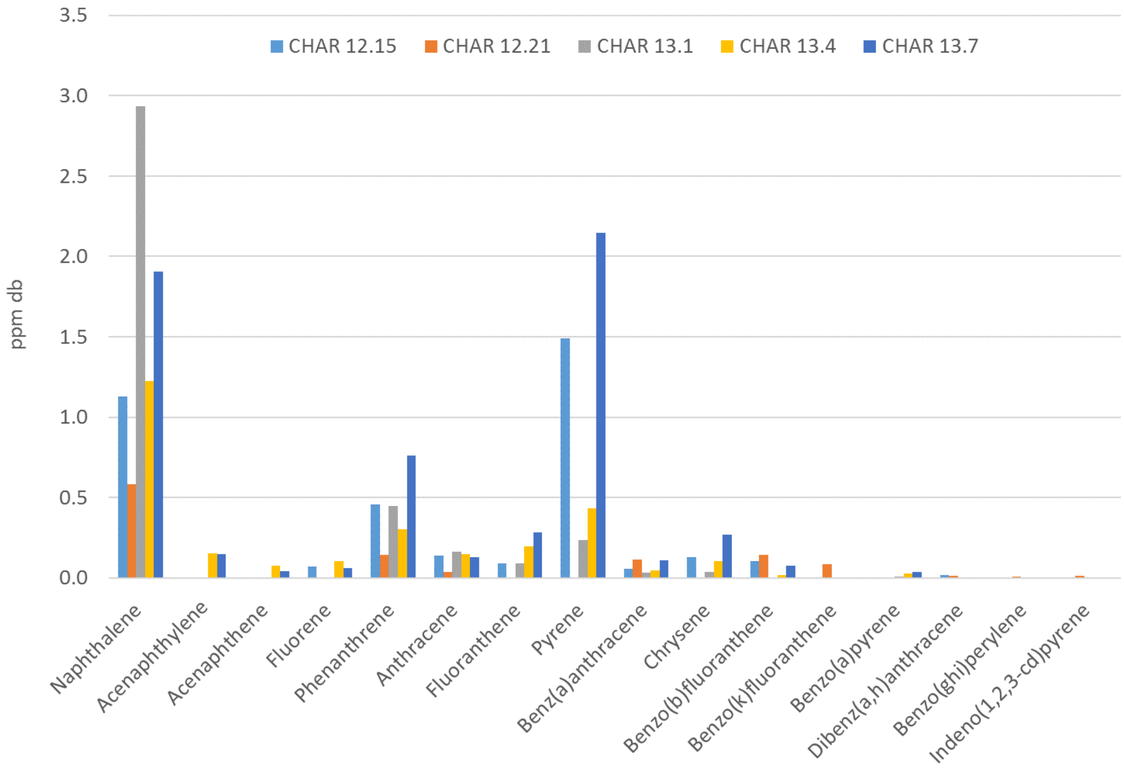

Figure 93. PAHs extraction result from char of test 12 (samples 15 and 21) and test 13

3.3 Conclusion

The two-test (11 and 12) achieved important results in benchmarking biomass carbonization in downdraft fixed bed reactor, verifying and confirming already existing literature results and providing also a full and detailed characterization of whole process and by-products.

Two different types of woodchips, large (mixture) and small (chestnut), were tested in a long run (approx. 8 h) with good performance stability and reliability of the pilot unit and many interesting feedbacks were obtained in obtained in view of the further development to an industrial carbonization demo unit rated to 250 kg/h.

Reactor peak temperatures were in the range of 500-650°C, higher for test 11 due to higher gas flow rate regulation to overcome problem of ejector clogging. Large woodchip retained a char carbon yield (dry) of 24 %wt, higher than small woodchip 22,4 %wt, and in general comparable with the most advanced industrial carbonization plant such as Lambiotte. Superficial velocity was around 0,1 – 0,2 m/s and reactor pressure drop was <0,1 mbar for both tests. Biomass carbonization is traditionally necessary long residence time from several hours up to days, instead calculated travelling time of char samples within the entire plant was around 5 -6 hours among which more than 3 hours in reactor only, meaning that is possible to manufacture high quality charcoal with shorter times. Fixed carbon content achieved (80-90%) is largely higher than the average considered for commercial charcoal (around 75%). Obtained charcoal can be suitable for biochar and industrial applications, such as metallurgy or activated carbon manufacturing. For BBQ application char should be briquetted before being sold on the market to comply with EN 1860-2 technical standard regarding lump size, but this issue could be overcome testing larger woodchip size already identified.

Permanent gas composition in pyrolysis vapour were rich in CO (>15%), H2 (>10%) and hydrocarbons CH4+ (>8%) which held an important energy content to be recovered throughout downstream combustion, as well as to incinerate harmful pollutants before being discharged in atmosphere.

Test 12 characterized also pollutant emissions and vapour phase of pyrolysis gas via tar sampling. CO and NO emissions where extremely low (<100 ppm) after incineration with reactor working at steady state condition. CO concentration was strictly dependant to temperature at stack and thus reactor stability.

Tar sampling results displayed that process water mass fraction in condensate was 78%wt and that 47%wt organics compounds were identified mostly Phenols, Aromatics and Acetic Acid. This achievement was perfectly in compliance with Daouk's result which adopted a lab scale of ten time less capacity (36,5 kg/h db instead of 3,34 kg/h dry) while Equivalent Ratio were almost the same: 0,15 for Re-Cord and 0,13 Daouk et al. [44].

In conclusion, the autothermal continuous process of Re-Cord reactor demonstrated to be able to produce top quality charcoal, with a very high fixed charcoal yield and relative low solid retention time, as well as provided a new benchmark for biomass carbonization in downdraft reactor at pre-industrial scale.

4 Process evaluation and scale-up

This chapter aims to follow up the experimental campaign in order to firstly evaluate the mass and energy balance of the tests and in particular focussing on the complete test 12. On the results of this last test it has been investigated the combustion of pyrolysis vapour as well as VOCs incineration, in view of designing an industrial demo carbonization plant of 250 kg/ capacity. A complete system solution has been proposed with a layout and process scheme. At the end, an economic scenario of a possible adoption of the demo unit coupled with a SRF plot was studied to estimate the investment profitability.

4.1 Mass and energy balance

4.1.1 Test 11

Mass balance of test 11, performed with large size woodchip, has been evaluated by means of measured data and some assumptions based on literature and experience. All data are expressed in wt/wt% on dry biomass input and Nitrogen free. Since no characterization of process vapours is available for this test, it has been assumed that process water, organics and permanent gas mass fractions in pyrogas are the same obtained by Daouk on his experimental result (*“Etudes Expérimentale et Numérique de la Pyrolyse Oxydante de la Bioimasse en Lit Fixe”*, 2015) [44]. Oxygen input of 15,7%wt has been calculated considering Nitrogen as trace gas and its relative ER is 0,12.

The 24,0 % of dry biomass input is converted in charcoal and the remain 91,7 % (calculated by difference of total inputs and charcoal) is a low calorific value pyrogas composed of water (24,5%wt), organics (8,3%wt) and permanent gas (58,9%wt). Permanent gas concentration of test 11 suffered of instability and high CH4 concentration, so it has been considered the mass fraction measured in test 6 owing to its stability and result comparable to Daouk. A Sankey diagram of test 11 mass balance is illustrated in Figure 94.

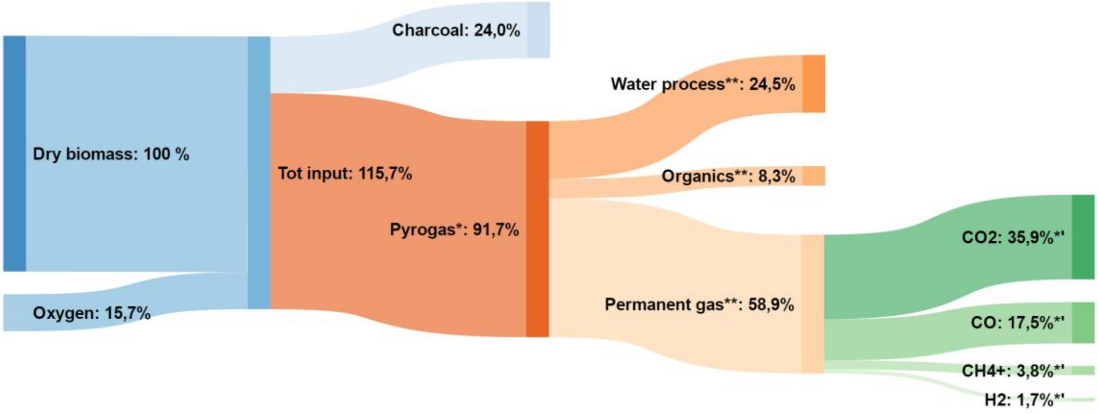

Figure 94. Mass balance of test 11[4]

Energy balance of test 11 is based on previous estimated mass balance. Thermal power of biomass input is 228,1 kWt, charcoal and pyrogas have approximately the same energy content of 44%, respectively 101,5 kWt and 100,2 kWt. Energy lost is 26,4% due to thermal losses 3,9 kWt (1,7 %) and 22,5 kWt (9,9 %).

Total thermal power at stack is 105,2 kW including 5 kWt of pilot burner, more than 100 kWt can be recovered and used for adjacent installation. Utilities consumption is 6,5 kWe (2 kW air heater, 3,5 kWcompressor and 1 kW others). Sensible heat of charcoal is only 0,6% which is negligible and can be dissipate. In Figure 95 and in Figure 96 are reported Sankey diagram and energy output distribution of energy balance of test 11.

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[4] Note: data expressed w/w% of dry biomass input; * calculated by difference; ** based on E. Daouk experiment (ER = 0,13); *' test 6 gas measurements

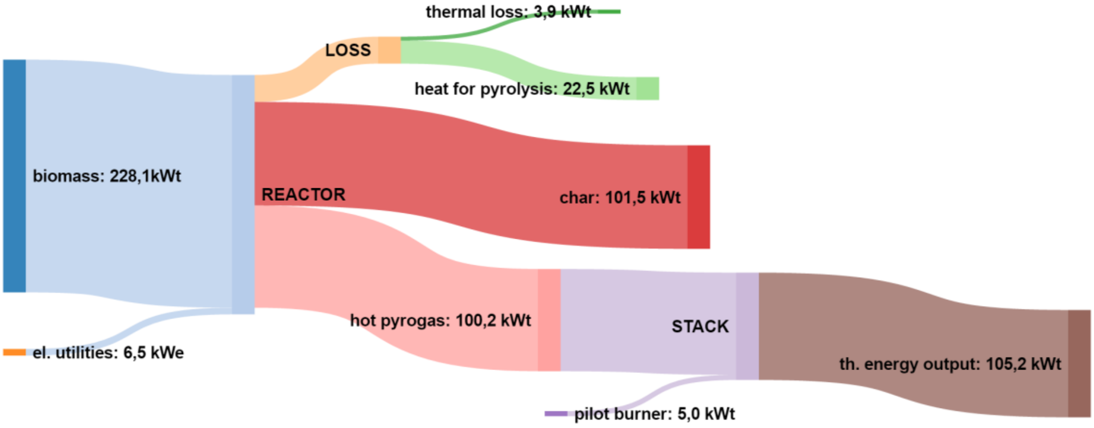

Figure 95. Energy balance of test 11

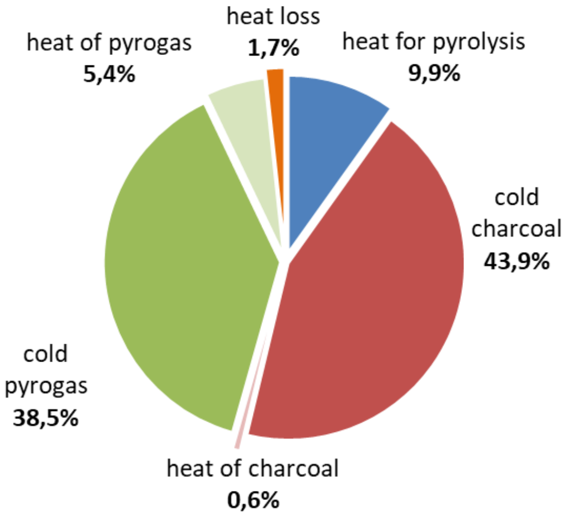

Figure 96. Energy output of carbonization test 11

4.1.2 Test 12

Mass balance of test 12, performed with small size woodchip, has been evaluated by means all information available of the extensive characterization carried out. All data are expressed in wt/wt% on dry biomass input and Nitrogen free. As seen in Test 12 results, charcoal yield is 22,4% confirming that small woodchip is more reactive and it has a lower conversion efficiency in comparison with larger pieces, due to its more surface/volume ratio. Oxygen input of 20,4% has been calculated considering Nitrogen as trace gas and its relative ER is 0,15.

