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Development of a thermochemical/biological process to convert waste biomass into new resources

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Biocarburanti e Bioraffinerie

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CHAPTER 1: INTRODUCTION

This work started on March 16th 2017, at the laboratories of analytical chemistry, the thesis deals with a thermo-chemical/biological process divided into two phases, in the thermochemical phase the biomass is pyrolysed thus obtaining pyrolysis products (solids, liquids and gasses) that will subsequently be used in the biological phase as "food" for methanogenic bacteria, capable of converting prospects into a rich methane gas (biomethane).

GLOBAL WARMING AND GREENHOUSE EFFECT

Global warming, also referred to as climate change, is the observed century-scale rise in the average temperature of the Earth's climate system and its related effects. Multiple lines of scientific evidence show that the climate system is warming (Hartmann D., et al. 2013). Many of the observed changes since the 1950s are unprecedented in the instrumental temperature record which extends back to the mid-19th century, and in paleoclimate proxy records covering thousands of years.

In 2013, the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report concluded that "It is extremely likely that human influence has been the dominant cause of the observed warming since the mid-20th century." The largest human influence has been the emission of greenhouse gases such as carbon dioxide, methane and nitrous oxide. Climate model projections summarized in the report indicated that during the 21st century, the global surface temperature is likely to rise a further 0.3 to 1.7 °C in the lowest emission scenario, and 2.6 to 4.8 °C in the highest emission scenario.

Future climate change and associated impacts will differ from region to region. Anticipated effects include increasing global temperatures, rising sea levels, changing precipitation regime, and expansion of deserts in the subtropical regions. Warming is expected to be greater over land than over the oceans and greatest in the Arctic, with the continuing retreat of glaciers, permafrost and sea ice. Other likely changes include more frequent extreme weather events such as heat waves, droughts, heavy rainfall with floods and heavy snowfall, ocean acidification and species extinctions due to shifting temperature regimes. Significant effects to humans include the threat to food security from decreasing crop yields and the abandonment of populated areas due to rising sea levels. Because the climate system has a large "inertia" and greenhouse gases will remain in the

atmosphere for a long time, many of these effects will persist for not only decades or centuries, but for tens of thousands of years to come (Peter U., et al. 2016).

The greenhouse effect is the process by which absorption and emission of infrared radiation by gases in a planet's atmosphere warm its lower atmosphere and surface. On Earth, an atmosphere containing naturally occurring amounts of greenhouse gases causes air temperature near the surface to be about 33 °C warmer than it would be in their absence. Without the Earth's atmosphere, the Earth's average temperature would be well below the freezing temperature of water. The major greenhouse gases are water vapor, which causes about 36–70% of the greenhouse effect; carbon dioxide (CO_2), which causes 9–26%; methane (CH_4), which causes 4–9%; and ozone (O_3), which causes 3–7%. Clouds also affect the radiation balance through cloud forcing similar to greenhouse gases.

Human activity since the Industrial Revolution has increased the amount of greenhouse gases in the atmosphere, leading to increased radioactive forcing from CO_2, methane, tropospheric ozone, chlorofluorocarbon (CFCs) and nitrous oxide. The concentrations of CO_2 and methane had increased by 36% and 148%, respectively, since 1750 (EPA, 2007). These levels are much higher than at any time during the last 800,000 years, the period for which reliable data has been extracted from ice cores. Less direct geological evidence indicates that CO_2 values higher than this were last seen about 20 million years ago.

Fossil fuel burning has produced about 3/4 of the increase in CO_2 from human activity over the past 20 years. The rest of this increase is caused mostly by changes in land-use, particularly deforestation. Coal burning was responsible for 43% of the total emissions, oil 34%, gas 18%, cement 4.9% and gas flaring 0.7% (Le Quéré C., et al. 2012).

In May 2013, it was reported that readings for CO_2 taken at the world's primary benchmark site in Mauna Loa surpassed 400 ppm. The first time CO_2 levels have been this high for about 4.5 million years. Monthly global CO_2 concentrations exceeded 400 ppm in March 2015, probably for the first time in several million years. On 12 November 2015, NASA scientists reported that human-made CO_2 continues to increase above levels not seen in hundreds of thousands of years; currently, about half of the CO_2 released from the burning of fossil fuels is not absorbed by vegetation and the oceans and remains in the atmosphere.

Over the last three decades of the twentieth century, gross domestic product per capita and population growth were the main drivers of increases in greenhouse gas emissions. CO_2 emissions are continuing to rise due to the burning of fossil fuels and land-use change (World Bank, 2010).

RENEWABLE ENERGY - BIOMASS

To achieve a sustainable development model, it is essential to replace non-renewable resources with renewable resources, which are evenly distributed on the planet and allow CO_2 emissions to be reduced.

By using renewable energy resources, such as solar energy, wind energy and biomass, whose exploitation is not associated with CO_2 emissions, most of man's energy needs can be met.

The use of biomass, for example, can make a valuable contribution to the energy sector, guaranteeing much lower effects in terms of GHGs gas emissions (Goyal et al., 2006). Biomass is a sophisticated form of solar energy storage: plants convert solar energy through the photosynthesis process, with an average yield of 0.1%, accumulating it permanently in leaves, stems and flowers. Among renewable energies, biomass is the only one that can be converted into solid fuels (for example wood, pellets, wood chips, charcoal), in liquid fuels (bioethanol, biodiesel, bio-oil), gaseous fuels (biogas, synthesis gas, hydrogen). Additionally, biomass can be also converted into materials and chemical compounds, becoming an ideal input for a multi-outputs biorefinery.

Plants are the most common form of biomass. They have been used in the form of wood, peat and straw for millions of years, until they have been supplanted by the use of fossil fuels considered for years "clean" energy sources. In the preindustrial society, biomass was the dominant source of energy. Today it is estimated that, in developing countries, biomass contributes to meet 33% of primary energy needs while in industrialized countries only 3%.

A careful exploitation of biomass can be an excellent source of energy. Plants can be grown directly for energy production or harvested in the natural environment. In general, plants capable of reproducing in a short time are chosen, both trees (pines, poplars, eucalyptus trees) and annual low-stem plants (sugar cane, corn, soybeans). The researchers are oriented towards the optimization of the energy potential of the plants, going to identify the crop species characterized by a high rate of photosynthetic efficiency and a limited need for agronomic practices such as soil tillage, fertilization, irrigation.

However, the main drawback is connected to the land use competition for food production. Indeed, an intensive production of energy from biomass needs great quantity of arable land shifting the land use away from food to agro-energy (Rathmann R., et al 2010). For this reason, European Commission issued Directive 2015/1513/EC promoting energy recovery from lignocellulosic residues and bio-wastes.

In addition, poorer quality lands and marginal lands could be utilized, but keeping in mind that any crop grown without adequate water and nutrient replenishment cannot maintain high oil yields over the longer term (Sims R. E., et al 2010).

BIOMASS CONSTITUENTS

The terrestrial vegetable biomass is mainly constituted by cellulose, hemicellulose and lignin with small quantities of inorganic materials. These constituents can vary considerably depending on the type of biomass.

Cellulose is a non-branched linear homopolysaccharide formed by the repetition of glucose units bound through B (1-4) glycosidic bonds that allow the cellulose to form sufficiently large and linear molecules that can give rise to highly ordered and crystalline areas (figure 1.1).

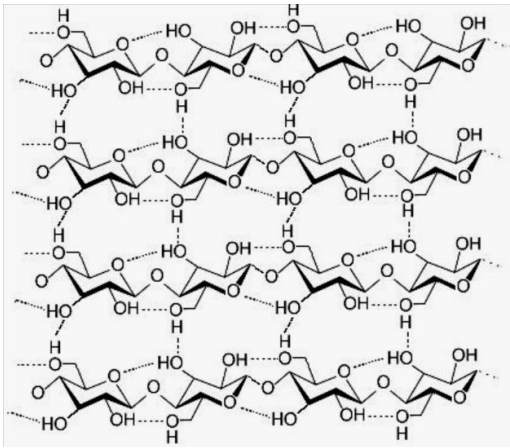


Figure 1.1: cellulose structure (source:www.chemistry.gcsu.edu).

A cellulose chain contains about 10,000 glucose units with an approximate molecular weight of 1.5-2 million u.m.a.

The hemicellulose consists instead of a large number of hetero polysaccharides (figure 1.2) hexose (D-glucose, D-mannose, D-galactose) and pentose (D-xylose, L-arabinose and D-arabinose).

It's a branched polymer consisting of about 50-200 monosaccharides and has a mostly amorphous structure. Because of their amorphous structure, the hemicelluloses have a remarkable ability to absorb water.

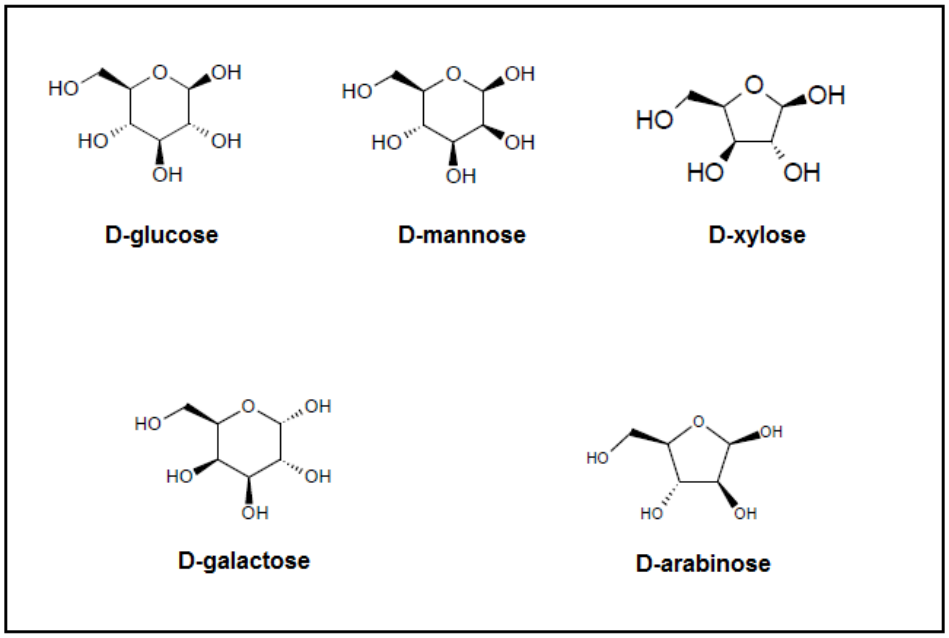


Figure 1.2: the main monomers constituting the hemicellulose

Finally, lignin is the third component and constitutes 16-33% by weight of dry mass. It is found in all plants in the walls and provides a mechanical support to the cellulose to which it is linked by covalent bonds or hydrogen bridges. It's the largest fraction of non-carbohydrate origin constituting the lignocellulosic materials and it has an amorphous structure that leads to a large number of possible interconnections between the individual units (Sjostrom, 1993).

It's a three-dimensional macromolecule composed of phenylpropanoid units and more precisely of phenolic, guaiacyl (2-methoxy-phenolic) and syringylic (2,6-dimethoxyphenolic) units (figure 1.3).

These phenylpropane molecules derive directly from three cinnamyl alcohols: 4-hydroxycinnamyl alcohol, coniferyl alcohol and synapyl alcohol (Figure 1.4).

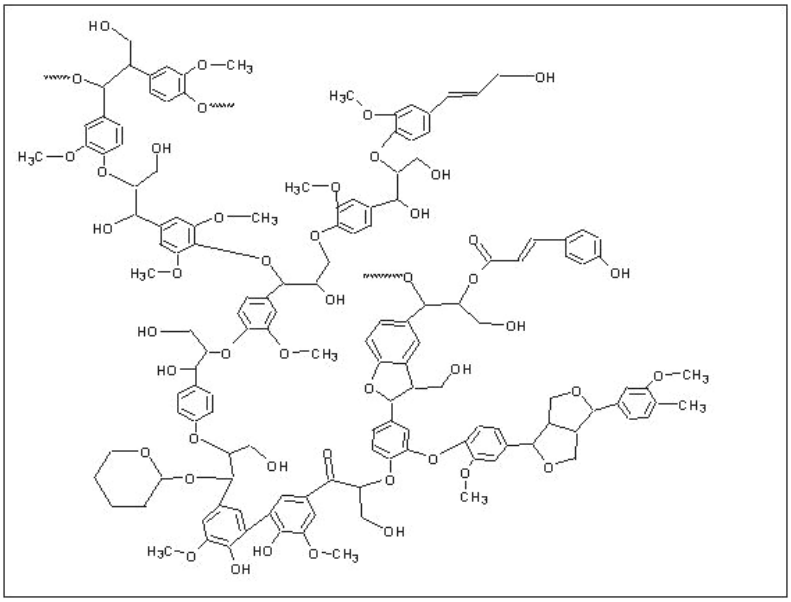


Figure 1.3: hypothetical lignin structure (source: http//academic.uofs.edu)

The structure of lignin can vary between different plant species and is strongly linked to the taxonomy of the plant. The lignin of gymnosperms (lignin G), in particular that of conifers, is composed only of guaiacyl units (2-methoxyphenol and derivatives). Within the angiosperm family, on the other hand, there are monocotyledons consisting of a lignin containing guaiacol and hydroxybenzene (lignin HG) units; dicotyledonous also contain the units of syringol (HGS lignin) (Das L. et al., 2016).