Water process (21,6%), organics (5,8%) and permanent gas (73,9%) mass fractions of pyrogas vapour (101,3%), have been calculated using tar sampling results.

Mass fractions yields are comparable to Daouk's result, in particular, permanent gas fractions present same values of CO and H2 which are 23% and 1,2%. CO2 and CH4+ are higher in Re-Cord experiment with respectively 41,1% and 7,7%, last one probably due to measure accuracy. In Table 27 is reported a full comparison of Re-Cord and Daouk mass balances.

Table 27. Mass balance comparison: Re-Cord test 12 with Daouk (2015)

	Re-Cord Test 12	**Daouk E., (2015)**
Biomass capacity (kg/h db)	36,5	3,34
Biomass type	Chestnut	Maritime pine
Process Equivalence Ratio (ER)	0,15	0,13
Inputs		
Dry biomass	100%	100%
O2 Input	20,4%	17,27%
Outputs		
Permanent gas	73,9%	60,37%
Water	21,6%	25,10%
Char	22,4%	17,23%
Organics	5,8%	8,48%
Permanent gas mass fraction		
CO2	41,1%	31,77%
CO	23,0%	22,80%
CH4+	7,7%	4,54% [a]
H2	1,2%	1,26%
O2	0,9%	-

[a]: sum of: CH4 = 3,04%, C2H4=1,08%, C2H6=0,42%
data expressed as wt/wt%

A Sankey diagram of test 12 mass balance is illustrated in Figure 97. Difference in total inputs (sum of dry biomass and oxygen or pyrogas and charcoal) is related to accuracy of measures within the test.

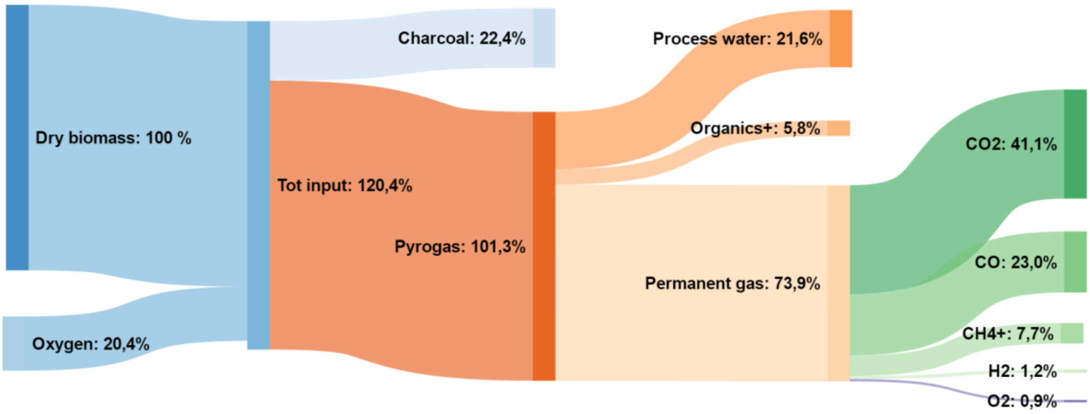

Figure 97. Mass balance of test 12[5]

Energy balance of test 12 is based on related previous estimated mass balance.

Thermal power of biomass input is 190,3 kWt. In comparison with test 11 which has larger size woodchip, more power is addressed in pyrogas 98,1 kWt (51,5%) and less in charcoal 69,1 kWt (36,4 kWt), owing to more reactivity of small pieces. Energy lost is 23,4% due to thermal losses 3,9 kWt (2,0 %) and 19,5 kWt (10,1 %).

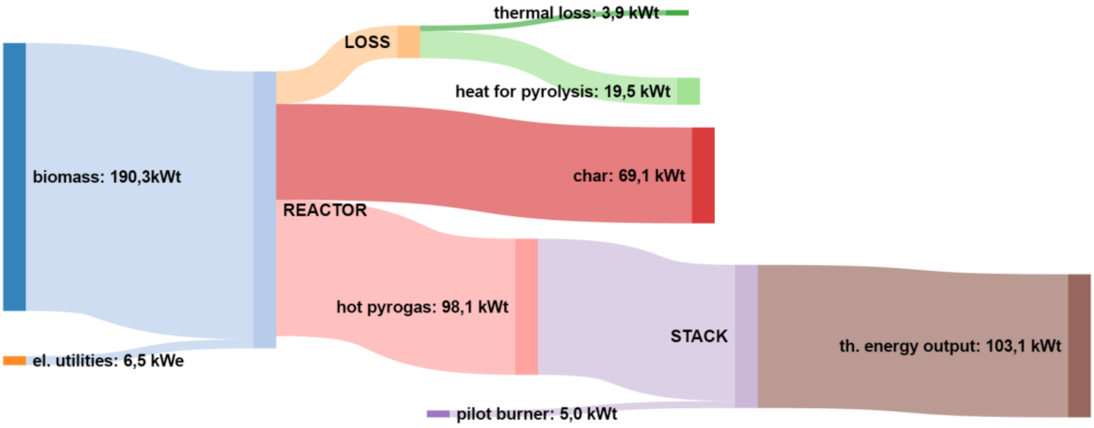

Figure 98. Energy balance of test 12

Total thermal power at stack is 103,1 kW including 5 kWt of pilot burner, which confirm test 11 heat recovery potential. Utilities consumption is 6,5 kWe. In Figure 98

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[5] Note: data expressed w/w% of dry biomass input

and in Figure 99 are reported Sankey diagram and energy output distribution of energy balance of test 12.

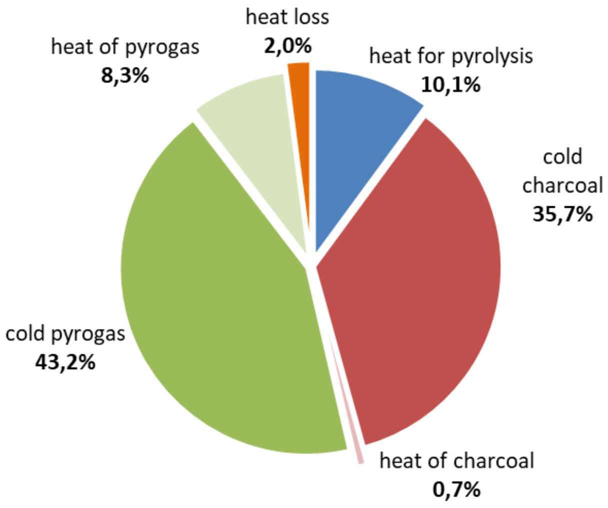

Figure 99. Energy output of carbonization test 12

4.2 Pyrogas combustion and VOCs destruction

There are several technologies to remove and control VOCs emissions in atmosphere. When is not possible to prevent the production of VOCs at source, destruction (oxidation or bio-filtration), and recovery (absorption, adsorption, condensation and separation) represent the state of the art to limit these hazardous and polluted compounds [95]. Thermal oxidation is basically the simplest and viable option which can be adopted to incinerate VOC retained in pyrolysis vapour, with additional scope of generating and recovering heat to benefit other adjacent installation and auxiliary processes. Complete combustion of a typical organic compound produces water vapour and carbon dioxide as described by the following formula [96]:

$$C_xH_yO_z + \left(x + \frac{y}{4} - \frac{z}{2}\right) O_2 = xCO_2 + \frac{y}{2} H_2O \tag{17}$$

Taking in to account experimental result of test 12 and opportunely upscale flow rate up to 250 kg/h of biomass input, it was recreated a possible scenario in order to investigate on handling and combustion of pyrogas mixture for an industrial carbonization system.

It was assumed that other aromatics were considered as Benzene and Ketones and unknown organics were considered as PAHs and in turn Anthracene (C14H10) the heaviest of its compounds. In Table 28 is reported the adjusted gas flow rate for each specie, with a total mass flow rate of 394 kg/h.

Chemical and physical characteristics and safety parameters, of each chemical specie existing in pyrolysis vapour, were listed in order to calculate the value representative of the entire gas mixture. Most of data were found on the following litarature: Yaws [97], Crowl [98], Lewandosky [99], EES database [100], Reaxys database [101], Wiley [102], NIST [103], Phyllis ECN [100]. For all species which no data were available, the missing value was calculated according the formulae here below.

Heating value (higher [99] and lower [100]) expressed in MJ/kg are :

$$LHV = HHV - 2{,}443 \cdot\ 8{,}936 \cdot \frac{H\ wt\%}{100} \tag{18}$$

$$\begin{aligned} HHV = \Big\{ & 15410 + 100 \\ & \cdot \left[\left(H \cdot \frac{1{,}01}{MW} \right) \cdot 323{,}5 - \left(S \cdot \frac{32{,}04}{MW} \right) \cdot 115 - \left(O \cdot \frac{32}{MW} \right) \cdot 200{,}1 \right. \\ & \left. - \left(Cl \cdot \frac{35{,}45}{MW} \right) \cdot 162 - \left(N \cdot \frac{14{,}01}{MW} \right) \cdot 120{,}5 \right] \Big\} \cdot 0{,}002326 \end{aligned} \tag{19}$$

with:

MW = molecular weight of chemical compound

H, S, O, Cl, N = number of atoms of each element

Lower heating value of gas mixture is:

$$LHV_{mix} = \frac{\sum(m_i \cdot LHV_i)}{\sum m_i} \tag{20}$$

Where m_i is chemical compound mass fraction.

Stochiometric oxygen moles necessary to burn organic compound is [99]:

$$\begin{aligned} C_aH_bN_cO_dS_eX_f + [(a + e + 0{,}25(b - f) - 0{,}5d]O_2 \\ = aCO_2 + 0{,}5(b - f)H_2O + fHX + eSO_2 + 0{,}5cN_2 \end{aligned} \tag{21}$$

Stoichiometric air fuel ratio α of gas mixture is calculated as:

$$\alpha_{mix} = \frac{\sum(m_i \cdot \alpha_i)}{\sum m_i} \tag{22}$$

Density is calculated by the average specific volume of the mixture, starting from each single species value. It has been assumed that the average among Methanol, Benzene and Toluene (available compounds) was representative of the entire condensate mass fraction.

LHV of gas mixture is 5,3 MJ/kg slightly higher than a product gas of downdraft gasifier owing to large amount of tar retained. Stoichiometric air fuel ratio is 1,61 kg_{air}/kg_{fuel} due to large quantity of inert compounds (water, Nitrogen, Carbon dioxide). Since, measured gas temperature T4 of gas out of reactor was 556°C in test 12, it was assumed a temperature of 500°C of pyrolysis gas. At this temperature, resultant density and specific heat of mixture are respectively 0,39 kg/m^3 and 1,57 kg/kJK that are different from air density 0,46 kg/m3 and specific heat 1,09 kg/kJK. Auto-ignition temperature (AIT) is also reported for each specie which is a parameter to take in to account for emission control and VOCs destruction. In Table 25 are reported the main characteristics parameter of the gas mixture at 500°C.

Table 28. Main characteristics of gas mixture and single specie at 500°C

Specie	Formula	Flow rate (kg/h)	AIT (°C)	LHV (MJ/kg)	α stoich. (kg/kg)	Density (kg/m3)	Spec. Heat (kJ/kgK)
Carbon dioxide	CO2	89	0	0	0	0,693	1,14
Carbon monoxide	CO	50	609	10,1	2,45	0,441	1,13
Methane +	CH4	17	600	50,1	17,16	0,252	3,88
Hydrogen	H2	3	580	122	34,32	0,032	14,68
Nitrogen	N2	143	0	0	0	0,441	1,12
Water	H2O	80	0	0	0	0,284	2,14
Methanol	CH4O	0,41	470	19,9	6,44	0,506	2,44
Acetaldehyde	C2H4O	0,12	185	25,1	7,8	n.a.	2,26
Acetic acid	C2H4O2	1,39	426	13,1	4,58	n.a.	2,07
Propionic acid	C3H6O2	0,21	485	18,8	6,49	n.a.	2,23
Furans	C4H4O	0,99	390	29,3	9,08	n.a.	2,07
Levoglucosan	C6H10O5	0,7	n.a.	17,5	5,08	n.a.	n.a.
Benzene	C6H6	1,01	592	40,1	13,2	1,234	2,39
Toluene	C7H8	0,2	536	40,5	13,43	1,457	2,09
Styrene	C8H8	0,17	491	40,5	13,2	n.a.	2,44
Indene	C9H8	0,06	n.a.	39,8	13,02	n.a.	2,52
Phenol	C6H6O	0,52	715	31	10,22	n.a.	-0,75
Anthracene	C14H10	7,03	538	38,4	12,73	n.a.	2,25
Gas mixture		**394**	**-**	**5,3**	**1,61**	**0,39**	**1,57**

4.2.1 Destruction efficiency and residence time

In real combustion process, reactions do never complete itself as totally, but a small quantity of chemical compounds remain uncombusted at discharge. To limit hazardous emissions and to comply with emission standards, it is important to reach an adequate efficiency level of combustion process.

VOCs destruction end combustion efficiency are related to many factors but generally only two are considered in combustion chamber: temperature and residence time. The first one must be at least above AIT to start incineration and the second should be sufficiently long to allow reaction happening.

Destruction Removal Efficiency DRE (or Destruction Efficiency DE) is defined by the following formulation [99]:

$$DRE = \frac{VOC_{in} - VOC_{out}}{VOC_{in}} \cdot 100 \qquad (23)$$

Given as input a certain quantity of VOC_{in} compound to bring in combustion and given a threshold limits VOC_{out} ruled by standards, it is possible to obtain Destruction Efficiency to set in incineration process.

Lewandowski [99] proposed a correlation between DRE and combustion parameters. Temperature must be considered up to 343°C higher than AIT and residence time might varies up to 2 s to satisfy DRE of 99,99%. In Table 29 is reported the correlation proposed by Lewandowski. Despite VOC destruction rates are difficult to quantify from a purely theoretical standpoint this method represents an efficacy guideline to preliminary evaluate and approach the gas combustion.

Table 29. VOC destruction efficiency versus time and temperature [99]

DRE [%]	Degrees Above AIT [°C]	Residence Time [s]
0	0	0
95	149	0,5
98	204	0,5
99	246	0,75
99,9	288	1
99,99	343	2

This method assumes that at least 3% in excess of oxygen concentration is maintained in combustion products and a sufficient turbulence exists in combustion chamber (Re > 10.000). Since CO is more difficult to destroy than most VOCs, its emission is extremely related to peak of temperature and it depends less on excess of oxygen. It has been demonstrated that CO emissions increase exponentially below 870°C [99].

Taking into account threshold limits prescribed by the Italian law D.Lgs.152:2006 which is equal to the EU Directive PE-CONS42/15, it was calculated destruction efficiency for each compounds as well as required destruction temperature and residence time.

Table 30. Threshold limit values for biomass combustion plant according to Italian law D.Lgs.152:2006

	Nominal thermal power installed [MW]			
	0,15 – 3	3 – 6	6 – 20	>20
Pollutant	**TLV [mg/Nm^3]**			
Solid particles	100	30	30	30
Volatile Organic Content (VOC)	-	-	30	20
Carbon Monoxide (CO)	350	300	150	150
Nitrogen Oxides (expressed as NO_2)	500	500	300	200
Sulphur Oxides (expressed as SO_2)	200	200	200	200
NOTE: TLVs is referred to a dry gas with O2 conc. of 11% at temp. of 0°C and pressure 101,3 kPa				

Italian D.Lgs.152 prescribed for biomass combustion plants the following TLV for main pollutants (Table 30). In case of carbonization unit of 250 kg/h the maximum thermal power achievable theoretically is around 1,1 MW and for this rated power there is no limit VOCs emissions except for hazardous species mentioned specifically in the law for which a certain TLV must be respected.

In Table 31 is reported the destruction efficiency calculation for the species considered by Italian TLV. Destruction temperature and residence time required to bring pollutants concentration in flue gas at emission limit are respectively 961°C and 1,0 s which represent a feasible target for an industrial process.

As expected, Carbon Monoxide and Benzene required 1,0 s of residence time due to their high concentration before combustion and in fact DRE is 99,8% and 99,4 %.

Phenol is instead critical for its high destruction temperature (961°C) which is the maximum within the other species. Although Toluene is listed among the hazardous compounds, its concentration in raw gas of 557 mg/Nm3 is below TLV. Other species considered, such as: Acetic Acid and Acetaldehyde are no critical and their requirements are included within the overall prescribed combustion parameters.

Table 31. Calculated residence time and destruction temperature for each chemical specie

specie	*concenc before combustion (mg/Nmc)*	*TLV Dlgs152 (mg/Nmc)*	*DRE %*	*temp of destruction (°C)*	*residence time (s)*
CO	196.383	350	99,8	897	1
Acetaldehyde	336	20	94,0	334	0,5
Acetic acid	3.942	150	96,2	630	0,5
Benzene	819	5	99,4	879	1
Toulene	557	600	0	685	0,5
Phenol	1.466	20	98,6	961	0,75

Since residence time is parameter that can be easily managed and taking into account in design process of volume and shape of combustion chamber, destruction temperature is instead strictly related to oxidation chemical reactions and temperature achievable in combustion. For this purpose, it has been evaluated the Adiabatic Flame Temperature (AFT) of the pyrogas at different oxygen concentration in flue gas to verify if the temperature is enough to incinerate pollutants or an auxiliary fuel is needed.

AFT calculation is based on heat balance of chemical reaction of each specie at equilibrium, in adiabatic condition and constant pressure. The balance is referred to a reference temperature of 25°C and it can be written as follow:

$$\begin{cases} \sum\left[(H_T - H_{25})_{reagents} + (H_T - H_{25})_{products} + \Delta H_{comb}\right] = 0 \\ (H_T - H_{25})_{products} = \sum n_i \int_{25}^{T} c_{p_i}\, dT \end{cases} \tag{24}$$

In the calculus, it has been assumed to bring in combustion pyrogas at 500°C and oxidant at 20°C, with 5% of loss in combustion chamber.

Max AFT calculated in stoichiometric condition is 1.666°C which is enough higher to the temperature required by DRE. In Figure 100 is reported trend of AFT and oxygen concentration in flue gas at different ER. For typical values of biomass furnaces with ER of 1,6 [104], temperature is 1.304°C and O2 in flue gas is 5,62 %vol.

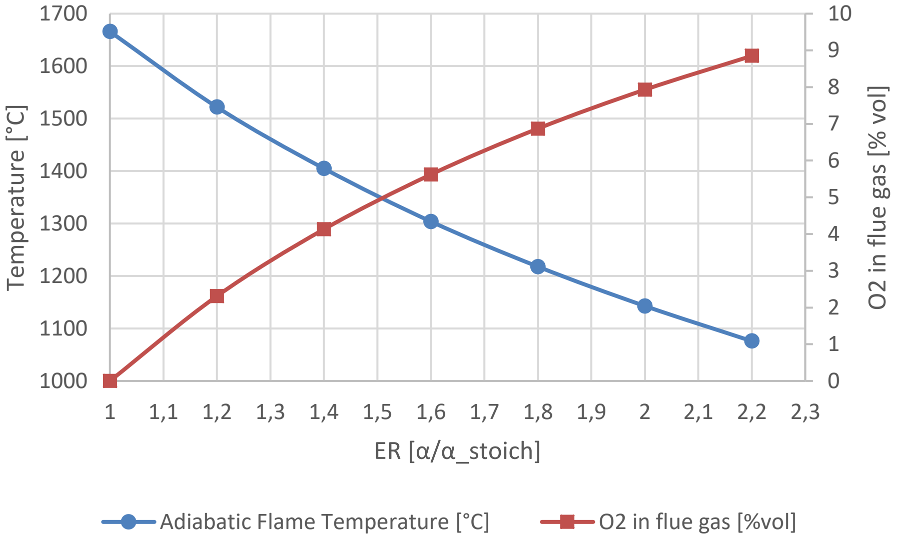

Figure 100. Adiabatic flame temperature and oxygen concentration in flue gas at different ER

According to Lewandowski, an excess of air is usually added to thermal oxidation to produce 3% (by volume) of oxygen in the combustion products [99]. Considering a reasonable temperature of 1200°C in combustion chamber we have a O2 concentration in flue gas of 7,13%vol. and a thermal power of 657 kW of which 82 kW of sensible heat and the remaining 575 kW chemical. In Table 32 are summarized combustion process parameters in combustion chamber with flow rates.

Table 32. Summary of main process parameters at Post-combustion chamber

Post-Combustion process parameters		
Pyrogas temp.	°C	500
O2 in flue gas	%vol.	7,13
Adiab. Flame Temp.	°C	1.200
ER (equiv. Ratio)		1,85
Pyrogas flow rate	kg/h	394
Total air input	kg/h	1.174
Total flue gas	kg/h	1.563
Power at CC	**kW**	**657**

A thermal oxidizer is generally composed of three sections: a burner, a mixing chamber and a residence chamber (Figure 101).