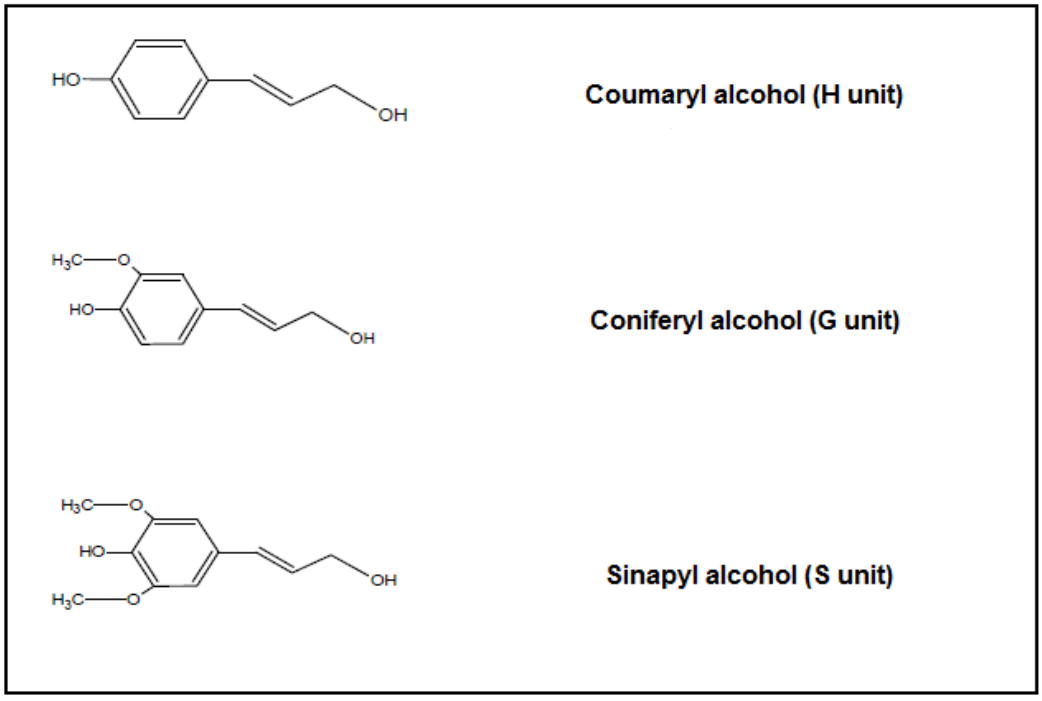


Figure 1.4: monolignol alcohols.

Cellulose, hemicellulose and lignin have a different behavior related to thermal degradation that depends on the heating rate. The main pyrolytic processes of cellulose are: the elimination of water that occurs at low temperatures (200-220 °C) with the formation of double bonds (fig 1.5). The elimination usually takes place in 2-3 position on the glucose monomer, and the hydroxyl in position 2 or 3 can be eliminated.

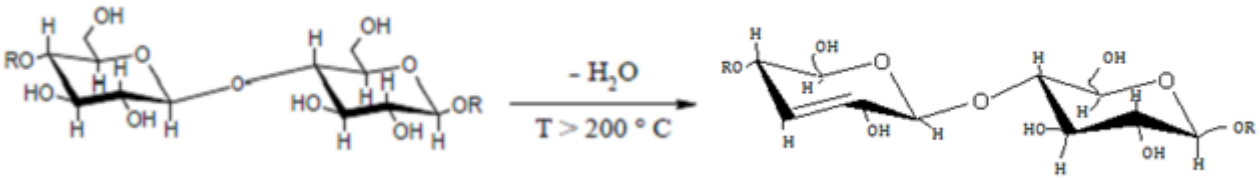


Figure 1.5: elimination of water in the pyrolytic process of cellulose. (Moldovenau, 1998).

At higher temperatures (350-500°C) other reactions start: cleavage reactions leading to depolymerization processes by transglycosidation leading to the formation of smaller molecules including the levoglucosan, the main cellulose pyrolysis product (figure 1.6).

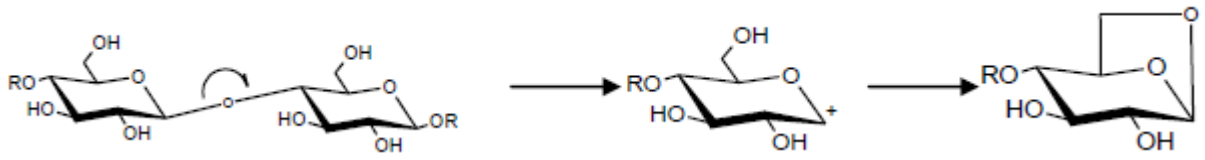


Figure 1.6: depolymerization of the cellulose chain with formation of levoglucosan (moldovenau, 1998).

Finally there are a series of retro-aldol reactions that cause the rupture inside the monomer with the formation of smaller fragments (figure 1.7).

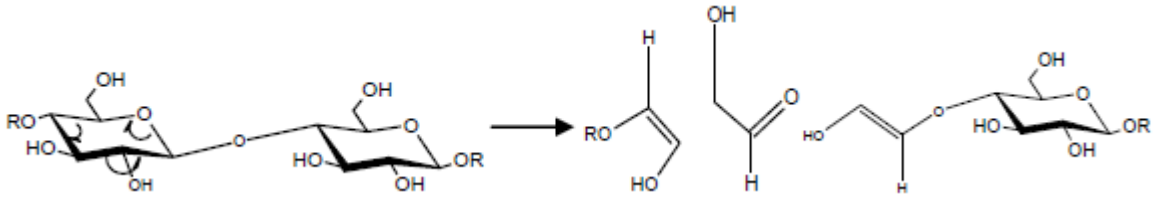


Figure 1.7: chain splitting with retro aldol reactions and minor fragments (moldovenau, 1998).

The hemicellulose begins to break down thermally at lower temperatures than cellulose, moreover there is less information on the degradation processes. This has led many authors to consider the degrading process of cellulose and hemicellulose the same, considering them in a single general

structure called "holocellulose". Finally at higher temperatures the fragmentation of the polyphenolic lignin structure takes place, leading to the formation of phenols, catechols, guaiacoles and syringes.

Based on data from Yang et al. 2007 (figure 1.8) shows the dependence on the temperature of the decomposition of cellulose, hemicellulose and lignin by thermo gravimetric analysis (TGA) carried out with a thermal gradient of 10 ° C min^{-1} and under the flow of N_2.

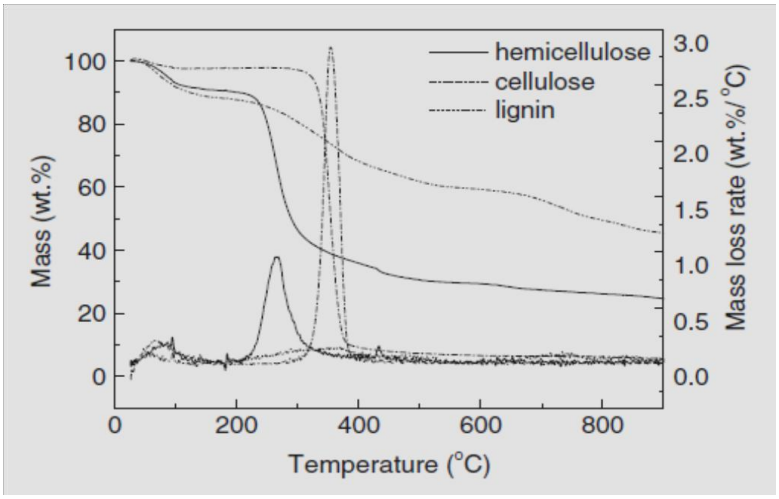


Figure 1.8: Decomposition of cellulose wood components by TGA (adapted from Yang et al., 2007).

Hemicellulose is the first component to decompose, starting at about 220°C and completing the decomposition process at 315°C.

The cellulose does not start to decompose before reaching the temperature of 315°C ending at 400°C.

Lignin begins to degrade at 160°C but is a very slow and constant process that extends up to 900°C. Lignin, therefore, is more difficult to dehydrate than cellulose and hemicellulose. At the same temperature the weight loss of lignin is typically less than half of the cellulose.

PYROLYSIS

Pyrolysis is a process of thermochemical decomposition in an inert atmosphere (without the presence of oxygen) that allows the conversion of an organic material in three products: a solid rich in carbon (char), a liquid fraction (bio-oil) and a mixture of gas (syngas).
Pyrolysis of biomass starts at 350–550 °C and goes up to 700 °C. Different condition leads to formation of products in different proportions.

PYROLYSIS PROCESS TYPES

- Slow pyrolysis: characterized by very low biomass heating rates, with reaction temperatures that are also quite low (200 - 350 °C), and with very long residence times. This particular type of pyrolysis can be used to produce high amounts of char (over 30%).

- Intermediate pyrolysis: which can be achieved by means of moderate heating rates (about 20°C/s) and equally moderate reaction temperatures (less than 600°C), with residence times varying from 10s to 10 min. This second type of pyrolysis gives rise to comparable quantities of char, gas and liquid.

- Fast pyrolysis: characterized by very high heating rates (of the order of 100°C/s), which can be reached by means of a very fine particle feed, it uses very short residence times of the gas phase (< 2 s), and produces very low yields in char.

The yields of gas, liquid and char depend, as well as on the type of biomass, on the residence time and the temperature inside the reactor (Di Blasi et al., 1999; Di Blasi et al., 2001). There are quantitative differences in the yield of the products from different modes of pyrolysis, showing the considerable flexibility achievable by changing process conditions (table 1.1). The observed differences suggest that residence time affects the development of secondary reactions that lead to a decrease in the yield of liquid in favor of the formation of volatiles and char.

Regarding the temperature dependence, the liquid yield shows a non-monotonous trend characterized by the presence of a maximum of around 500 - 600°C. The liquid consists of an organic fraction and water; the yield of the organic fraction reaches a maximum of about 450°C (Aguado et al., 2000). The solid residue, on the other hand, decreases rapidly to reach a value that remains constant at high temperatures. An increase in pyrolysis temperature leads to an increase in

the content of fixed carbon and ash and a decrease in volatile matter in the solid residue (Encinar et al., 1996).

Finally, the yield of the gaseous phase tends to increase with temperature. This trend depends on the fact that initially there is a certain competition between the reactions of charring and those of devolatilization that take the upper hand at high temperature. It follows that the yields in liquid and gas increase with temperature, while that in char decreases. At temperatures close to 500°C, secondary degradation reactions of tar vapors with the production of gaseous species begin.

Table 1.1: Typical product weight yields (dry wood basis) obtained by different modes of pyrolysis of wood (A.V. Bridgwater).

Mode	Conditions	Liquid	Solid	Gas
Fast	~ 500 °C, short hot vapour residence time ~1 s	75%	12%	13%
Intermediate	~ 500 °C, hot vapour residence time ~ 10 - 30 s	50% in 2 phases	25%	25%
Carbonisation (slow)	~ 400 °C, long vapour residence hours → days	30%	35%	35%
Gasification	~ 750 - 900 °C	5%	10%	85%
Torrefaction (slow)	~ 290 °C, solids residence time ~ 10 - 60 min	0% unless condensed, then up to 5%	80%	20%

PYROLYSIS PRODUCTS

BIOCHAR

The term "biochar" refers to a material rich in carbon obtained from the "combustion" of biomass in an environment free of oxygen (pyrolysis) that can be applied both for agronomic and environmental management purposes (Lehmann, 2006). The benefits associated with biochar are manifold. In particular, when applied to soils, biochar is a powerful soil improver. In fact, its high porosity increases the water retention and that of the nutritive elements, which remain thus longer available for the plants; also improves the structure of the soil and its mechanical properties (Chan et al., 2007). Many studies have already shown the positive impact of applying biochar on agricultural yields. In fact, it determines the reduction in water and fertilizer requirements (Lehmann et al., 2003; Yamato et al., 2006; Chan et al., 2007; Rondon et al., 2007; Baronti et al., 2010; Vaccari et al., 2011) thus allowing the reduction of the use of synthetic high-intensity chemicals. Another potential of biochar is represented by climate change mitigation. In fact, the compact structure of the biochar allows this product not to be degraded by soil microorganisms and

therefore to store carbon instead of returning it to the atmosphere in the form of CO_2 (Sohi et al., 2009).

On the other hand, in literature there are some studies (Garcia-Perez M. et al., 2008) on the potential development of dangerous toxic substances in biochar as a result of the biomass pyrolysis process and the potential impact of these products on the environment. In particular, the possible formation was studied, during the pyrolysis, of polychlorinated dibenzofurans (PCDFs), polychlorodibenzo-p-dioxins (PCDDs) and polycyclic aromatic hydrocarbons (PAHs), and it was concluded that their presence is not found in biochar produced by fast pyrolysis and slow pyrolysis (Rombolà A. G., 2010). With regard to PAHs, in particular, it is known that they are formed in large quantities by secondary thermo-chemical reactions at temperatures above 700°C (Ledesma et al., 2002). However, small amounts of these compounds can be also produced at the temperatures used in pyrolysis reactors (350 - 600°C). Further studies have shown the formation of PAHs and dioxins in biochars that may therefore be bioavailable for organisms. Total and bioavailable concentrations were quantified, demonstrating their dependence on the starting biomass type, the temperature and the pyrolysis time. Concentrations decrease with increasing time and pyrolysis temperature (Hale et al., 2012). On the other hand it is known that the application of biochar is able to improve the overall absorption capacity of soils towards common organic compounds of anthropic origin (for example PAHs, pesticides and herbicides), and therefore influence the toxicity, transport and the fate of these contaminants (Verheijen et al., 2012).

BIO-OIL

Bio-oil is dark brown, free-flowing organic liquid that is comprised of highly oxygenated compounds. The synonyms for bio-oil include pyrolysis liquids, pyrolysis oils, liquid wood, liquid smoke, pyroligneous acid, wood distillates, and bio-crude oil (BCO).

Pyrolysis liquid is formed by rapidly and simultaneously depolymerizing and fragmenting cellulose, hemicellulose, and lignin with a rapid increase in temperature (Fabbri D., 2016). Rapid quenching then “freezes in” the intermediate products of the fast degradation of hemicellulose, cellulose, and lignin. Rapid quenching traps many products that would further react (degrade, cleave, or condensate with other molecules) if the residence time at high temperature was extended (Mohan et al. 2006).

Bio-oils contain many reactive species, which contribute to unusual attributes. Chemically, bio-oil is a complex mixture of water, syringols, catecols, guaiacols, vanillins, pyrones, isoeugenol,

furancarboxaldehydes, formic acid, acetic acid, and other carboxylic acids. It also contains other major groups of compounds, including hydroxyketones, hydroxyaldehydes, carboxylic acids, phenolics and sugars.

SYNGAS

Pyrolysis gas is a gaseous mixture consisting primarily of: N_2 (50%), H_2 (15-20%), CH_4 (3-5%), CO and CO_2 (each 15 - 20%). The other components present are propane, propylene, butane, butenes, C5, ethane, etc.

THE CARBON NEGATIVE PROCESS

To face climate change it is a widely used strategy to make energy consumption more efficient, and thereby reduce the net amount of GHGs released per quantity of products produced, kilometers driven, etc. In this way the carbon-balance can be shifted from a given positive value closer to zero – a neutral carbon level. In most energy-production processes the carbon balance is positive, but some processes – like the combustion of biomass, are considered carbon neutral. The difference between a carbon positive and a carbon neutral energy production is exemplified in figure 1.9. The black arrow in scenario “A” indicates a net supply of carbon to the production – rendering the production carbon positive, which is compared to the closed carbon neutral production in “B” with no net carbon change. The positive net flux of carbon into scenario “A” will result in a build-up of carbon within the cycle. In modern business-as-usual settings this build up will take place in the atmosphere. For carbon-positive processes, there are large differences in the level of positivity (the size of the black arrow in scenario “A”) depending on the fossil fuel, process efficiency, and many other aspects.

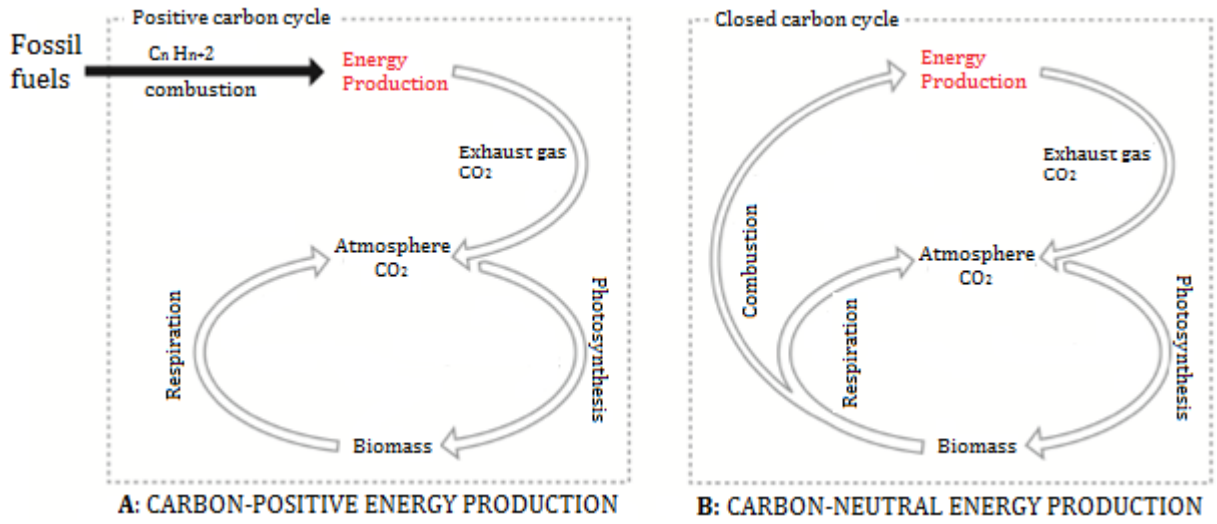


Figure 1.9: a schematic difference between a carbon positive ("a") and a carbon neutral ("b") process.

The carbon negative process requires that carbon is removed from the atmosphere as energy is produced. The main approach to meet this requirement is a validated carbon negative energy production method from pyrolysis of biomass and the concomitant production and use of biochar.

In this process biomass is turned into biochar – a carbon rich char similar to coke or charcoal, with bio-oil or combustible gases as energy output. Amending the char in farm soil will sequester the carbon for a very long time, as well as replenish the contents of nutrients and carbon in the soil.

In figure 1.10 the impact of biochar carbon sequestration on the overall carbon cycle is illustrated. Scenario "B" is a carbon neutral energy production with a completely closed carbon cycle. This neutrality is shifted towards negative in scenario "C", where carbon is removed from the cycle in the form of biochar and sequestered on a long term basis. Running the "C" cycle repeatedly will slowly drain carbon from the atmosphere, and thus lower the CO_2 concentration, as energy is produced.

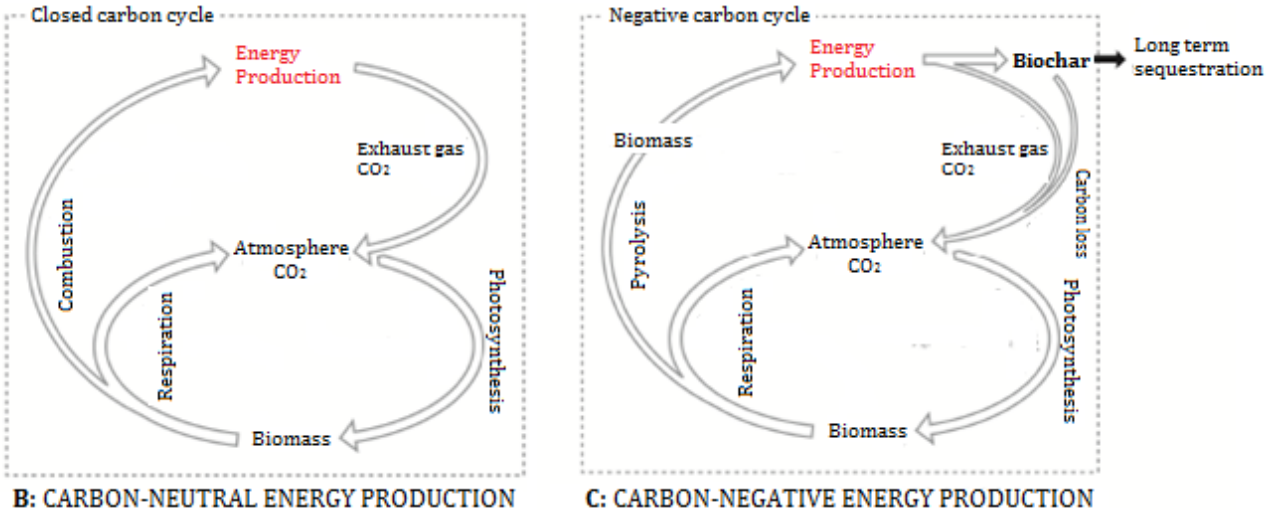


Figure 1.10: schematics of a carbon-neutral energy production ("b") and a carbon negative energy production ("c").

BIO-CHAR AND CARBON NEGATIVITY

In regard to climate change mitigation, the main effect from application of biochar is the carbon-negativity of the production process. In this process, the energy output reduces GHG emissions by fossil fuel displacement, and is in itself an example of carbon-neutral energy production. The long term sequestration of carbon in soil renders the overall-process carbon-negative. Any additional effects of biochar amendment – e.g. reduction of soil emissions of CH_4 and N_2O or increased crop production and thereby carbon capture through photosynthesis, are regarded as a significant plus in the struggle for reducing GHG emissions.

The pyrolysis process produces less electricity and heat than the full combustion process, but maintains or even rebuilds soil fertility and structure. It also mitigates climate change in the energy producing process by sequestering atmospheric carbon, where combustion of biomass is normally slightly carbon-positive (conventional farming) or soil degrading (organic farming). This draws up an important difference: full combustion of biomass yield the highest amount of immediate energy, but has increased costs on the long term (reducing soil quality and depleting the carbon storage), where energy production including biochar use gives a smaller immediate energy yield, but addresses the problems of soil fertility and long term crop productivity in the same process.

SPECIFIC INFLUENTIAL FACTORS ON CARBON-NEGATIVITY CALCULATIONS

In addition to the large-scale influence of the replacement energy source, another parameter, namely the stability of the char in the soil is also very important when addressing the carbon-balance. The char is expected to be substantially more recalcitrant than the feedstock. However, it is a fact that the char will not last forever, and that it will degrade eventually.

How fast this degradation happens is very important to the carbon-balance. Process design and parameters are highly important to the overall balances. Among the most important parameters are whether the process is fast, slow or intermediate, the feedstock- and gas retention times, the heating rate and the maximum temperature.

However, also the overall efficiency of the plant, the integration of heat exchangers, the use of process utilities, the production of the biomass and finally any transportation and storage-requirements are influential on the total carbon-balance (Thomsen T., et al., 2011).

ANAEROBIC DIGESTION

Anaerobic digestion is an attractive waste treatment practice in which both pollution control and energy recovery can be achieved.
Many agricultural and industrial wastes are ideal candidates for anaerobic digestion because they contain high levels of easily biodegradable materials (Jay J. Cheng et al. 2007).

Anaerobic digestion is a collection of processes by which microorganism break down biodegradable material in the absence of oxygen. The digestion process begins with bacterial hydrolysis of the input materials. Insoluble organic polymers, such as carbohydrates, are broken down to soluble derivatives that become available for other bacteria. Acidogenic bacteria then convert the sugars and amino acids into CO_2, H_2, NH_3, and organic acids. These bacteria convert these resulting organic acids into acetic acids, along with additional NH_3, H_2, and CO_2. Finally, methanogens convert these products to CH_4 and CO_2.

PROCESS

Many microorganisms play a role in the anaerobic digestion, including acetic acid-forming bacteria (acetogens) and methane-forming archaea (methanogens).These organisms promote a number of chemical processes in converting the biomass to biogas (figure 1.11).

Gaseous oxygen is excluded from the reactions by physical containment. Anaerobes utilize electron acceptors from sources other than oxygen gas. These acceptors can be the organic material itself or may be supplied by inorganic oxides from within the input material. When the oxygen source in an anaerobic system is derived from the organic material itself, the 'intermediate' end products are primarily alcohols, aldehydes, and organic acids, plus carbon dioxide. In the presence of specialised methanogens, the intermediates are converted to the 'final' end products of methane, carbon dioxide, and trace levels of hydrogen sulfide. In an anaerobic system, the majority of the chemical energy contained within the starting material is released by methanogenic bacteria as methane.

Populations of anaerobic microorganisms typically take a significant period of time to establish themselves to be fully effective. Therefore, common practice is to introduce anaerobic microorganisms from materials with existing populations, a process known as "seeding" the digesters, typically accomplished with the addition of sewage sludge or cattle slurry.

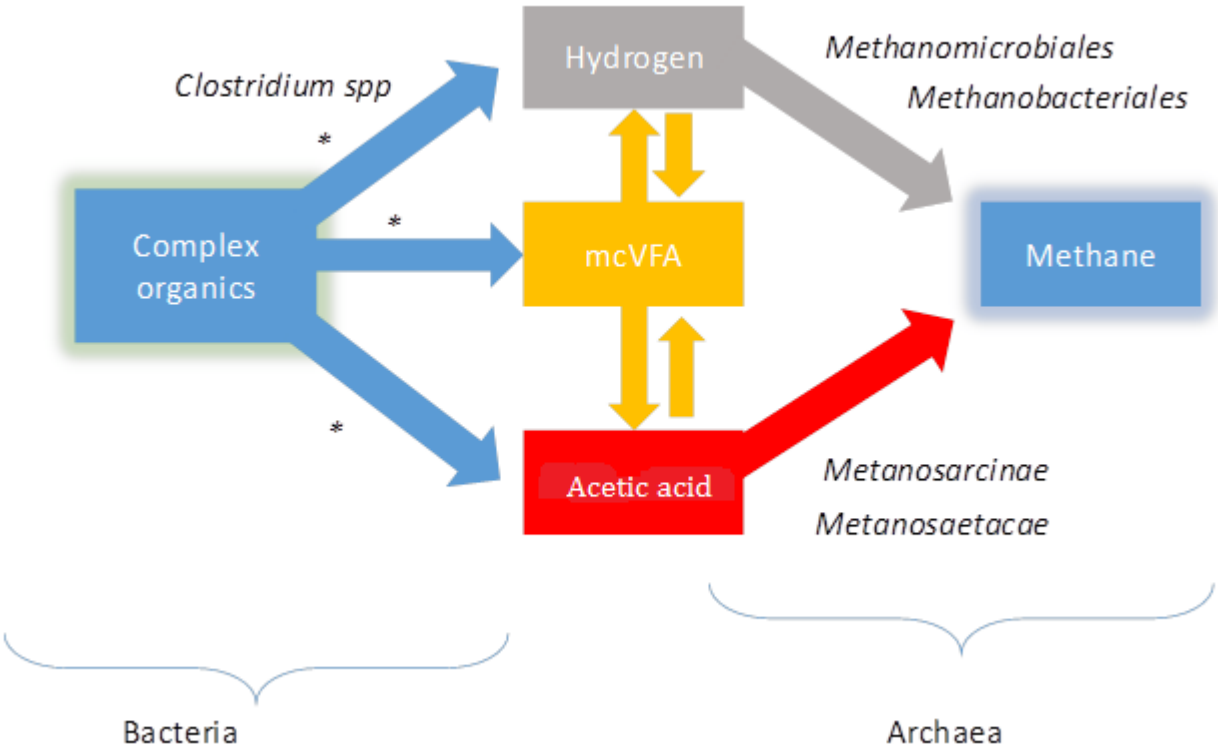


Figure 1.11: the biological process of anaerobic digestion carried out by microorganisms.

PROCESS STAGES

The four key stages of anaerobic digestion involve hydrolysis, acidogenesis, acetogenesis and methanogenesis. The overall process can be described by the chemical reaction, where organic material such as glucose is biochemically digested into carbon dioxide (CO_2) and methane (CH_4) by the anaerobic microorganisms.

$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$$

HYDROLYSIS

It's the formation of low molecular weight substances such as monomers (sugars) from more complex substrates (large organic polymers). Bacteria colonize solid particles and degrade them, producing extracellular hydrolysis enzymes. The typical bacteria may be *Clostridium*, *Ruminococcus*, *Anaerovibrio*, *Bacillus*, etc. Through hydrolysis the complex organic molecules are broken down into simple sugars, amino acids, and fatty acids. Hydrogen and acetate produced in the

first stage can be used directly by methanogens. Other molecules, such as volatile fatty acids (VFAs) with a chain length greater than that of acetate must first be catabolized into compounds that can be directly used by methanogens.

ACIDOGENESIS

This is the transformation of monomers into volatile fatty acids (VFA). The simple compounds produced in the hydrolytic phase are transformed into pyruvic acid which in turn is converted into acetic acid, propionic acid, etc. The microorganisms involved are called Acidogens. The process is typically fast. The intermediates produced in this reaction are not however used as substrates by methanogens, which require simpler molecules (C1 and C2). These are formed in the next phase of acetogenesis.

ACETOGENESIS

This is the transformation of VFAs into acetic alcohol, hydrogen and CO_2. The process involves the acetogens, obliged producers of hydrogen, and the homoacetogens that instead consume it. Homoacetogens are bacteria that produce acetate using hydrogen as a source of energy or other substrates and CO_2 as an electron acceptor.