Optimal criteria to design the residence chamber is to maintain gas mixture for a necessary time to complete the combustion in according to DRE thus a certain internal volume should be addressed. Gas speed velocity should be preferably between 7,6 and 12,2 m/s and volume chamber L/D ratio in range of 2 – 8 [99]. Mixing chamber volume depends on fluid dynamic and it requires detailed CFD studies [105,106].

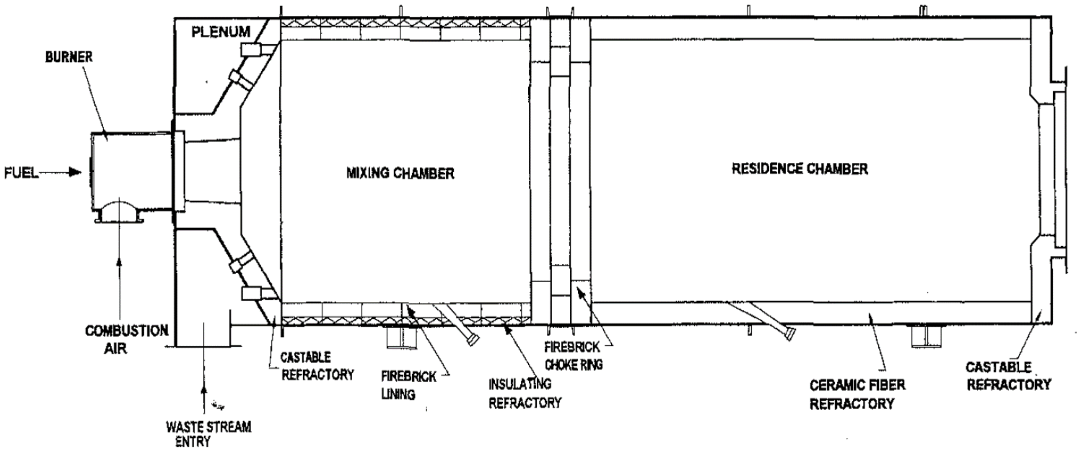

Figure 101. Typical thermal oxidizer refractory installation [99]

In case of a carbonization unit of 250 kg/h, it has been evaluated volume and dimensions of thermal oxidizer in order to assess feasibility and cost impact on demo unit final price. According to a burner manufacturer for such application and working parameters, mixing chamber volume should be around 0,2 m3. Residence chamber volume is instead 1,8 m3, considering a reasonable diameter of 0,68 m, length 5 m with gas flow speed of 5 m/s. Total internal volume is therefore 2,00 m (Table 33).

Table 33. Combustion chamber geometry

Combustion chamber geometry		
max residence time	s	1
mixing chamber volume	m3	0,20
residence chamber volume	m3	1,80
total internal volume	m3	2,00
Residence chamber parameters		
Gas flow speed	m/s	5
Diameter	m	0,68
length	m	5,00
L/D ratio		7,4
Reynolds number		17.420

4.2.2 Explosion limit and safety of gas mixture

An air fuel mixture combustion happens when their concentration must be within two limits, which are called LEL (Lower Explosion Limit) and UEL (Upper Explosion Limit). In order to provide useful data for a possible following design of a demonstration unit, it has been calculated explosion limits and LOC (Limiting Oxygen Concentration) of gas mixture at 500°C. Explosion limit for each specie is calculated by means of the following formula [107]:

$$\begin{cases} LEL_T = LEL_{25} - \dfrac{0,75}{\Delta H_c}(T-25) \\ UEL_T = UEL_{25} + \dfrac{0,75}{\Delta H_c}(T-25) \end{cases} \tag{25}$$

Where ΔHc is enthalpy of combustion [kcal/mol]

LEL and UEL of gas mixture are calculated according to Le Chatelier formula [98]:

$$\begin{cases} LEL_{mix} = \dfrac{1}{\sum \frac{y_i}{LEL_i}} \\ UEL_{mix} = \dfrac{1}{\sum \frac{y_i}{UEL_i}} \end{cases} \tag{26}$$

LOC is calculated according to Crowl [98]with

$$\begin{cases} LOC = z \cdot LEL \\ z = \dfrac{x_{O2\,stoich}}{x_{fuel}} \end{cases} \tag{27}$$

Where z is oxygen volume fraction in gas mixture at stoichiometric conditions.

Calculated explosion parameters of gas mixture are at 500°C: LEL = 5,22%, UEL = 34,16% and LOC =5,22%. For species which values are unavailable from literature it has been assumed with precautionary criteria a LEL of 1,00% at 25°C. In Table 34 are reported explosion limits, LOC and Flash temperature of each specie.

Table 34. Explosion limits and Flash temperature of gas mixture at 500°C

specie	LEL @500°C (%vol. fuel)	UEL @500°C (%vol. fuel)	LOC @500°C (%vol. O2)	T flash (°C)
Carbon monoxide	12,20	74,30	6,10	
Methane +	4,89	15,11	9,79	-187,78
Hydrogen	3,65	75,35	1,82	
Methanol	5,87	36,63	8,80	11,11
Formaldehyde	6,84	73,16	6,84	-53,33
Acetaldehyde	4,02	60,08	10,06	-37,78
Glycolaldehyde	1,00 [a]	55,42 [a]	2,00	
Hydroxyacetone	1,00 [a]	87,10 [a]	3,50	
Cyclopentenone	0,95 [a]	36,54 [a]	5,71	
Acetic acid	5,29	16,11	10,58	42,78
Propionic acid	2,84	14,86	9,94	55,00
Furans	2,26	14,34	10,16	-35,56
Levoglucosan	0,98 [a]	45,91 [a]	5,88	
Guaiacols	1,28	9,62	10,20	81,67
Benzene	1,37	8,03	10,30	-11,11
Toluene	1,38	6,72	12,39	4,44
Styrene	1,08	6,12	10,80	32,22
Indene	0,98	7,22	10,80	55,00
Phenol	2,97	10,03	20,80	42,78
Anthracene	0,59	5,31	9,69	-17,78
Gas Mixture	**5,22**	**34,16**	**1,71**	

[a]: values calculated from initial precautionary assumption

4.3 Demonstrative carbonization plant of 250 kg/h

This paragraph describes and resumed preliminary steps and design criteria to scale up the pilot unit to an industrial carbonization demo system of 250 kg/h. Core item of the entire process is the reactor where conversion occurs and which represents in most cases the biggest and tallest components, and for this reason a critical part of the small bioenergy plant.

Reactor size is directly related to biomass flow rate and the new demo has a volume of 2,34 m3, thus fifth times larger than the existing pilot unit (0,47 m3). Chosen criteria to scale up the reactor was set to maintain the same SV of 0,12 m/s of the pilot unit in order to replicate same conversion condition, as much as possible, and to limit in height the reactor. It is known from gasification literature that low SV ratio favourites production of char and tar [86], thus toward to carbonization process, as well as reactors characterized of low L/D ratio do not performed properly in gasification [93] due to channelling problems and temperature distribution. Lower temperature of carbonization process compared to gasification can make viable the adoption of a wide reactor allowing in any case to use a mechanical steerer on the top to make uniform the biomass bed. The new reactor is therefore characterized by: D=1,4 m; L=1,52 m and L/D = 1,08. In Table 35 are resumed all data of 50 kg/h and 250 kg/h reactors and compared to different upscale criteria.

Table 35. Upscale scenario of 250kg/h carbonization reactor

Reactor	**D [m]**	**L [m]**	**A [m^2]**	**V [m^3]**	**L/D**	**SV [m/s]**
50kg/h pilot unit	0,63	1,5	0,31	0,47	2,38	0,12
250 kg/h - upscale criteria						
same D	0,63	7,50	0,31	2,34	11,90	0,61
same L/D	1,078	2,56	0,91	2,34	2,38	0,21
same SV	**1,4**	**1,52**	**1,54**	**2,34**	**1,08**	**0,12**

An annular jacket chamber can be designed to minimize gas flow velocity and to keep heated part of the reactor itself, as well as to overcome some issues faced during the experimental campaign on the pilot unit: particle dragging and homogeneous gas sucking from reactor.

As already investigated in previous paragraph, regarding pyrogas combustion and VOCs destruction, it has been evaluated the viability of product gas utilization for heat generation to benefit of adjacent installation. Aiming to design an innovative, industrial and reliable carbonization plant, the gas line and incineration system represents a bottleneck of the technology due to risk of tar condensation and consequently clogging must be avoided. New gas line, such as for the pilot unit, must regulate automatically the gas flow rate extracted from reactor and consequently oxidant air drawn to sustain the autothermal process. An advanced gas line, proposed and schematized in Figure 102, is composed of: a cyclone, a complete combustion chamber with burner, a heat exchanger to recovery off-gas thermal load, a blower and a stack/chimney.

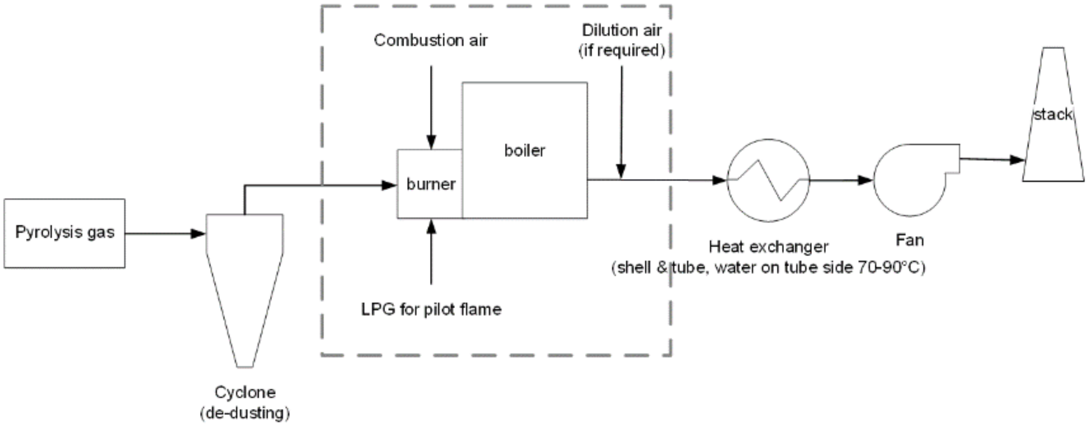

Figure 102. Proposal scheme for recovery heat and pyrogas combustion of 250 kg/h carbonization plant

Taking in to account, thermal power at CC of 657 kWt calculated in the previous paragraph considering mass end energy balance of test 12, it has been evaluated the net thermal power recovered by a heat exchanger place downstream the combustion chamber which produces hot water at 80-90°C for wood drying application. Global efficiency of combustion chamber and heat exchanger is assumed to be 0,7 and exhaust gas temperature is sent to chimney at 200°C. Net recovered thermal power is 381kWt which allows to supply a drier with an output capacity of 423 kg/h of woodchip at less than 10%wt wb starting from a biomass at 45%wt wb [108] (Table 36).

Table 36. Waste heat recovery scenario

Heat recovery data	***Unit***	
Thermal power input at combustion CC	kWt	657
Global efficiency of CC and HE	%	70
Net thermal power at boiler	kWt	460
Exhaust temperature after HE	°C	200
Net recovered thermal power	kWt	381
Woodchip drier utilization scenario		
Specific power consumption [108]	kg/kWt	1,11
Drier output capacity (from 45% to <10%wt wb)	kg/h	423

According to manufacturer, a dedicated pyrogas burner for this application should consider an auxiliary burner of approx.120 kW fed with LPG or natural gas to sustain flame stability and to heat all components in the start-up. A typical combustion system for this application can integrate a heat exchanger such as a three-pass fire tube boiler.

In final carbonization plant scheme should be considered on gas line a bag-house filter to avoid any residual particle emission in atmosphere, as well as a by-pass with a parallel gas line and an ejector must be addressed for ignition and unsteady operations to avoid damages on components of main gas line.

Char extraction system is completely air tight and it is composed of a high temperature twin screw conveyor installed below the reactor and a belt conveyor with water spraying to cold down hot charcoal and avoid crushing of particles. In general, the 250 kg/h system adopts some technologies of 50 kg/h pilot unit.

A complete and detailed P&iD of the Re-Cord carbonization demo unit of 250 kg/h is reported in Figure 103.

Target price for this industrial carbonization unit is estimated around 400-450 k€ (CAPEX).

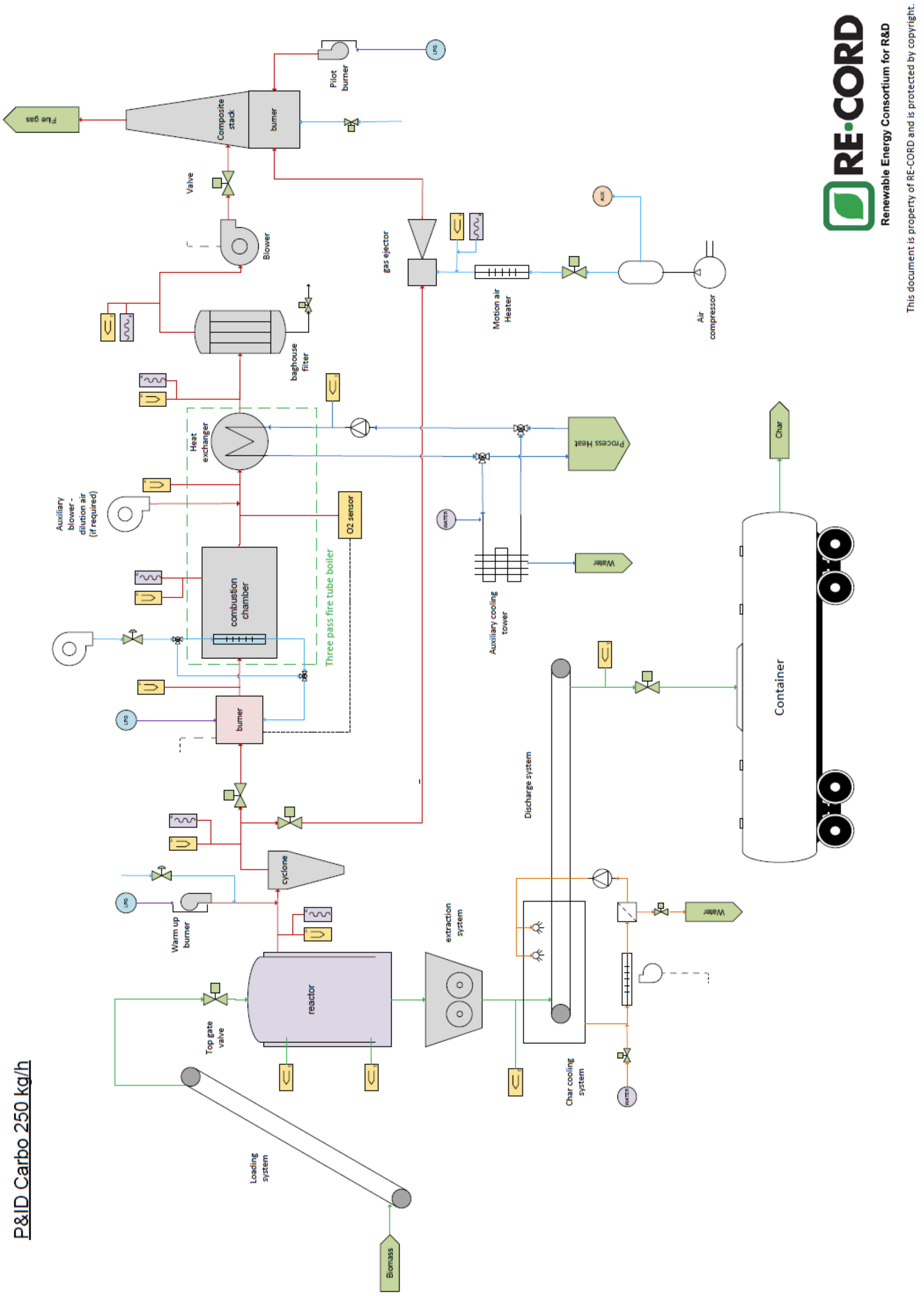

Figure 103. P&iD of Re-Cord carbonization demo unit of 250 kg/h

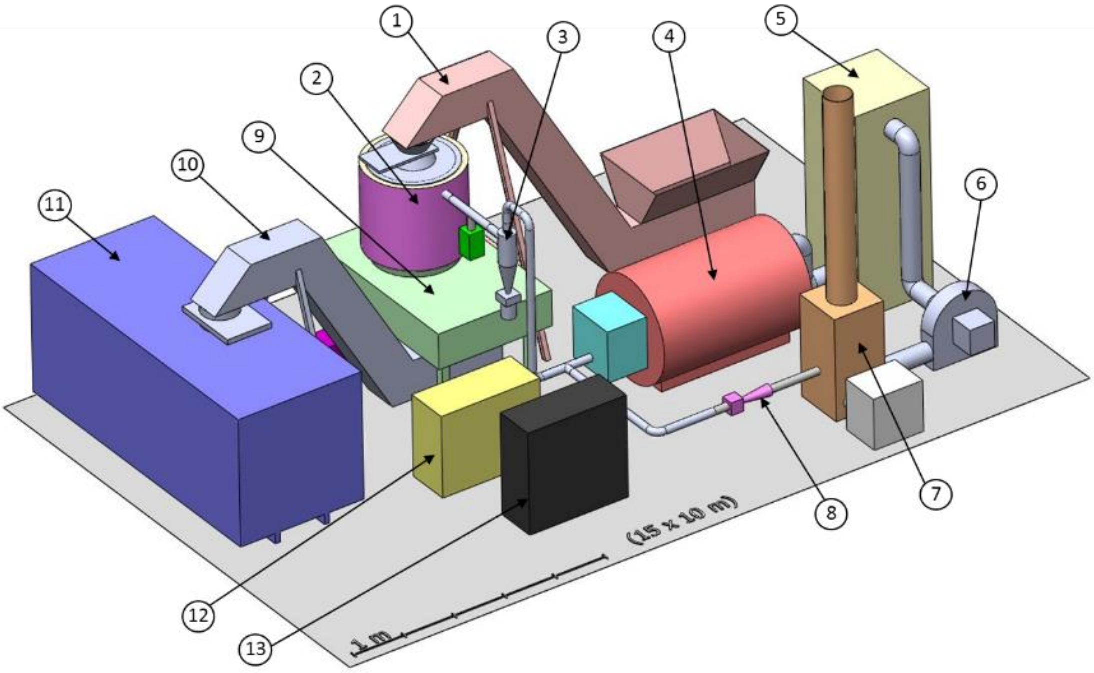

Figure 104. 3D layout of Re-Cord demo carbonization unit 250 kg/h

Expected demo unit has a footprint of 15x10 m max without considering woodchip stock and in Figure 104 is proposed a 3D layout. Equipment and components list are the following:

1. Biomass loading system
2. Reactor
3. Cyclone
4. Three-pass fire tube boiler
5. Bag house filter
6. Inverter driven blower
7. Composite stack
8. Gas ejector
9. Charcoal extraction system
10. Char cooling and discharge system
11. Storage container
12. Air compressor
13. Control panel

4.4 Short rotation forestry coupling with demo unit: economic scenario

Short rotation forestry (SRF) consists of planting a site and then felling the trees when they have reached a size of typically 10-20 cm diameter at breast height. Depending on tree species this usually takes between 8 and 20 years, and is therefore intermediate in timescale between short rotation coppice and conventional forestry [109].

Backed by the aforementioned performance data collected during the operation of 50 kg/h pilot unit, the present work reports the technical viability and economic profitability of coupling SRF and the demo carbonization plant, sized at a scale that can properly match the size of an average forestry company operating in central Italy (250 kg/h feed).

This paragraph is an extract of our conference proceeding paperwork presented at the 8th International Conference on Applied Energy – ICAE2016 [110].

4.4.1 Performance and cost estimate of the carbonization demo unit (250 kg/h)

As a conservative hypothesis, it was assumed that the demo plant attains the same performance of the pilot unit using large size woodchip, in term of all the four yields of the test 11, thus neglecting the beneficial scale effect. While the pilot unit simply burn the off-gases, the up-scaled demo plant entails some more refined features that enhance the energy recovery and mitigate the environmental impact of the system; therefore, the larger system considered in this study includes a pyrogas burner, a heat recovery boiler and bag-house filter for exhaust de-dusting before stack and all the heat generated by the combustion of the pyrogas is fed to an external process. Net boiler efficiency (overall) was assumed equal to 90%.

A cost estimate of first-plant construction was drawn basing on the design constraint and operation scenario, and was supported by quotation of individual components from individual manufacturers. The estimate of operating expenditure was based on the use scenario of 5 days per week over three shift of 8 hours each; the heat recovered from the boiler was assumed to be sold at 6 €c/kWh, and the amount of estimated available heat after the internal consumption for biomass drying. The cost of labour was estimated at 12 €/h, cost of service calculated as 4% of capex, and cost of insurance 2% of capex; the carbonization plant operates automatically, and the workload has been considered to be 6 h per day.

Thermal energy required for drying biomass from 45 to 10 wt% (wb) was estimated at approx. 4MJ/kg_{dry} (1.1 kWh/kg_{dry}) [108]. Charcoal was assumed to be sold on the wholesale market at 0.65 €/kg.