METHANOGENESIS

The bacterial fermentation of fermentation products leads to the formation of acetate, carbon dioxide and hydrogen, these products act as substrates for the Archea methanogens. In the end, the most oxidized and the most reduced form of carbon are obtained which cannot be further fermented. The latter products of anaerobic decomposition are therefore carbon dioxide and methane. Methanogenesis is sensitive to both high and low pHs and occurs between pH 6.5 and pH 8. The remaining, indigestible material the microbes cannot use and any dead bacterial remains constitute the digestate. The Archea are the most important microorganisms able to use CO_2 as an electron acceptor in anaerobic respiration. In particular, methanogens acetoclasts convert acetic acid into methane without involving the use of hydrogen (Ali Bayané, Serge R. Guiot, 2010).

PRODUCTS

The three principal products of anaerobic digestion are digestate, wastewater and biogas.

DIGESTATE

Digestate is the solid residue of the original input material to the digesters that the microbes cannot use. It also consists of the mineralized remains of the dead bacteria from within the digesters. Digestate can come in three forms: fibrous, liquor, or a sludge-based combination of the two fractions. In two-stage systems, different forms of digestate come from different digestion tanks. In single-stage digestion systems, the two fractions will be combined and, if desired, separated by further processing.

The second byproduct (acidogenic digestate) is a stable, organic material consisting largely of lignin and cellulose, but also of a variety of mineral components in a matrix of dead bacterial cells.

The third byproduct is a liquid (methanogenic digestate) rich in nutrients, which can be used as a fertiliser, depending on the quality of the material being digested. Digestate typically contains molecules, such as lignin-based compounds, that cannot be broken down by the anaerobic microorganisms. Also, the digestate may contain ammonia that is phytotoxic, and may hamper the growth of plants if it is used as a soil-improving material. For these two reasons, a maturation or composting stage may be employed after digestion. Lignin and other materials are available for degradation by aerobic microorganisms, such as fungi, helping reduce the overall volume of the material for transport. During this maturation, the ammonia will be oxidized into nitrates, improving the fertility of the material and making it more suitable as a soil improver. Large composting stages are typically used by dry anaerobic digestion technologies.

WASTEWATER

The final output from anaerobic digestion systems is water, which originates both from the moisture content of the original waste that was treated and water produced during the microbial reactions in the digestion systems. This water may be released from the dewatering of the digestate or may be implicitly separate from the digestate.

The wastewater exiting the anaerobic digestion facility will typically have elevated levels of biochemical oxygen demand (BOD) and chemical oxygen demand (COD). These measures of the reactivity of the effluent indicate an ability to pollute. Some of this material is termed 'hard COD', meaning it cannot be accessed by the anaerobic bacteria for conversion into biogas. If this effluent were put directly into watercourses, it would negatively affect them by causing eutrophication. As such, further treatment of the wastewater is often required. This treatment will typically be an oxidation stage wherein air is passed through the water in a sequencing batch reactors or reverse osmosis unit.

BIOGAS

The nature of the raw materials and the operational conditions used during anaerobic digestion, determine the chemical composition of the biogas (Holm-Nielsen J.B. et al. 2009) Raw biogas consists mainly of CH_4 (40-75%) and CO_2 (5-10%), H_2S (0.005-2%), halogenated hydrocarbons (<0.6%), siloxanes (0-0.2%), CO (<0.6%), NH_3 (<1%), N_2 (0-2%) and O_2 (0-1%) can be present and might be inconvenient when not removed (figure 1.12).

Impurity	Possible Impact
Water	Corrosion in compressors, gas storage tanks and engines due to reaction with H_2S, NH_3 and CO_2 to form acids Accumulation of water in pipes Condensation and/or freezing due to high pressure
Dust	Clogging due to deposition in compressors, gas storage tanks
H_2S	Corrosion in compressors, gas storage tanks and engines Toxic concentrations of H_2S (>5 cm^3 m^{-3}) remain in the biogas SO_2 and SO_3 are formed due to combustion, which are more toxic than H_2S and cause corrosion with water
CO_2	Low calorific value
Siloxanes	Formation of SiO_2 and microcrystalline quartz due to combustion; deposition at spark plugs, valves and cylinder heads abrading the surface
Hydrocarbons	Corrosion in engines due to combustion
NH_3	Corrosion when dissolved in water
O_2/air	Explosive mixtures due to high concentrations of O_2 in biogas
Cl^-	Corrosion in combustion engines
F^-	Corrosion in combustion engines

Figure 1.12: biogas impurities and their consequences.

TRANSFORMING BIOGAS INTO BIOMETHANE

In order to transform biogas into biomethane, two important steps are performed, the first one consists in a cleaning process to remove the harmful trace components and the second one is an upgrading process, in which CO_2 is removed to adjust the heating value and relative density. Upgrading is generally performed in order to meet the standards for use as vehicle fuel or for injection in the natural gas grid. After transformation, the final product is referred to as "biomethane", containing 1-3% CO_2 and at least 95-97% methane. Biomethane can be used as an alternative for natural gas. In general, the type of end use of the biogas sets its quality demand (Ryckebosch E., et all 2008).

HYBRID PROCESS, PYROLYSIS COUPLED WITH ANAEROBIC DIGESTION (PY-AD)

Biorefineries are gaining more and more attention among researchers all the way to their ability to valorize different feedstocks, thus obtaining numerous products. In agreement with the IPCC and the International Energy Agency (IEA), it has been estimated that the consumption of biofuels in the transport sector will increase to 10-20% by 2030 (Cherubini F., 2010). Furthermore, a large amount of municipal solid waste is currently produced despite the efforts of many countries to limit the production of waste. In 2013, the total amount of municipal solid waste was estimated to be 1.3 billion tonnes from the World Bank, and an increase of up to 2.2 billion tonnes a year is expected for 2025 (Hoornweg D. 2013). Different technologies are currently under development (anaerobic digestion, gasification, combustion, pyrolysis, etc.) to transform waste into energy and renewable products.

Anaerobic digestion is a technology widely used worldwide for the production of biogas from organic waste (for example, municipal solid waste), composed of 30-70% organic matter. Organic waste is highly biodegradable and is already widely used as feedstock in anaerobic digestion plants. However, about 30% of these wastes are lignocellulosic green waste, which cannot be exploited through anaerobic digestion because lignin acts as a barrier and protects cellulose from degradation by inhibiting cellulose enzymes. For this reason the MSWs are separated into non-biodegradable and biodegradable fractions according to their content of lignocellulosic components, using only the latter as a substrate for anaerobic digestion (Chaudhary Awais S., 2017).

The coupling of anaerobic digestion to pyrolysis allows the maximum valorization of waste regardless of their lignocellulosic composition, valorizing even the fraction with a high content of

lignin. This is confirmed by numerous studies, for example Chaudhary et al. have shown that the use of these two technologies in pairs leads to an increase in the volume yield of the biomethane produced by 20% and a general efficiency of the process of 67% where instead using only anaerobic digestion was only 52%. Fabbri and Torri have identified the two main configurations that can have a pyrolyser coupled to anaerobic digester (Py-AD) (figure 1.13).

In the first configuration the pyrolysis products are converted into biogas by the digester; pyrolysis is therefore, applied "upstream" to allow the breakdown of the chemical bonds of hemicellulose and lignin thus obtaining smaller compounds more accessible to biomethanation.
In the second configuration the products derived from anaerobic digestion are transformed by pyrolysis in a "downstream" configuration able to convert residual solid digested from biogas plants into fuels and materials (Fabbri et al., 2016).

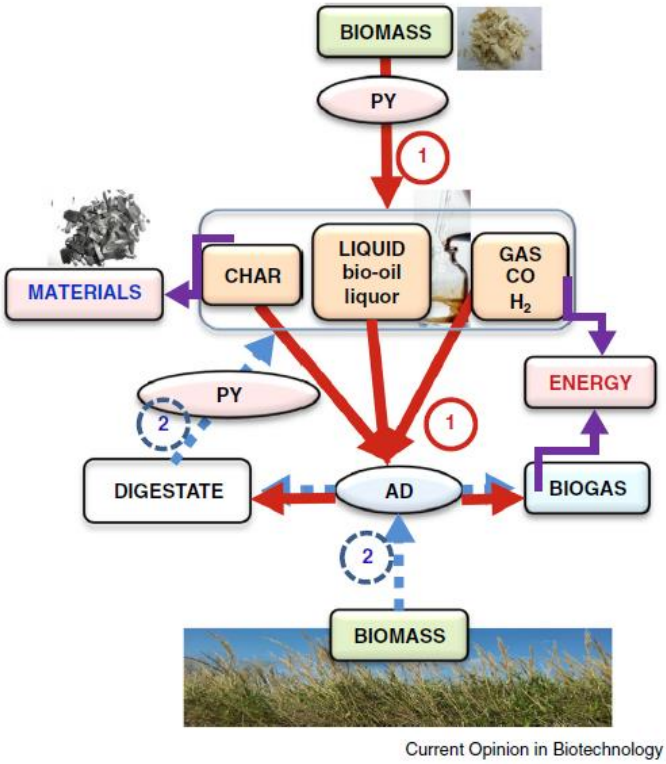


Figure 1.13: Pathways in the Py-AD approach. Path (1) Py of input lignocellulosic feedstocks including recycled solid digestate followed by AD upgrading of liquids and syngas into biogas; the addition of biochar can favour biomethanation. Path (2) Py upgrading of AD co-products (solid digestate) into fuels (charcoal, bio-oil, syngas) and materials (soil fertiliser, sorbent, functionalised materials).

CHAPTER 2: AIM OF THE THESIS

The increasing attention to environmental issues of recent times encourages us to find new methods for the production of energy from renewable sources, and to improve existing ones, increasing their energy yield. Most of the waste and agricultural residues, with a high content of lignin and non-hydrolysable polymers, cannot be effectively transformed into biofuels with existing technology. This thesis has as its objective the production of biogas (a mixture of CH_4 and CO_2) through waste biomass with a high lignin content (therefore the most difficult to exploit them) through a process that couples pyrolysis with anaerobic digestion carried out by microorganisms (figure 2.1).

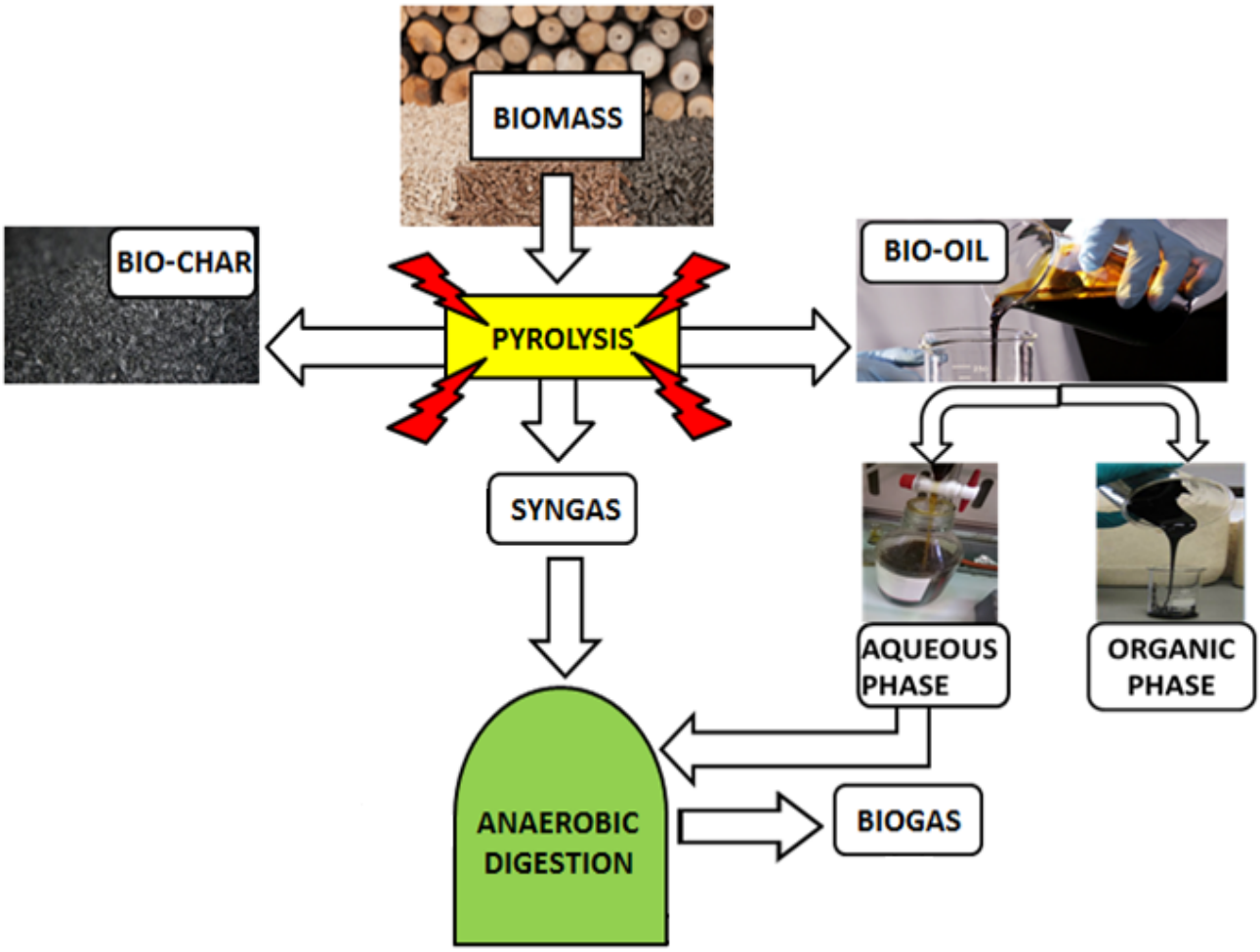


Figure 2.1: main phases of the Py-AD process.

CHAPTER 3: MATERIALS AND METHODS

The experiments presented in this thesis were carried out using equipment and pilot plants currently operating at the "R. Sartori" of the University of Bologna, appropriately modified by adding functional elements developed during the process and installed by Hera s.p.a.

The materials obtained from the process (char, bio-oil and gas) were analyzed through GC-MS and GC-TCD using methodologies developed in the laboratory of analytical chemistry of the laboratories "R. Sartori".

DESIGN AND CONSTRUCTION OF THE PY-AD PLANT

Figure 3.1 shows the structure of the plant that was subjected to the test, which consists in an intermediate pyrolysis reactor producing gas and liquid phase. The system is directly coupled to two biological reactors for the treatment of raw pyrolysis gas.