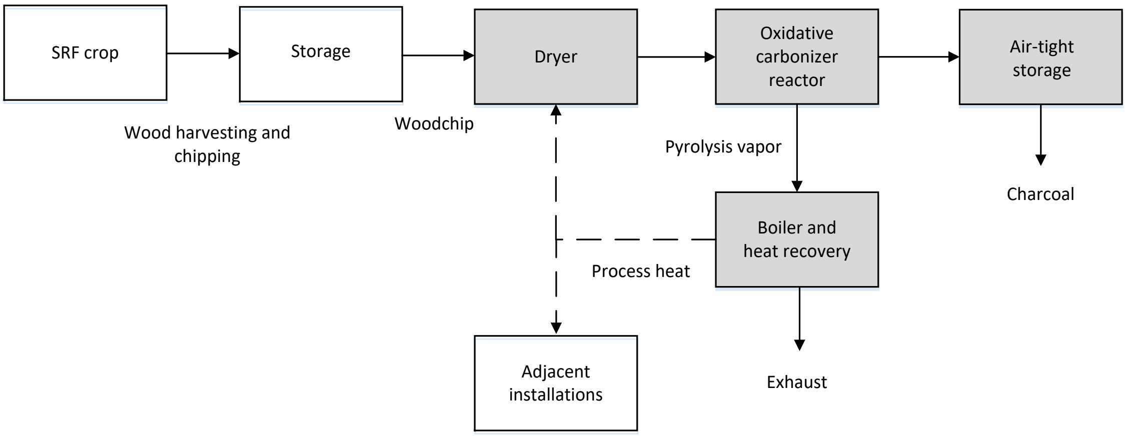

Figure 105. SRF-Carbonization demo unit coupling scheme

4.4.2 SRF plot

SRF is the ideal forestry management scheme to be coupled with a carbonization plant as it provides consistent size of feedstock, after field processing and size reduction, which in turns reflects in a less dispersed charcoal particle size.

For calculation, the agronomic data reported by Coaola and Grignetti [111] on the productivity and specific cost per hectare of poplar and robinia cultivated at SRF scheme have been adopted. In their study 2514 hectares over 350 plots, cultivated by 255 farms, distributed across eleven distinct Italian regions, have been evaluated between 2008 and 2010. In the present study we retain the same land management scheme proposed by the Authors: a cut every two year and a plantation lifespan of 10 years, without plot irrigation. The biomass yield per hectare and corresponding production cost, in 2010 €, were estimated at 8.55 tdry/ha/y and 68 €/tdry for poplar and 8.1 tdry/ha/y 58 €/tdry for robinia.

4.4.3 Demo Charcoal quality and carbonization yields in pilot unit

Considering the measured charcoal and biomass properties and mass yields achieved during test 11, it was possible to calculate the main performance parameters; the attained average charcoal yield (Cy) was 24.0 wt% (db), the fixed carbon yield (fCy) 20 wt%, the char carbon yield (CCy) was 42.8 wt% and the net energy conversion efficiency (ε) of 40.2 % (wb). Volume concentration of permanent gases in the pyrolysis vapours were also measured before incineration; dry pyrolysis vapor was composed of: CO2 17.4%; CO 13.3%; H2 17.8%; N2 46.3%; CH4+ 5.2% (including C2H4 and C2H6) [6].

4.4.4 Demo plant performance

Considering the demo plant, with a capacity of 250 kg/h of biomass at 15 wt% moisture content, and assuming to attain the same performance of the pilot, a production cycle of 5760 h/y (24 h a day for 5 days a week for 11 months), each unit will manufacture around 294 ton of high quality charcoal and generate around 8.4 x10^3 GJ of heat per year (either as steam or hot water); part of the heat will be used internally to dry the harvested wood chips, therefore the net heat available for the market is $3.5 \cdot 10^3$ GJ per year.

4.4.5 Land requirement for SRF plot

Considering that 90% of the harvested biomass can be used to feed the carbonization plant, the rest being leafs, branches and dust, and basing on the agronomic plot-yield data reported in section 2.6, the extent of land required for the

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[6] energy content in product gas has been estimated taking in to account permanent gas composition of test 6 and organics from Daouk experimental study performed at similar condition [44].

SRF plantation can be assessed between 159 ha and 168 ha, for poplar and robinia respectively.

4.4.6 Economic scenario

In a virtuous land management scenario, the carbonization plant of 250 kg/h has been coupled with a SRF crop to enhance viability and profitability of carbonization adoption among small and medium scale forestry industries. Investment cost (CAPEX) was estimated in 450 k€. Woodchip production via SRF was the predominant - among the others - cost component, and worth 92 k€/y for poplar and 79 k€/y for robinia, and the total annual costs, were respectively 137 k€/y and 123 k€/y. Revenue from charcoal selling on the gross market was 191 k€ and from heat selling was 58 k€/y, for a total revenue of 249 k€. Total annual value of production and payback time were respectively 94 k€ and 4.8 y for poplar and, 108 k€ and 4.2 y for robinia. Heat selling income represents 17% of total annual income and influence the investment pay-back time.

Here below are summarized in the table all the data accounted in the scenario:

Table 37. Integration of SRF with carbonization unit: economic scenario

Data			
biomass input (15% moisture)	kg/h w.b.	250	
charcoal yield	kg/h w.b.	24,1	
dry charcoal output	kg/h w.b.	51,1	
energy for drying	kWt/kg/h	1,11	
	MJ/kg dry	4,00	
operating hours	h/y	5760	
SRF net wood ratio	db	0,9	
annual dry biom. req. (1)	tdry/y	1224	
harv. annual dry wood biom. req.	tdry/y	1360	
annual char prod	t/y	294	
net thermal power recovered	kW	350	
annual energy recovered	GJ/y	7258	
total energy for drying (1) (45%-10%)	GJ/y	4891	
energy recovered - energy for drying	*GJ/y*	*2366*	
Specie		**Poplar**	**Robinia**
SRF harvesting yield	tdry/y	8,55	8,1
land required	ha	159	168
Production cost (gross cost)	€/tdry	68	58
cost of biomass (retail cost)	€/tdry	90	90
Tariffs			

charcoal price	€/kg	0,65	
specific price of heat	€/kWh	0,06	
	€/GJ/y	16,67	
labour cost	€/h	12	
labour per day	h/d	6,00	
cost of service	of CAPEX/y	4%	
cost of insurance	of CAPEX/y	2%	
CAPEX	€	450000	
Costs			
woodchip production	€/y	92480	78880
service and maintenance	€/y	18000	
insurance	€/y	9000	
labour	€/y	17280	
total costs	€/y	136760	123160
Incomes			
heat selling (total - drying)	€/y	39442	
charcoal	€/y	191302	
total income	**€/y**	**230744**	
Value of production	**€/y**	**93984**	**107584**
Gross Payback	**years**	**4,8**	**4,2**

In conclusion, a scenario in which a SRF land management scheme is coupled to a larger demo carbonization unit (250 kg/h), charcoal is sold to the market and the produced heat is partly recovered for wood drying, and partly sold to nearby plant for process demand, has been evaluated; the whole system is profitable, with short payback time (approx. 4 years) and marginal risks.

Conclusions

Charcoal making could represent a viable opportunity for forestry companies to diversify the source of income as well as to create new stable business opportunities rather than the typical decentralized power generation. Bioenergy generation for small scale application can be economically sustainable only in case economic incentives are made available, thus grid parity is unrealistic and financial capability of small scale farmers is often limited. For this reason, biomass carbonization might be as an interesting alternative to bio-power because it shifts the focus from energy to product and charcoal is a well-known product still manufactured in traditional ways.

Prerequisite conditions for successful biomass based systems in the forestry sector are: (I) system must be incentive-independent as much as possible; (II) renewable power generation – if present – should represent the co-product of a different primary production, i.e. a real additional income; (III) plant capital cost must be affordable for small scale farmers, and operation should require technical skills normally available in the forestry sector; (IV) reliability of the system must be proven and credible; (V)system must be environmentally friendly.

An innovative continuous carbonization pilot unit of 50 kg/h capacity has been designed and built addressing all constraints above mentioned and to evaluate performance of the system in view of the further upscale to 250 kg/h, as well as providing a new literature benchmarking on continuous oxidative pyrolysis vapour characterization. The proposed pilot plant leverages the simplicity and effectiveness of autothermal operations and open top, downdraft design, to bring to the small scale the performance of larger installations. In autothermal operation, heat for the process is internally provided by combusting part of the feedstock and evolved volatiles inside the reactor, the so called oxidative pyrolysis. Beyond bringing significant simplification in the process layout, autothermal operation also allows for process intensification in biomass pyrolysis.

An extensive test campaign comprising 13 tests for a total of 65 h was carried out on the pilot unit to validate its functioning, reliability and performances. In test 4 and 6, reported in chapter 2, was proved the effective functioning of the system and preliminary results showing that high fixed carbon yields were achieved with reactor properly working. Some technical improvements on the pilot unit were also proposed and realized to overcome bridging and ejector clogging issues.

Two tests were taken in to account to characterize in detail the entire process. Those tests, reported in chapter three, achieved important result in benchmarking biomass carbonization in downdraft fixed bed reactor, verifying and confirming already existing literature results and providing also a full and detailed characterization of whole process and by-products.

Two different types of woodchips, large (test 11 - mixture) and small (test 12 - chestnut), were tested in a long run (approx. 8 h) with good performance stability and reliability of pilot unit and significative feedbacks in view of the further upscale to an industrial carbonization demo unit of 250 kg/h.

Reactor temperatures were in the range of 500-650°C, higher for test 11 due to higher gas flow rate regulation to overcome problem of ejector clogging. Large woodchip retained a char carbon yield (dry) of 24 %wt, higher than small woodchip 22,4 %wt, and in general comparable with the most advanced industrial carbonization plant such as Lambiotte. Superficial velocity was around 0,1 – 0,2 m/s and reactor pressure drop was <0,1 mbar for both tests. In biomass carbonization is traditionally necessary long residence time (from several hours up to days), instead the calculated travelling time of char samples within the whole pilot unit was around 5 -6 hours, and 3 hours in reactor only, meaning that is possible to manufacture high quality charcoal with short times. Fixed carbon content achieved (80-90%) is largely higher than the average considered for commercial charcoal (around 75%).Obtained charcoal can be suitable for biochar and industrial applications, such as metallurgy or activated carbon manufacturing.

Permanent gas composition in pyrolysis vapour were rich in CO (>15%), H2 (>10%) and hydrocarbons CH4+ (>8%) which held an important energy content to be recovered throughout downstream combustion, as well as to incinerate harmful pollutants before being discharged in atmosphere.

Test 12 characterized also pollutant emissions and vapour phase of pyrolysis gas by means of tar sampling. CO and NO emissions were extremely low (<100 ppm) after incineration with reactor working at steady state condition. CO concentration was strictly dependant on temperature at stack and reactor stability in consequence.

Tar sampling results displayed that process water mass fraction in condensate was 78%wt and that 47%wt organic compounds were identified as mostly: Phenols, Aromatics and Acetic Acid. This achievement was perfectly in compliance with Daouk's result which adopted a lab scale of ten time less capacity (36,5 kg/h db instead of 3,34 kg/h dry) and while Equivalent Ratio were almost the same: 0,15 for Re-Cord and 0,13 Daouk et al..

The Mass balance for small woodchip (test 12) showed that considering 100% of dry biomass input, permanent dry gases were the major part of output (74%), water and char were both around 20% and organics 6%. Regarding energy balance, thermal power input due to biomass was 190 kW, of which 35,7% was retained in cold charcoal and 51% in hot pyrogas, making available to be recovered at stack more than 100 kW. Despite mass and energy balance for large woodchip (test 11) was based on some assumptions due to lack of reliable data on gas analysis and unavailability of tar sampling, cold charcoal retained the same energy of pyrogas (approx. 44%) owing to more char yield was achieved.

Following work on pyrogas combustion, based on test 12 characterization, put the basis to approach design of combustion chamber and of the entire gas line for a carbonization demo unit of 250 kg/h. Pyrogas combustion, as well as VOCs incineration, were investigated to meet low emissions requirements in accordance with TLV prescribed by Italian regulation. Gas mixture to burn (394 kg/h) was characterized by a valuable LHV of 5,3 MJ/kg, owing to tars and higher than dry product gas of downdraft gasifiers, a low stoichiometric air fuel ratio (α) of 1,61, and specific heat of 1,57 kJ/kgK at 500°C. Taking in to account Destruction Removal Efficiency method were calculated residence time and destruction temperature for each specie and were respectively 961°C and 1,0 s which represent a feasible target for an industrial process. Other parameters such as, density, explosion limits, limit oxygen concentration and adiabatic flame temperature were also investigated. Proposed combustion chamber was rated for 657 kWt and had an internal volume of 2 m^3. Reactor was upscaled maintaining the same SV ratio, limiting the height and cost of the system owing to temperature control into the reactor is less challenging than in gasification.

For the 250 kg/h demo plant a new advanced gas line comprised: a cyclone, a complete combustion chamber with burner and heat exchanger (three pass fire tube boiler), a bag house filter, an inverter driven blower and a composite stack. Considering to recover heat by means of hot water for feeding a woodchip drier, its capacity is 423 kg/h, larger than the quantity necessary to feed the carbonizer itself. P&iD and 3D layout were also proposed. Target price for this industrial carbonization unit has been estimated around 400-450 k€.

A scenario in which a SRF land management scheme is coupled to a larger demo carbonization unit (250 kg/h), charcoal is sold to the market and the produced heat is partly recovered for wood drying, and partly sold to nearby plant for process demand, has been evaluated; the whole system is profitable, with short payback time (approx. 4 years) and marginal risks.

In conclusion, the autothermal continuous process of Re-Cord reactor demonstrated to be able to produce top quality charcoal, with a very high fixed charcoal yield and relative low solid retention time, as well as provided a new benchmark for biomass carbonization in downdraft reactor at pre-industrial scale.

The manufactured product can be used for various purposes, such as metallurgy, complies with standard EN 1860-2 for BBQ lump charcoal and therefore can be sold on the market for barbequing applications and activated carbon manufacturing, but also biochar production for carbon sequestration can be considered as a viable product destination.

The scale of operation makes the process technically and economically viable for the small to medium sized SME operating in the forestry sector, that could locally exploit the potential of this technology to add value to their main business. The process brings significant advantages toward competing alternatives, that are operated batch-wise, in particular with respect to energy recovery, evenness of product quality and gaseous pollutant emission.

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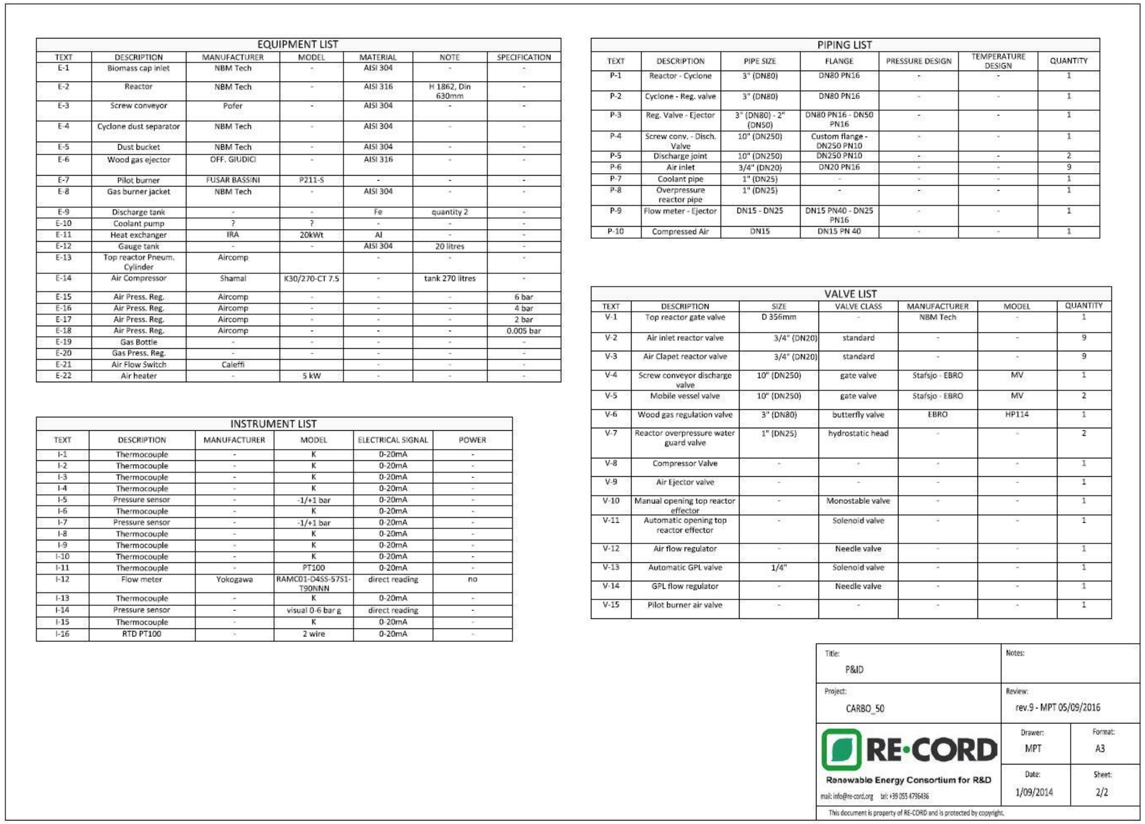
Appendix A: CarbON pilot unit - Piping & Instrumentation Diagram



EQUIPMENT LIST

TEXT	DESCRIPTION	MANUFACTURER	MODEL	MATERIAL	NOTE	SPECIFICATION
E-1	Biomass cap inlet	NBM Tech	-	AISI 304	-	-
E-2	Reactor	NBM Tech	-	AISI 316	H 1862, Din 630mm	-
E-3	Screw conveyor	Pofer	-	AISI 304	-	-
E-4	Cyclone dust separator	NBM Tech	-	AISI 304	-	-
E-5	Dust bucket	NBM Tech	-	AISI 304	-	-
E-6	Wood gas ejector	OFF. GIUDICI	-	AISI 316	-	-
E-7	Pilot burner	FUSAR BASSINI	P211-S	-	-	-
E-8	Gas burner jacket	NBM Tech	-	AISI 304	-	-
E-9	Discharge tank	-	-	Fe	quantity 2	-
E-10	Coolant pump	?	?	-	-	-
E-11	Heat exchanger	IRA	20kWt	Al	-	-
E-12	Gauge tank	-	-	AISI 304	20 litres	-
E-13	Top reactor Pneum. Cylinder	Aircomp		-	-	-
E-14	Air Compressor	Shamal	K30/270-CT 7.5	-	tank 270 litres	-
E-15	Air Press. Reg.	Aircomp	-	-	-	6 bar
E-16	Air Press. Reg.	Aircomp	-	-	-	4 bar
E-17	Air Press. Reg.	Aircomp	-	-	-	2 bar
E-18	Air Press. Reg.	Aircomp	-	-	-	0.005 bar
E-19	Gas Bottle	-	-	-	-	-
E-20	Gas Press. Reg.	-	-	-	-	-
E-21	Air Flow Switch	Caleffi		-	-	-
E-22	Air heater	-	5 kW	-	-	-

INSTRUMENT LIST

TEXT	DESCRIPTION	MANUFACTURER	MODEL	ELECTRICAL SIGNAL	POWER
I-1	Thermocouple	-	K	0-20mA	-
I-2	Thermocouple	-	K	0-20mA	-
I-3	Thermocouple	-	K	0-20mA	-
I-4	Thermocouple	-	K	0-20mA	-
I-5	Pressure sensor	-	-1/+1 bar	0-20mA	-
I-6	Thermocouple	-	K	0-20mA	-
I-7	Pressure sensor	-	-1/+1 bar	0-20mA	-
I-8	Thermocouple	-	K	0-20mA	-
I-9	Thermocouple	-	K	0-20mA	-
I-10	Thermocouple	-	K	0-20mA	-
I-11	Thermocouple	-	PT100	0-20mA	-
I-12	Flow meter	Yokogawa	RAMC01-D4SS-57S1-T90NNN	direct reading	no
I-13	Thermocouple	-	K	0-20mA	-
I-14	Pressure sensor	-	visual 0-6 bar g	direct reading	-
I-15	Thermocouple	-	K	0-20mA	-
I-16	RTD PT100	-	2 wire	0-20mA	-

PIPING LIST

TEXT	DESCRIPTION	PIPE SIZE	FLANGE	PRESSURE DESIGN	TEMPERATURE DESIGN	QUANTITY
P-1	Reactor - Cyclone	3" (DN80)	DN80 PN16	-	-	1
P-2	Cyclone - Reg. valve	3" (DN80)	DN80 PN16	-	-	1
P-3	Reg. Valve - Ejector	3" (DN80) - 2" (DN50)	DN80 PN16 - DN50 PN16	-	-	1
P-4	Screw conv. - Disch. Valve	10" (DN250)	Custom flange - DN250 PN10	-	-	1
P-5	Discharge joint	10" (DN250)	DN250 PN10	-	-	2
P-6	Air inlet	3/4" (DN20)	DN20 PN16	-	-	9
P-7	Coolant pipe	1" (DN25)	-	-	-	1
P-8	Overpressure reactor pipe	1" (DN25)	-	-	-	1
P-9	Flow meter - Ejector	DN15 - DN25	DN15 PN40 - DN25 PN16	-	-	1
P-10	Compressed Air	DN15	DN15 PN 40	-	-	1

VALVE LIST

TEXT	DESCRIPTION	SIZE	VALVE CLASS	MANUFACTURER	MODEL	QUANTITY
V-1	Top reactor gate valve	D 356mm	-	NBM Tech	-	1
V-2	Air inlet reactor valve	3/4" (DN20)	standard	-	-	9
V-3	Air Clapet reactor valve	3/4" (DN20)	standard	-	-	9
V-4	Screw conveyor discharge valve	10" (DN250)	gate valve	Stafsjo - EBRO	MV	1
V-5	Mobile vessel valve	10" (DN250)	gate valve	Stafsjo - EBRO	MV	2
V-6	Wood gas regulation valve	3" (DN80)	butterfly valve	EBRO	HP114	1
V-7	Reactor overpressure water guard valve	1" (DN25)	hydrostatic head	-	-	2
V-8	Compressor Valve	-	-	-	-	1
V-9	Air Ejector valve	-	-	-	-	1
V-10	Manual opening top reactor effector	-	Monostable valve	-	-	1
V-11	Automatic opening top reactor effector	-	Solenoid valve	-	-	1
V-12	Air flow regulator	-	Needle valve	-	-	1
V-13	Automatic GPL valve	1/4"	Solenoid valve	-	-	1
V-14	GPL flow regulator	-	Needle valve	-	-	1
V-15	Pilot burner air valve	-	-	-	-	1