Pyrolysis vapors, generated by a pyrolysis at 400 °C (average temperature at the top of the biomass) for 20 minutes of residence time, are cooled inside a heat exchanger reaching an approximate temperature of 60°C. Pyrolysis vapors cooling induces the condensation of a liquid phase (hereafter called bio-oil) and produces a raw pyrolysis gas, consisting in gas and residual aerosols. This raw pyrolysis gas is subsequently injected at a depth of 1 meter below the liquid level of the first CSTR (Continuous-flow Stirred-Tank Reactor) reactor (R1, 300L suspended biomass). R1 is mixed intermittently by a biogas blower that withdraws biogas from the top dome and pump it to the reactor base. The pyrolysis vapors are then recirculated several times through the R1 and flows to the top of second (R2) reactor. R2 is a trickle bed reactor optimized for conversion of uncondensable gases (e.g. CO and H_2). R2 consist in a stainless steel tank filled with a small amount of liquid (30L) and 250 L of high surface area polypropylene elements (150 m^2/m^3). The liquid, accumulated at the base of R2 is sprayed on the top of filling elements (covered with bacterial biofilm) and exit just above the liquid in the R2 base. Finally the biogas/syngas mixture is collected into a 150 L gasometer that automatically release the gas when full.

As mentioned above, in the heat exchangers there is the collection of the high-boiling part of the pyrolysis products, which has been collected through a tap. The liquid obtained was separated into a water-soluble fraction (of density close to water) and an insoluble fraction (denser). The bio-oil (formed from aqueous liquid and organic phase) was quantified and analyzed and (see section

below) subjected to anaerobic digestion (aqueous liquid) and detailed chemical characterization (organic phase). Figures 3.2, 3.3 and 3.4 show details of the equipment used.

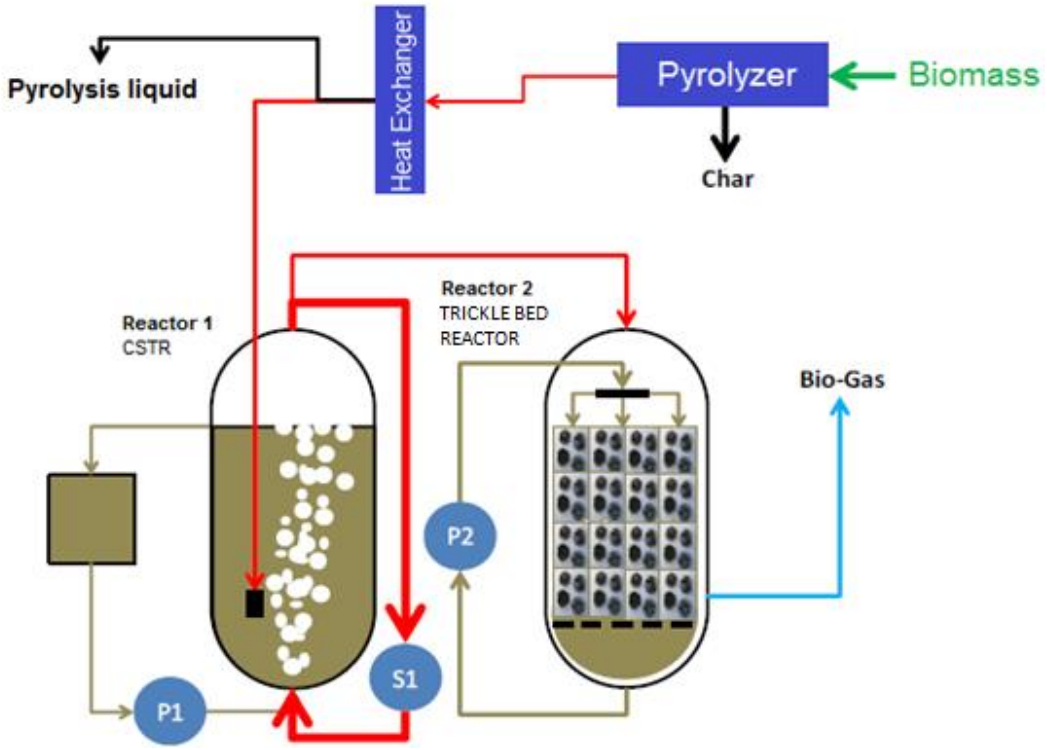


Figure 3.1: planting structure of the testing phase.

Figure 3.2: overview of the experimental site

Figures 3.3 - 3.4: detail of the two-stage digestion system

BIOMASS AND BIO-CHAR

The experimental phase of this study was carried out through the use of coniferous pellet.

The pellet was pyrolyzed without undergoing any preliminary treatment, however the resulting biochar sample was then ground manually using a mortar to facilitate subsequent analyzes.

ELEMENTAL ANALYSIS

An elemental Flash 2000 series CHNS/O (thermo scientific) analyzer was used for providing the values of C, H, N and S of the input (wood pellets) and outputs obtained after pyrolysis (bio-char and bio-oil).

The samples (about 4-5 mg) analyzed in duplicate are placed in a tin crucible and mixed with about 10 mg of vanadium pentoxide (catalyst to obtain a better identification of the sulfur) and burned at a temperature of 900 ° C under a stream of nitrogen.

The oxygen content was calculated as follows:

O = 100 - (C + N + H + S + A) expressed as a percentage. The calorific value (HHV) was calculated on the basis of the elemental composition by means of the equation proposed by Channiwala and Parikh (2002):

HHV (MJ kg-1) = 0.3491 C + 1.1783 H + 0.1005 S - 0.1034 O - 0.0151 N - 0.0211 A with C, H, S, O, N and A expressed as a percentage.

The ash content was calculated for weight loss after calcination at 600°C for 2 hours.

DETERMINATION OF THE WATER CONTENT OF THE BIO-OIL USING THE KARL-FISCHER TITRATION TECHNIQUE

Karl Fischer titration is a classic titration method in analytical chemistry that uses volumetric titration to determine trace amounts of water in a sample.

Five samples were prepared, each analyzed in duplicate:

• two bio-oil samples, one from 10 μL and the second from 50 μL;

• two samples of THF (tetrahydrofuran, a solvent with almost zero water concentration); one of 0.5 mL and the second one of 1 mL;

• a sample of 0.12 g of pyrolytic lignin dissolved in 1.2 mL of THF;

DETERMINATION OF MICRO-POLLUTANTS (PAHS) IN THE BIOCHAR SAMPLE

For the determination of PAHs in the biochar, an analysis procedure was carried out, based on extraction using Soxlhet with acetone/cyclohexane (1: 1, v/v), evaporation of the extraction solution by Rotavapor and clean up solid phase extraction (SPE) over silica gel (Rombolà, 2010).

TOTAL ORGANIC CARBON MEASUREMENT

TOC content was measured using a carbon analyzer equipped with a module for liquid analysis (mod. TOC VCPH + SSM-5000A, SHIMADZU) (figure 3.5). Half quartz filter was oxidized at 900 °C with ultrapure oxygen (0.5 L min^{-1} at 20 °C). In these conditions all carbon was converted in carbon dioxide and quantified by infrared detector. Preliminary treatment was performed using bidistilled water to dilute the samples and eliminate the coarse particles by filtration.

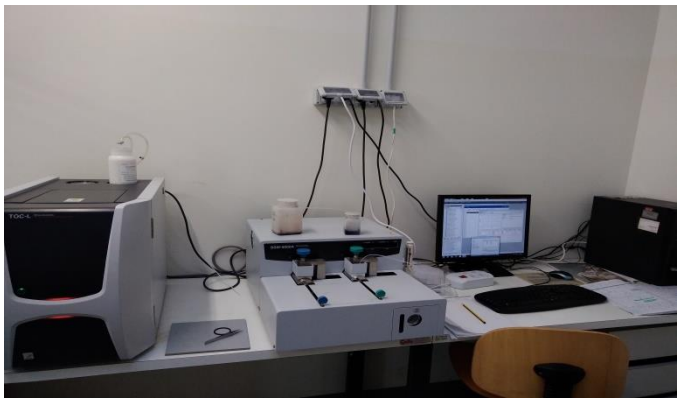


Figure 3.5: instrument for the analysis of total organic carbon concentration.

SILYLATION PROCEDURE

A direct analysis of bio-oil was performed with a 6850 Agilent HP gas chromatograph connected to a 5975 Agilent HP (figure 3.6) quadrupole mass spectrometer (EI 70 eV, at frequency of 1.55 scan s^{-1} within the 10-450 m/z range). Analytes were separated by a HP-5 fused-silica capillary column (stationary phase poly [5% diphenyl/95%dimethyl] siloxane, 30 m, 0.25mm i.d., 0.25mm film

thickness) using helium as carrier gas with the following thermal program: 50 °C with a hold for 5 min, then ramping up with a heating rate of 10 °C min^{-1} until 325 °C followed by a column cleaning at 325 °C for 10 min.

For the silylation procedure, 100 µL of sample added to 100 µL of sorbitol in ethanol at 160 ppm (the internal standard) are prepared in a sampling vial and left to dry by nitrogen flow; subsequently, 100 µL of BSTFA and 100 µL of acetonitrile are added, heating the solution obtained for 45 minutes at 70 °C; then 5 µL of pyridine is added and heated again for 30 minutes at 70 °C; at the end of the procedure, 500 µL of ethyl acetate are added and the sample is sent to analyze in GC/MS.

Bio-oil solution (5% concentration) was analysed after silylation using the following thermal program: 100°C with a hold for 5 min, then ramping up with a heating rate of 5 °C min^{-1} until 310 °C.

Figure 3.6: instrument for the bio-oil analysis and silylation procedure

VFAs ANALYSIS

For the quantitative analysis procedure of the VFA, 100 µL of sample is prepared in a sampling vial, in which:

• 200 µL of a saturated aqueous solution of KHSO4 (potassium sulphate);

• 100 µL of NaCl brine (sodium chloride);

• 100 µL of 1 g/L solution of 2EB (2-ethylbutyrate, used as internal standard);

• 1 mL of DMC (dimethylcarbonate);

once the sample preparation is finished, the biphasic sample was let settle and analysis is carried out by GC/MS of the upper DMC phase. Calibration was performed by applying the same procedure to standard solutions containing known amount of the five VFA analyzed (acetic acid, propionic acid, isobutyric acid, butyric acid, isovaleric acid, valeric acid).

GC-MS AND GC-TCD ANALYSIS

GC-MS analyses were performed with a 7820A Agilent HP gas chromatograph (figure 3.7a) connected to a 5977E Agilent HP quadrupole mass spectrometer (EI 70 eV, at a frequency of 1.55 scan s^{-1} within the 10-450 m/z range). Analytes were separated by a DB-FFAP column (stationary phase nitroterephthalic acid modified polyethylene glycol, 30 m, 0.25 mm i.d., 0.25 mm film thickness) using helium as carrier gas with the following thermal programme: 50°C with hold for 5 min, then ramping up with a heating rate of 10 °C min^{-1} until 250 °C.

Syngas and biogas obtained from anaerobic digestion were analysed using a gas chromatograph (GC Agilent 7820A) equipped with a thermal conductivity detector (TCD) (figure 3.7b). Gases were separated using a three packed columns system: a pre-column Hayesep N (SS. 80-100 mesh, dimension: 8 ft. x 1/8”), a Hayesep Q (SS. 80-100 mesh, dimensions: 3 ft. x 1/8”) and a molecular sieve 5A (SS. 60-80 mesh, dimensions: 6 ft. x 1/8”). Oven program: 50 °C for 9 min then 8°C/min to 80 °C for 10 min.

Figure 3.7: instruments for the analysis of digested liquids (a) and digestion gases (b)

DEVELOPMENT OF AN ANAEROBIC DIGESTION SYSTEM FOR THE AQUEOUS PHASE OF BIO-OIL THROUGH A UASB REACTOR

For a detailed study of anaerobic digestion of the aqueous phase (AP), 100 ml UASB reactor was used, where daily amounts of AP and bacterial inoculum (used to provide a kind of food supplement for microorganisms), were dosed through an automated peristaltic pump (figure 3.8).

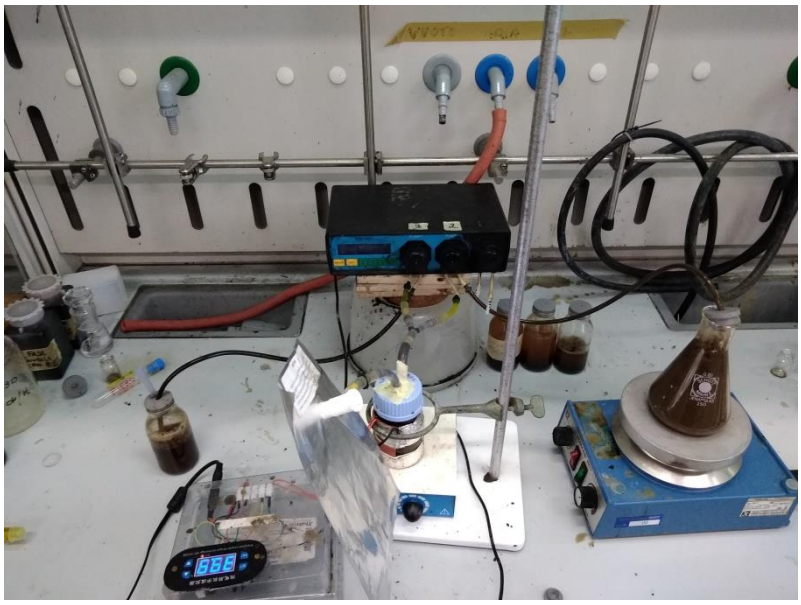


Figure 3.8: overview of the anaerobic digestion system.

The products derived from anaerobic digestion (digestate, waste water and biogas) were subsequently collected in a tedlar bag and extracted using a syringe, after marking the quantity of gas and liquid produced, were then analyzed through GC-MS and GC-TCD to follows volatile fatty acids (VFA) concentration and biogas production.

The AP concentration was expressed as chemical oxygen demand (COD_{AP}, gCOD l^{-1}) of AP which was calculated using the following formula:

$$AP_{COD} = 2660 \cdot C_{AP}$$

Where C_{AP} is the carbon fraction present in the AP.

COD_{added} indicates the total concentration of the incoming material (AP and bacterial inoculum) fed into the reactor. It was calculated using the following formula:

$$COD_{ADDED} = \sum_i V_i \cdot C_i$$

where V_i is the volumes of liquid digestate released every day by the reactor and C_i is the concentration of the relative day of the input material expressed in terms of COD.

COD_{biogas} is the total volume of biogas produced by the reactor in terms of COD during anaerobic digestion. It was calculated using the following formula:

$$COD_{BIOGAS} = \sum_i \left(H_{2i} \cdot H_{2\,COD}\right) + \left(CH_{4i} \cdot CH_{4\,COD}\right)$$

where H_2 and CH_4 are the cumulative production of hydrogen and methane (ml) during the experiments, H_{2COD} and CH_{4COD} are the COD values of hydrogen and methane respectively.

The VFA concentration was expressed as chemical oxygen demand (COD_{VFA}, gCOD l^{-1}) of VFA which was calculated from the ThOD of each VFA using the following formula:

$$COD_{VFA} = \sum_i ThOD_i \cdot VFA_i$$

Where $ThOD_i$ (gThOD $g^{-1}_{substance}$) is 1.07, 1.51, 1.82, 2.04 for acetic acid, propionic acid, butyric/isobutyric acid, valeric/isovaleric acid respectively and VFA_i is the concentration of different VFA in g l^{-1}. All reagent and chemicals were purchased from Sigma-Aldrich and used without purification.

The COD transformed into methane (COD_{CH4}, gCOD l^{-1}) was calculated from density of gaseous methane (0.62 g l^{-1} at 40 °C) and its ThOD (4.0 gCOD g^{-1}) using the following formula:

$$COD_{CH4} = 2.48 \cdot \frac{V_{CH4}}{V_{reactor}}$$

where V_{CH4} is the cumulative production of methane (ml) during the experiment and $V_{reactor}$ is the volume of reactor (100 ml).

The COD transformed into hydrogen (COD_{H2}, gCOD l^{-1}) was calculated from density of gaseous methane (0,09 g l^{-1}) and its ThOD (8.0 gCOD g^{-1}) using the following formula:

$$COD_{H2} = 0.71 \cdot \frac{V_{H2}}{V_{reactor}}$$

where V_{H2} is the cumulative production of hydrogen (ml) during the experiment and $V_{reactor}$ is the volume of reactor (100 ml).

CHAPTER 4: RESULTS AND DISCUSSION

The system has been continuously fed for 50 days with wood pellet. The throughput capacity of pyrolyser (1-10 kg/h) was in excess with respect to the maximum biological reactor load capacity (approximately evaluated in a preliminary test, 0.5-1 kg/d). Therefore, the pyrolyser was operated continuously 1 hour per day and biological reactors (including mixing) were kept on all the time.

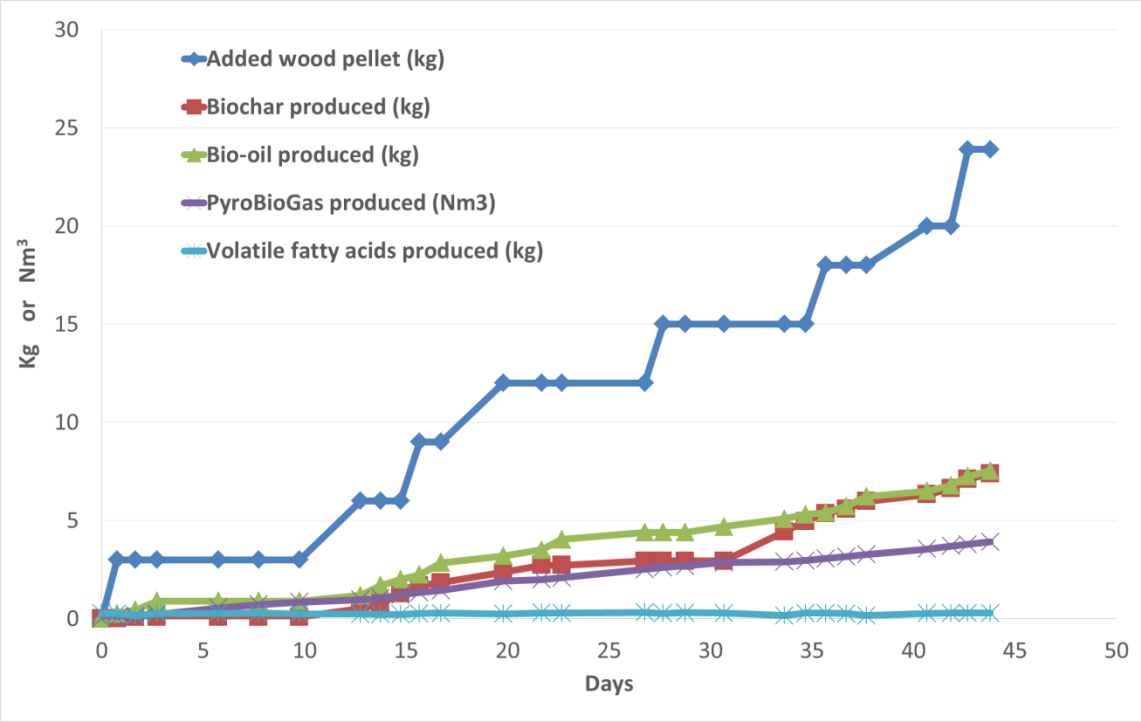


Figure 4.1: general trends of input and output material.

The pyrolyser was preloaded with weekly wood loads (3 kg per week of coniferous pellets), subsequently fed automatically three days a week. Figure 4.1 shows results from wood pellets digestion test, blue line shows the total amount of biomass inserted in the Py-AD system, red, green, purple and light blue lines shows the biochar , bio-oil, biogas and VFAs productions respectively. Pyrobiogas productions followed the addition of raw pyrolysis gas, without significant accumulation of anaerobic digestion intermediates in both reactors. It is interesting to notice that the concentration has never gone beyond 1 g/L, this suggest an adequate stability of the digestion of raw pyrolysis gas.

Making the overall balance, 24 kg of material were pyrolized, with the production of 7.62 kg of biochar (31.7% yield), 5.96 kg of biogas (24.8% yield) and 7.81 kg of liquid (32.5% yield). The remaining 2.6 kg (11% of the total) were probably converted in waste water and digestate. Pyrolysis was conducted at 400 °C (average temperature at the top of the biomass) for 20 minutes of

residence time. By comparing these results with the data reported in literature at the same pyrolysis temperature/conditions (slow) but different feedstock and pyrolyser configuration, it is possible to note that the yields of biochar and bio-oil are in line with those reported by other studies, whereas we observe a significant increase in gas yield (table 4.1).

Table 4.1: yields comparison of pyrolysis products using different feedstock at the same temperature.

BIOMASS	YIELD AT 400°C (%)		
	Char	**Bio-oil**	**Gas**
Coniferous pellets	**32**	**32**	**25**
Rapeseed (Onay and Kockar)	24	42	26
Euphorbia rigida (Putun et al.)	44	37	19
Sunflowers bagasse (Putun et al.)	35	48	17
Hazelnut shell (Putun et al.)	47	34	19
Cottonseed cake (Ozbay et al.)	29	47	24
Switchgrass (Imam and Capareda)	48	22	8
Average	**38**	**38**	**19**

Pyrolysis temperature has been found to be a crucial parameter for achieving good yields of the three man pyrolysis products: Onay and Kockar, Imam and Capareda and Ozbay et al. (table 4.2) reported that 550-600 °C is the temperature at which the maximum oil yield is obtained, whereas the char yield decreases and gas yield increases with rising temperature according to the data present in the literature (Antal and Gronli, 2003, Demirbas, 2004, Kim et al., 2012, Song et al., 2012).

Table 4.2: comparison of pyrolysis yields of different biomasses.

Temp. (C°)	**Rapeseed** (Onay and Kockar)			**Cottonseed cake** (Ozbay et al.)			**Switchgrass** (Imam and Capareda)		
	Char	**Oil**	**Gas**	**Char**	**Oil**	**Gas**	**Char**	**Oil**	**Gas**
	Yield (%)			**Yield (%)**			**Yield (%)**		
400	24	42	26	29	47	24	48	22	8
500	22	46	25	28	46	26	43	28	10
600	19	47	27	26	48	26	25	37	26

The pyrolysis process and the process parameters, especially the temperature and residence time, are therefore particularly important, but, has highlighted in the work of Putun et al. (table 4.3), it should however be stressed that determining the final product also influences the type of biomass used.

Table 4.3: comparison of pyrolysis yields of different biomasses performed by Putun et al.

Temp. (C°)	*Euphorbia rigida* (Putun et al.)			Sunflower (Putun et al.)			Hazelnut shell (Putun et al.)		
	Char	**Oil**	**Gas**	**Char**	**Oil**	**Gas**	**Char**	**Oil**	**Gas**
	Yield (%)			**Yield (%)**			**Yield (%)**		
400	44	37	19	35	48	17	47	34	19
500	28	49	23	27	56	17	41	37	22
700	21	39	40	26	50	24	36	35	29

However, it should be noted that, as regards the yields of biochar, they show a greater dependence on temperature and residence time, while the type of original biomass is less influential.

CHEMICAL CHARACTERIZATION OF COMPOUNDS OF PYROLYSIS / ANAEROBIC DIGESTION

BIO-CHAR

The biochar produced by the process has been characterized in terms of:

1) Carbon and ash content through elemental analysis (table 4.5, 4.6);
2) Content of micro-pollutants (PAHs) to determine its agronomic applications.

Conti R. (2011) during his study pyrolized three types of biomasses (switchgrass, corn stalk pellets and poultry litter pellets) at seven temperatures, from a minimum of 400 °C to a maximum of 700 °C and five residence times (1, 2, 5, 10 and 20 minutes). Comparing the yields obtained with the same conditions (table 4.4), we can see how the wood pellet tested falls within the values, finding a greater resemblance to the yield obtained with the pellet derived from corn stalks.

As far as the elemental analysis of biomass is concerned, the wood pellet shows a higher content in carbon and oxygen and a lower content of nitrogen, hydrogen and sulfur. The ash content was found

to be considerably lower in the wood pellet, thus influencing the heating value (HHV) bringing it to a notably higher value. The elemental analysis of biochar reflects that of biomass, with values for wood pellets greater in carbon and oxygen and less for nitrogen, hydrogen and sulfur. Even here ashes are considerably lower, going to influence the heating value.

Table 4.4: comparison of biochar yields of different feedstocks at the same temperature and time of residence

BIOMASS	Biochar yield (400°C, residence time 20 min)
Wood pellet	**32%**
Switchgrass (*Panicum Virgatum*) (Conti R.)	28%
Corn stalks pellet (Conti R.)	39%
Poultry litter pellet (Conti R.)	45%

Table 4.5: elemental analysis of the original biomasses

BIOMASS	ELEMENTAL COMPOSITION (%)						HHV
	C	N	H	S	O	Ash	(MJ Kg^{-1})
Wood pellet	47.5 ± 0.2	0	2.4 ± 0.2	0	49.7 ± 0.3	0.4 ± 0	17.5
Switchgrass (*Panicum Virgatum*) (Conti R.)	42.5	0.7	5.7	0	44.2	6.9	17
Corn stalks pellet (Conti R.)	40.2	1	5.4	0	43.1	10.3	15.7
Poultry litter Pellet (Conti R.)	33.5	4.1	4.8	1.3	32.6	25	13.4
Average	**38.7**	**1.9**	**5.3**	**0.4**	**40**	**14.1**	**15.4**

Table 4.6: elemental analysis of the biochars

BIOCHAR	ELEMENTAL COMPOSITION (%)						HHV
	C	N	H	S	O	Ash	(MJ Kg^{-1})
Wood pellet	77.1 ± 0.7	0	1.2 ± 0.1	0	20.3 ± 0.3	1.37 ± 0.2	28.5
Switchgrass (*Panicum Virgatum*) (Conti R.)	67.8 ± 1.4	0.5 ± 0	3.8 ± 0.1	0	21.4 ± 2.5	6.6 ± 1	26
Corn stalks pellet (Conti R.)	46.3 ± 1.2	1 ± 0.3	2.8 ± 0.1	0	15.2 ± 0.6	34.7 ± 1	17.1
Poultry litter pellet (Conti R.)	34.7 ± 0.5	3.9 ± 0.2	2.5	2.2	5 ± 0.4	51.7 ± 1.2	13.6
Average	**49.6 ± 1.0**	**1.8 ± 0.2**	**3.0 ± 0.1**	**0.7**	**13.9 ± 1.2**	**31 ± 1.1**	**18.9**

Rombolà A. in 2010 carried out a study on the determination of PAHs in various samples of biochar produced by pyrolysis of herbaceous biomass (switchgrass) at different pyrolysis conditions thus being able to observe the effect of temperature and residence time on PAHs concentration.

Table 4.7: concentration of PAHs in the biochar samples produced by the pyrolysis of switchgrass and wood pellet

PAHs	400 °C RT = 20 min. Wood pellet		450 °C RT = 20 min. Switchgrass (Rombolà A.)	
	µg/g	RSD %	µg/g	RSD %
Naphthalene	7.51	10	0.20	7
Acenaphthylene	2.24	13	0.01	2
Acenaphthene	1.15	11	0.02	54
Fluorene	6.20	16	0.07	49
Phenanthrene	8.19	9	0.13	13
Anthracene	2.47	16	0.02	36
Fluoranthene	1.53	10	0.05	2
Pyrene	1.85	14	0.06	22
Chrysene	0.90	18	0.03	57
Benz[a]anthracene	1.81	17	0.03	59
Benzo[b]fluoranthene	0.71	3	0.06	103
Benzo[k]fluoranthene	0.81	10	0.05	80
Benzo[a]pyrene	0.77	14	0.09	75
Indeno[1.2.3-c,d]pyrene	0.33	15	0.04	30
Dibenzo[a.h]anthracene	0.37	11	0.03	67
Benzo[g,h,i]perylene	0.36	17	0.03	33
Total	37.20		0.92	

As shown in table 4.7 we can see that the total quantity of PAHs in the biochar derived from wood pellets is far greater than the biochar obtained from switchgrass. The reason for this difference is probably due to specific features of the pyrolyser; in fact whereas Rombolà A. used in his study a bench scale pyrolysis reactor that allows producing unpolluted biogas, the kg/h scale pyrolysis showed a large contamination of biochar. This contamination was probably due to improper design of biochar collection system (the biochar is downstream with respect to pyrolysis) and semi-continuous operation of pyrolyser used.

The levels of contaminants found exceed the limits imposed by the organizations that manage the trade of biochar in the world (IBI), in Europe (EBC) and in Italy with the Italian association ICHAR, which impose a limit maximum content of PAHs of 20, 12 and 6 µg/g, respectively (table 4.8).