Title: P&ID
Notes:
Project: CARBO_50
Review: rev.9 - MPT 05/09/2016
RE·CORD
Renewable Energy Consortium for R&D
mail: info@re-cord.org tel: +39 055 4796436
Drawer: MPT
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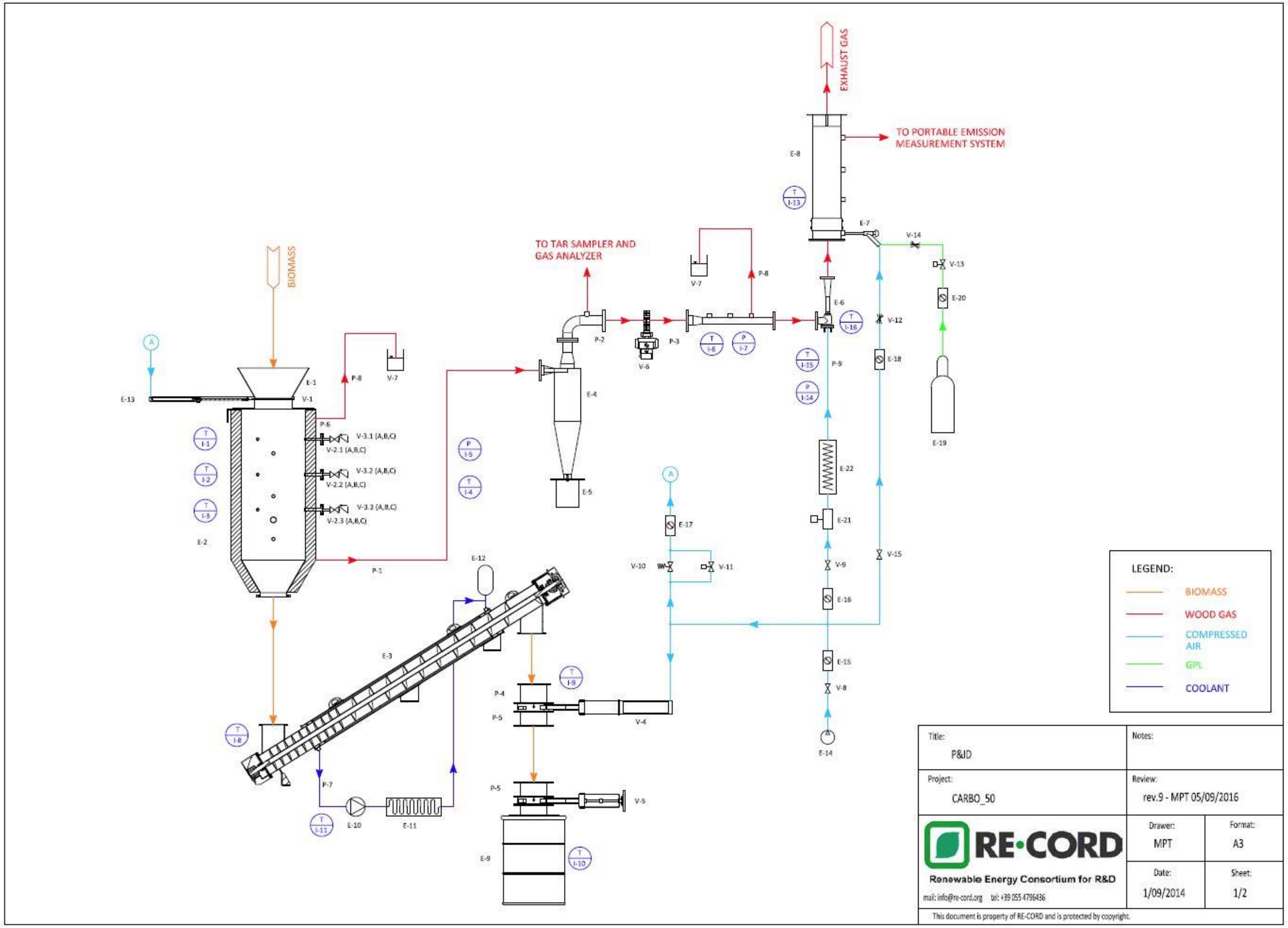
Date: 1/09/2014
Sheet: 2/2


EXHAUST GAS
TO PORTABLE EMISSION MEASUREMENT SYSTEM
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BIOMASS
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A
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BIOMASS
WOOD GAS
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GPL
COOLANT
Title:
P&ID
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Project:
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rev.9 - MPT 05/09/2016
RE·CORD
Renewable Energy Consortium for R&D
mail: info@re-cord.org tel: +39 055 4796436
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Appendix B: Charcoal and biochar standards

In the following tables are recapped the standards reference for BBQ charcoal (Table 38) and biochar (Table 39). A comparison between the existing standards methods and those adopted by Re-Cord is also present in the tables.

Standard EN 1860-2 [56] prescribed characteristics that a good charcoal for BBQ should have in terms of: calorific value, Fixed Carbon content, Ash, bulk density, moisture, volatiles and granulation. In the standard are mentioned also qualities for briquettes charcoal, but these are not listed in the table.

For biochar application, more parameters have been addressed by EBC and IBI [63,64]. In the table are listed existing methods and criteria and compared with those available in Re-Cord lab and performed during this study.

Table 38. Standards for charcoal application as fuel BBQ

Standards for Charcoal application as fuel for BBQ			
	EN 1860-2:2005 ***Charcoal for BBQ***		**Anallysed By Re-Cord**
Parameter	**Method**	**Criteria**	**Method**
Lower Calorific Value	EN 14918:2009. Processed in calorimeter for combustion at 400 psi for HHV determination. LHV is calculated as HHV-0,0212H-0,245M	Declaration	Same method used
Fixed Carbon C.	EN1860-2:2005 Mathematically calculated by the equation. $C(fix) = 100 - (F + A)$. F is the volatile matter content Wt. Db. (A): ash as a percentage by weight of water free material (WF)	At least 75% by mass	Same method used
Ash	EN1860-2:2005. Heated in air at a specified rate up to a temperature of (710 ± 10)° C and maintained at this temperature until constant in mass.	not exceed 8%	Same method used
Total moisture	EN14774-2:2009. Heated in air at 105°C - 110°C and maintained at this temperature until constant mass is obtained.	not exceed 8%	Same method used
Granulation	EN 15149-1:2010. Sieved with round test sieves with a hole diameter of 150 mm, 80 mm, 20 mm and 10 mm, in accordance with ISO 1953.	0 -150 mm No more than 10% > 80 mm in size. 80% shall > than 20 mm.	Same method used
Volatiles	EN 15148:2009. the sample is heated at 900° C out of contact with air for 7 min.	no limits are set	Same method used
Bulk density	EN15103:2009. Weighing a measuring container of 50 l (D 360 mm, H 491 mm) or 5 l (D 167 mm, H 228 mm) D/L=0,73	at least 130 kg/m3	internal: Weighing Cyinder of 4 l (D 170mm, H 172 mm).

Table 39. Standards for charcoal application as a soil improver

Standards for charcoal application as soil improver					
	EBC (2012) *Biochar*		IBI (2012) *Biochar*		Anallysed By Re-Cord
Parameter	**Method**	**Criteria**	**Method**	**Criteria**	**Method**
Carbon Content	Total C, H, N analysis by dry combustion IR detection (DIN 51732, ISO 29541). Inorganic C analysis by determination of carbonate-C content with HCl, as outlined in DIN 51726, ISO 925	Biochar ≥ 50% Bio Carbon Minerals (BCM) < 50% (% of total mass, dry basis)	Total C and H analysis by dry combustionIR detection. Inorganic C analysis by determination of CO2-C content with 1N HCl, as outlined in ASTM D4373	10% Minimum Class 1: ≥60% Class 2: ≥30% and	EN 15104:2011 (only total C, not organic)
Molar H/Corg ratio	See C	0.7 max. (molar ratio)	See C	0.7 maximum (molar ratio)	N/A
Molar O/Corg ratio	O calculated from ash content, C, H, N, S (DIN 51733, ISO 17247)	0.4 max.	N/A	N/A	N/A
Nutrients (N)	Dry combustion-IR detection following the same procedure for total C and H (DIN 51732)	Declaration required	Dry combustion-IR detection following the same procedure for total C and H	Declaration required	EN 15104:2011
Nutrients (P,K,Mg,Ca)	Digestion with Lithium metaborate on ash 550 °C according to DIN 51729-11 and determination with ICP-OES according to DIN EN ISO 11885 or ICP-MS according to DIN EN ISO 17294	Declaration	Digestion with Lithium metaborate on ash 550 °C according to DIN 51729-11 and determination with ICP-OES according to DIN EN ISO 11885 or ICP-MS according to DIN EN ISO 17294	Declaration Optional P,K	UNI EN 15290
PAH content	DIN ISO 13877 Soxhlet-extraction with toluene and determination with HPLC DIN CEN/TS 16181 Soxhlet-extraction with toluene und determination with GC-MS	Basic grade: < 12mg kg-1 Premium grade < 4mg kg-1 total (sum of 16 US EPA PAHs)	US EPA 8270 Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) using Soxhlet extraction (US EPA 3540) and 100% toluene as the extracting solvent	6 – 300 mg kg-1 total (sum of 16 US EPA PAHs) AND 3 mg kg-1 B(a)P-TEQ B(a)P Toxic Equivalency (TEQ) basis	DIN CEN/TS 16181 Soxhlet-extraction with toluene and HPLC
pH	DIN ISO 10390 with 1:5 biochar to 0.01 M CaCl2-solution, 60 min shaking, measuring directly in the suspension	Declaration (pH) If > 10, the delivery slip must feature appropriate handling information	US Composting Council TMECC Section 04.11, modified dilution of 1:20 biochar, according to Rajkovich et al (2011).	Declaration (pH)	N/A
Surface Area	milled < 50µm, 2h outgassing at 150°C, vacuum, N2 adsorption, multi-point BET method	Declaration (preferably higher Area by Nitrogen Adsorption' than 150 m2 g-1)	ASTM D6556 'Standard Test Method for Carbon Black – Total and External Surface Declaration (preferably higher Area by Nitrogen Adsorption'	Declaration (m2 g-1) Optional	ISO 9277 (multi point BET method)
PCDDs	Soxhlet-extraction with toluene and determination with HRGC-HRMS based on US EPA 8290 (2007-02)	<20 ng kg-1 I-TEQ	US EPA 8290 Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)	<17 ng kg-1 WHO-TEQ	N/A
Heavy Metals	All metals: microwave acid digestion with HF/HNO3 and determination of the metals with ICP-MS (DIN EN ISO 17294-2)	Required Metals: Pb, Cd, Cu, Ni, Hg, Zn, Cr	All elements except Hg and Cl: i. Microwave-assisted HNO3 digestion, or ii. HNO3 digestion, followed by determination with iii. ICP-AES, or iv. Flame AAS	Required Metals: Pb, Cd, Cu, Ni, Hg, Zn, Cr, Co, Mo Metalloids: B, As, Se, Others: Cl, Na	UNI EN 15297
PCBs	Soxhlet-extraction with toluene and determination with HRGC-HRMS based on US EPA 8290 (2007-02)	< 0.2mg kg-1	Analysis by GC or US EPA 8275 Semivolatile Organic Compounds (PAHs and PCBs) in Soils/Sludges and Solid Wastes Using Thermal Extraction/Gas	0.2 – 0.5 mg kg-1	N/A