Table 4.8: regulatory limits for soil application of biochar.

CONTAMINANT	Italy	IBI	EBC
PAH	$< 6\ \mu g\ g^{-1}$	$< 20\ \mu g\ g^{-1}$	$< 12\ \mu g\ g^{-1}$
PCB	$< 0.5\ \mu g\ g^{-1}$	$< 0.5\ \mu g\ g^{-1}$	$< 0.2\ \mu g\ g^{-1}$
PCDD/PCDF	$< 9\ ng\ kg^{-1}$	$< 9\ ng\ kg^{-1}$	$< 20\ ng\ kg^{-1}$

BIO-OIL

The 7.8 kg of liquid obtained from the pyrolysis of wood consist in a biphasic liquid that, subjected to fractionation found to be formed of 6.8 kg of aqueous phase (AP) (containing 5.4 kg of water) and 1 kg of organic phase (OP), revealed to a subsequent analysis to be mainly composed of pyrolytic lignin (figure 4.2).

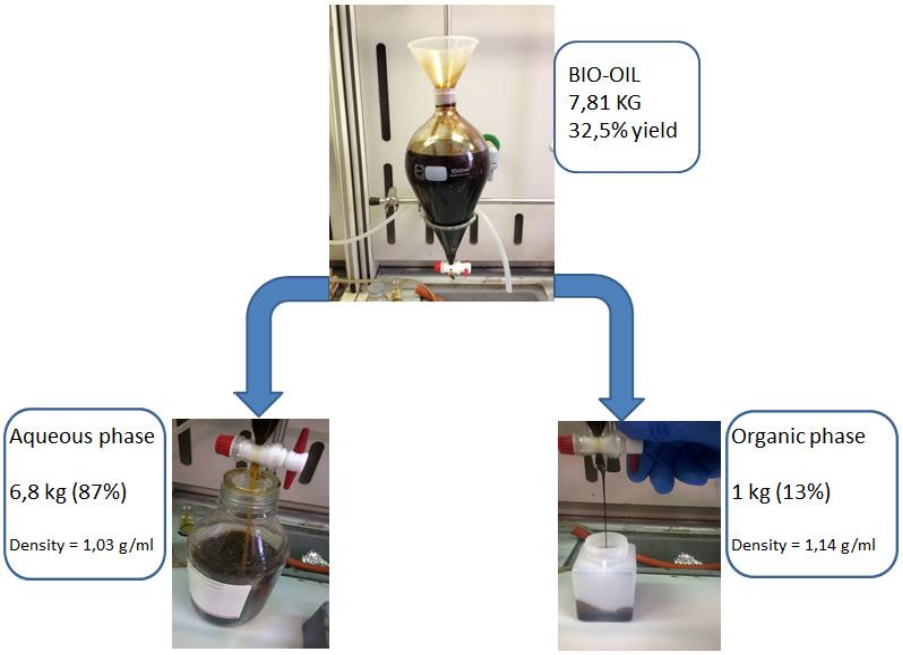
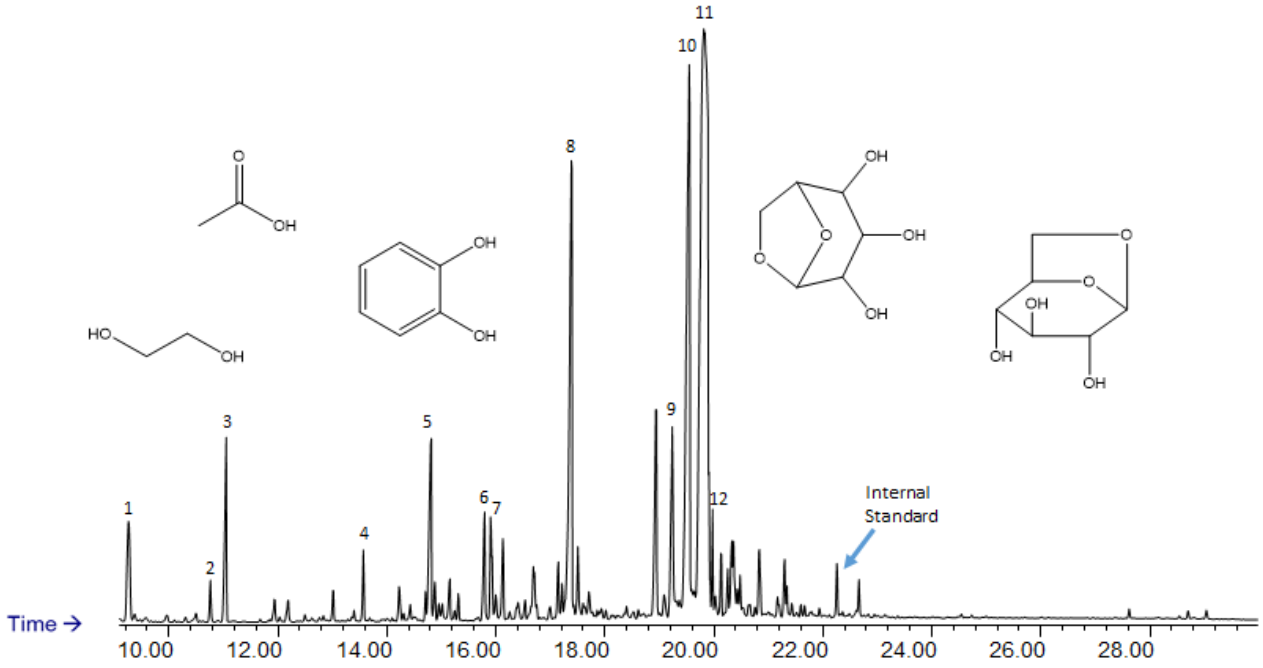


Figure 4.2: fractionation procedure performed on the bio-oil

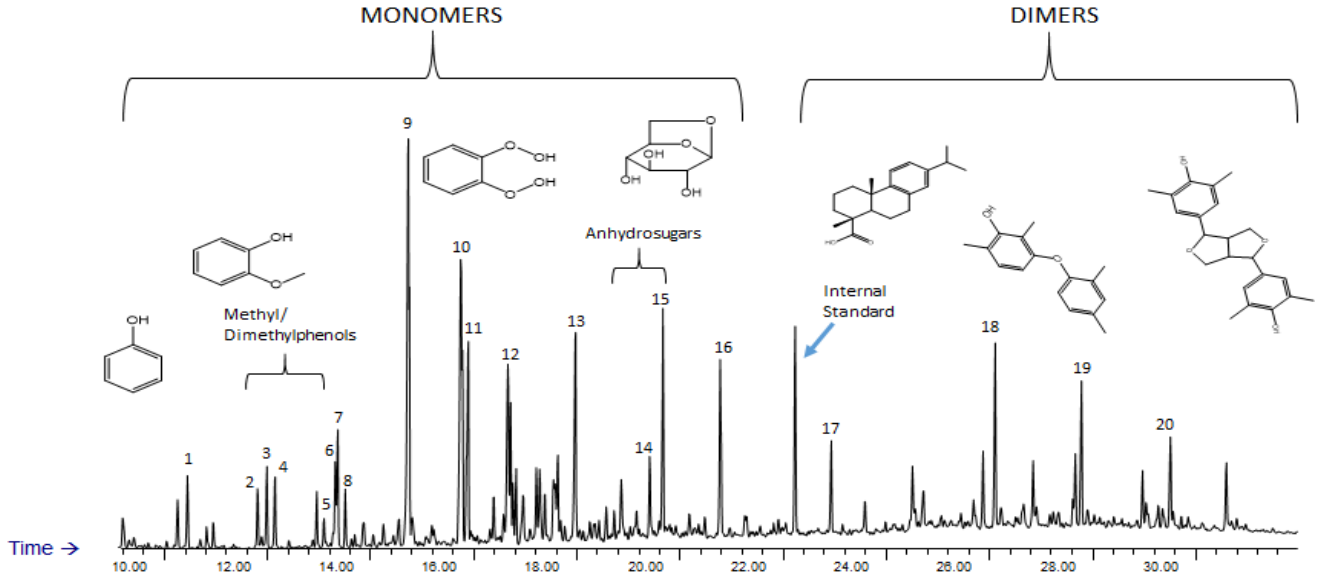
The resulting aqueous phase is a reddish liquid with a density slightly higher than that of water (1.03 kg/L) from the pungent smell of smoke. This fraction was subjected to analysis procedure (by silylation and GC-MS) aimed at determining the main chemical constituents shown in Figure 4.3. In the chromatogram, we can see that the most relevant GC-MS detectable compound is the levoglucosan, typical marker of pyrolysis of lignocellulosic biomass, followed by another anhydrosugar, the mannosan, deriving from hemicellulose. Among lignin markers, main product identified where low molecular weight phenol, pyrocatecol, 3-methyl-1,2-dihydroxy-benzene and 1,3 - dihydroxy-benzene.



N	Compounds	R.T.	Relative Abondance (%)	Absolute Abondance (µg)
1	Ethane-1,2-diol	9.267	2,10	55,34943
2	2-hydroxypropanoic acid	10.766	0,44	11,63501
3	Acetic acid	11.054	2,17	57,18551
4	Butanoic acid	13.572	0,75	19,84904
5	Pyrocatechol	14.812	3,35	88,27064
6	3-methyl-1,2-dihydroxy-benzene	15.791	1,44	38,06889
7	1,3 - dihydroxy-benzene	15.909	1,56	41,2846
8	Phytol	17.390	9,55	251,8894
9	Galactosan	19.305	0,28	7,403572
10	Mannosan	19.548	13,85	365,3569
11	Levoglucosan	19.820	32,16	848,6198
12	1,4 - anhydro-D-glucose	19.975	0,86	22,66012
Internal standard		22.257		16

Figure 4.3: list of the main components constituting the aqueous phase of the bio oil.

The organic phase is a relatively viscous black liquid (a behavior similar to heavy fossil oil) with a density of 1.14 kg/L. This fraction was subjected to GC-MS silylation in order to obtain a description of the main chemical constituents shown in Figure 4.4.



N	Compounds	R.T.	Relative Abondance (%)	Absolute Abondance (µg)
1	Phenol	10.510	1,94	4,7
2	o - cresol	11.867	1,29	3,1
3	m - cresol	12.043	1,97	4,8
4	p - cresol	12.202	1,95	4,7
5	Dimethyl phenol	13.150	0,94	2,3
6	Ethyl/dimethylphenol	13.370	2,58	6,3
7	Guaiacol	13.417	2,79	6,8
8	Hydroxybenzaldehyde	13.562	1,33	3,2
9	1,2 - dihydroperoxybenzene	14.781	17,07	41,5
10	2-(2,3-dimethoxyphenyl)acetic acid	15.800	14,18	34,5
11	3-methyl-1,2-dihydroxy-benzene	15.941	6,71	16,3
12	4-(2-hydroxyethyl)phenol	16.711	6,54	15,9
13	E-isoeugenolo	18.016	7,26	17,6
14	Mannosan	19.453	2,98	7,2
15	Levoglucosan	19.708	5,87	14,3
16	Eugenol	20.815	6,32	15,4
17	Palmitic acid	22.961	3,15	7,7
18	Isopropyl-1,4a-dimethyloctahydrophenanthrene-1-carboxylic acid	26.131	5,96	14,5
19	3-(2,4-dimethylphenoxy)-2,6-dimethylphenol	27.800	5,31	12,9
20	4,4'-(tetrahydro-1H,3H-furo[3,4-c]furan-1,4-diyl)bis(2,6-dimethylphenol)	29.520	3,86	9,4
Internal standard		22.263		16,0

Figure 4.4: list of the main components constituting the organic phase of the bio-oil.

On closer examination, it was found by NMR technique (Nuclear Magnetic Resonance spectroscopy) that pyrolytic lignin produced by intermediate pyrolysis is mainly composed of monomers, dimers and trimers (figure 4.5), which could have interesting applications as binders in

the production of wood pellets or as a substitute for Bisphenol A in epoxy resins and polycarbonates.

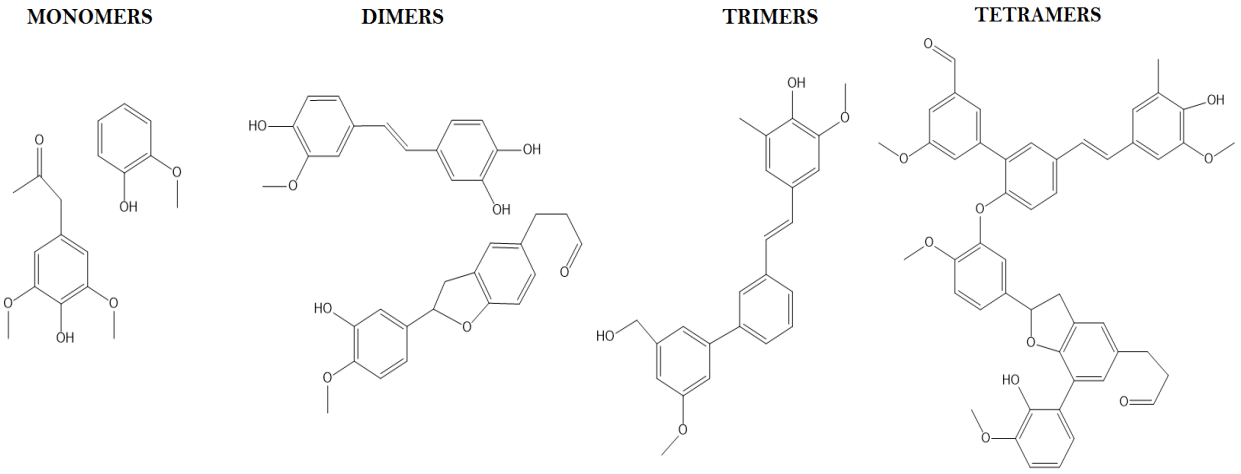


Figure 4.5: the representative compounds of the "pyrolytic lignin".

In tables 4.9 - 4.10 we can see the elemental analysis of the two phases that compose bio-oil derived from wood pellet. Unfortunately, for the analytical technique used for the elemental analysis of the AP, the hydrogen and oxygen data are not accurate.

Ba T. et al in a study of 2004 produced bio-oil from pyrolysis of softwood bark residues that were obtained from a wood shredding plant in Canada. Making a comparison between the aqueous and organic phase from softwood pellets and softwood bark we can see much higher carbon content for the two phases derived from the bark pyrolysis, it's probably due to the fact that softwood bark has a lignin content (richer in C) that is twice that of softwood.

Fagernas L. et al (2012) produced bio-oil from pyrolysis of hardwood bark-free birch residues from a plywood mill. Making a comparison between the organic phase from softwood pellet and hardwood bark-free materials we can see very similar values apart for hydrogen, where there is a slightly higher value for the hardwood material.

Table 4.9 - 4.10: elemental analysis of both aqueous and organic phase.

BIO-OIL Aqueous phase	ELEMENTAL COMPOSITION (%)				
	C	**N**	**H**	**O**	**Ash**
Wood pellet	9.4 ± 0.5	0.3 ± 0	N/D	N/D	0
Softwood bark (Ba T. et al)	51.7	1.2	6.3	40.8	0

Table 4.10

BIO-OIL Organic phase	ELEMENTAL COMPOSITION (%)				
	C	**N**	**H**	**O**	**Ash**
Wood pellet	54.2 ± 2.7	0.2 ± 0.1	3.9 ± 1.5	41.0 ± 1	0.7 ± 0.2
Softwood bark (Ba T. et al)	72.7	0.7	7.1	19.5	0.8
Hardwood free-bark birch (Fagernas L. et al.)	57.6	0.3	7.3	35	-

Table 4.11 shows the comparisons of the two aqueous phases in terms of TOC (Total Organic Carbon), TC (Total Carbon) and COD (Chemical oxygen demand). Note that the inorganic carbon content in both APs is irrelevant.

Table 4.11: TOC, TC and COD parameters of the APs deriving from wood pellet and hardwood free-bark birch.

	Wood pellet A.P.	Hardwood free-bark birch A.P (Fagernas L. et al. 2012)
TOC, g L^{-1}	130	130
TC, g L^{-1}	130	130
COD, g L^{-1}	342	340

Figure 4.6 shows the main components of AP and OP of hardwood free-bark birch; comparing it with the AP and OP of wood pellets shows in figure 4.7 we can see that the water content in the AP is almost identical while observing a lower value for sugars and a higher value for VFAs, instead, in the OP, we can notice a higher water content.

Both aqueous and organic fractions were subjected to Karl Fischer analysis to determine its content in water (figure 4.7). It is possible to detect how the AP is mainly formed of soluble carbohydrates (cellulose oligomers) and a small quantity of volatile fatty acids, while the OP, which contains a modest amount of moisture, is mainly composed of "pyrolytic lignin", or lignin oligomers, insoluble in water and with variable composition.

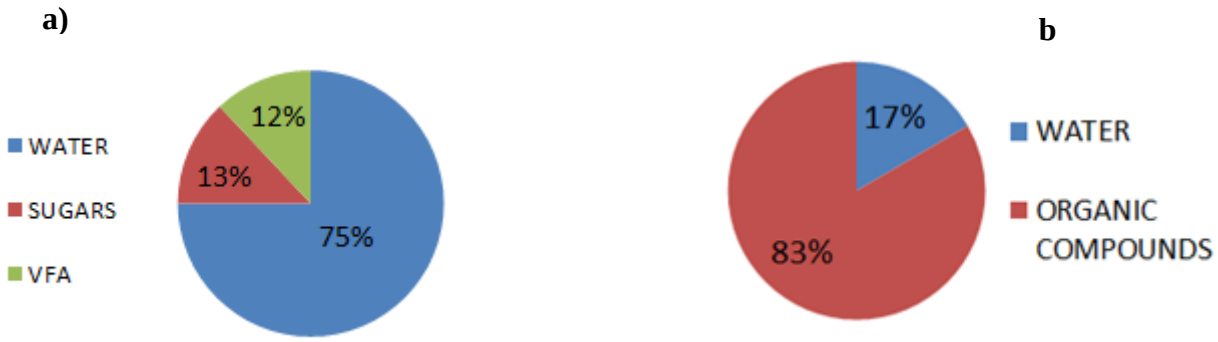


Figure 4.6: composition of the AP (a) and OP (b) of the bio-oil from hardwood free-bark birch (fagernas l. et al.).

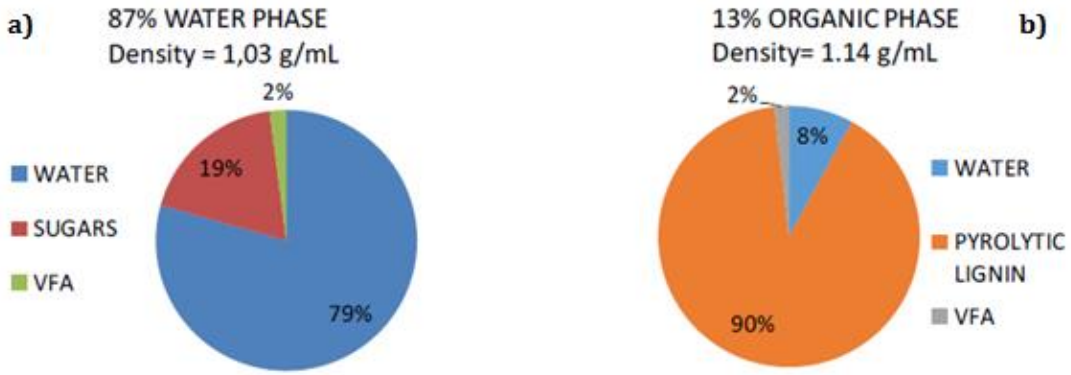


Figure 4.7: composition of the AP (a) and OP (b) of the bio-oil from wood pellet.

BIO-GAS

As mentioned above, the gaseous fraction of the pyrolysis process (syngas) once produced is bubbled into R1 and R2 (sequentially) for the digestion phase where hydrogen and carbon monoxide (and other minor impurities) should be biologically converted into the most thermodynamically stable products (CH_4 and CO_2).

Of the 24 kg of total biomass inserted in the pyrolyser 5.96 kg (24.8% yield) was converted into a raw pyrolysis gas (sampled before the R1) and finally upgraded biogas (thereafter called pyrobiogas) with a composition change represented in figure 4.8 (A before, B after R1+R2).

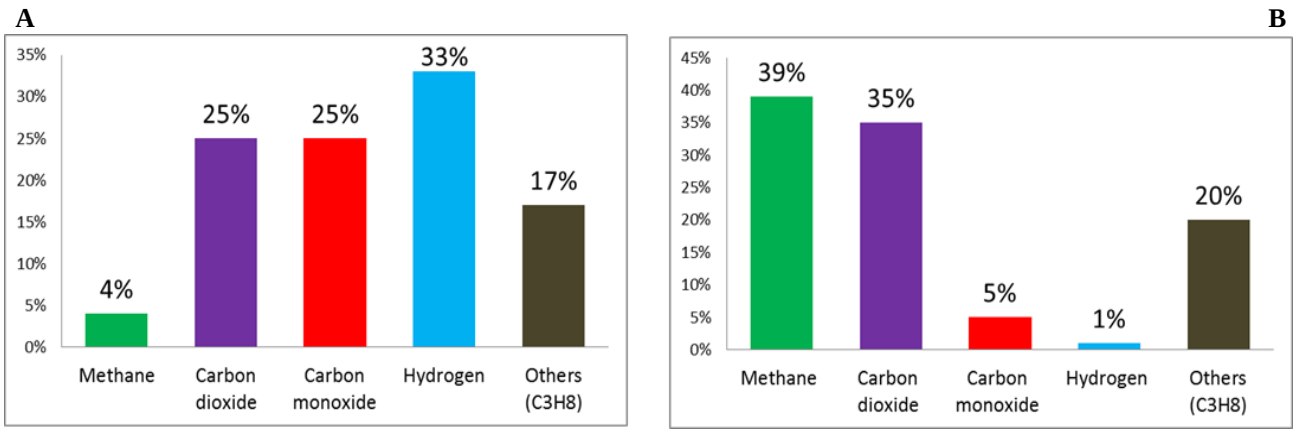


Figure 4.8: A shows the composition of the syngas after pyrolysis of wood pellet, B displays the pyrobiogas composition obtained from the Py-AD system after bacterial digestion.

As expected, the biological conversion drastically modifies the composition of the raw pyrolysis gases (syngas + impurities). Main change were the increases of the concentration of methane by 10 times and CO_2 by 40%, going from 4 to 39% and from 25 to 35% respectively, while CO decreases by 80% and H_2 of 97% going from 25 to 5% and 33 to 1%, respectively. Small hydrocarbons remain almost unchanged with a slight increase of 18%, from 17 to 20%, probably due to a decrease of volume due to reactions above (e.g. $4H_2+CO_2$ ➔ CH_4+2H_2O decreases by five times the moles of permanent gases).

Looking to the trend in final pyrobiogas concentration, the resulting gas has reached a relatively steady state composition in about 15 days of experiment (figure 4.9), with contents of CO and residual H_2 (< 5%) but still an important contribution by the C2-C4 compounds in biogas that are substantially undigested by both R1 and R2. The minimum content of CO and H_2 was 0.1% (1000 ppm) with the system in steady state, with considerable fluctuations in the composition of the gas, probably due to a certain degree of backflow (in turn due semi-continous operation of pyrolyzer).

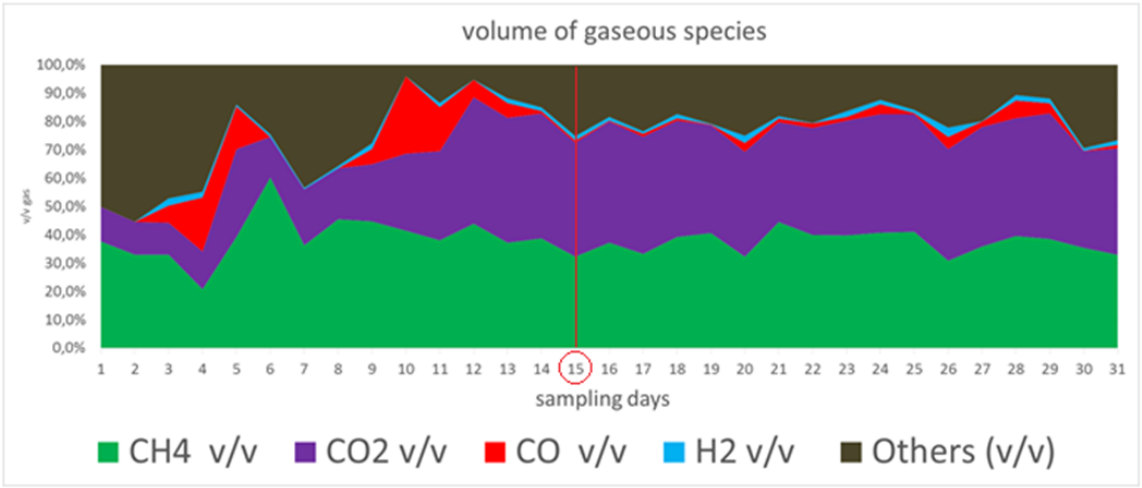


Figure 4.9: concentration of the gaseous species during the experiment.

When fully operational, the plant was able to process a quantity of biomass equal to 1 kg per day, equal to a specific capacity of 1.6 kg/m^3 digester. In light of the data obtained and considering the digestion of gas only, it is possible to estimate a pyrobiogas production (with methane content of 50%) equal to 170 Nm^3/ton (table 4.12).

Table 4.12: balance of matter and composition of the gaseous product obtained during the whole experiment.

Update date	18/07/2017
Experiment duration	50
Pyrolized biomass (kg)	23.98
Total moisture in the biomass (kg)	0.48
Bio-oil produced (kg)	7.81
Bio-char produced (kg)	7.62
Bio-gas produced (kg)	5.96
Hydrogen (kg)	0.004
Methane (kg)	1.16
Carbon dioxide (kg)	2.91
Carbon monoxide (kg)	0.007
Others (C_3H_8) (kg)	1.63
Bio-gas produced (m^3)	4.19
Biogas density (kg/m^3)	1.42

EVALUATION OF THE SOLUBILITY BEHAVIOR OF PYROLYTIC LIGNIN

In order to identify possible applications, the organic fraction of the bio-oil was submitted to solubility tests in various organic solvents (dimethylcarbonate DMC, chloroform $CHCl_3$, tetrahydrofuran THF, propylene carbonate PC) in order to evaluate possible applications for the synthesis of biopolymers and biofuels (table 4.13). The ability of these solvents to solubilize pyrolytic lignin (LP) was determined by adding aliquots of them to the organic fraction of the bio-oil until the total miscibility was observed (figure 4.10).

Figure 4.10: the four pyrolytic lignin samples flanked by their respective solvents.

Table 4.13: list of the solvents and respective amount of pyrolytic lignin tested.

N° VIAL	SOLVENT	PYROLYTIC LIGNIN (mg)
C1	DMC	131
C2	PROPYLENCARBONATE	99
C3	THF	121
C4	CHLOROFORM	138

For PC and THF, a complete solubility was observed immediately after the first 0.5 mL of solvent was inserted. For samples DMC and $CHCl_3$, up to 8.5 ml of solvent were necessary for being able to note a partial solubility of LP (table 4.14).

Table 4.14: solubility of the pyrolytic lignin to the four solvents examined.

N° VIAL	SOLVENT	SOLUBILITY w/w
C1	DMC	<1 %
C2	PROPYLENCARBONATE	>20 %
C3	THF	>20 %
C4	CHLOROFORM	>1 %

A similar experiment was performed to separate and then analyze the soluble and insoluble phase of LP in various solvents (DMC, H_2O and ethanol). In this case, the organic solvent phase was withdrawn and then dried under a constant flow of nitrogen to determine the soluble fraction (table 4.15).

Table 4.15: fractionation of the pyrolytic lignin in the soluble and insoluble phase carried out by means of the three solvents examined.

N°VIAL	SOLVENT	PL SAMPLE (mg)	SOLUBLE FRACTION (mg)	INSOLUBLE FRACTION (mg)
C1	DMC	109	52.7	56.7
C2	H_2O DIS.	128	4.7	124.1
C3	ETHANOL	108	78.8	29.2

Table 4.14 shows the ineffectiveness of DMC and water as solvents for LP. In fact, while DMC leads to a separation of about half between soluble and insoluble fraction, water shows how 98% of the LP sample remains in the insoluble fraction. On the other hand, ethanol acts very effectively as a solvent for LP leading to dissolution of 73% of the LP sample.

The 6 samples (3 soluble fractions and 3 non-soluble fractions) were then analyzed by GC-MS after silylation.

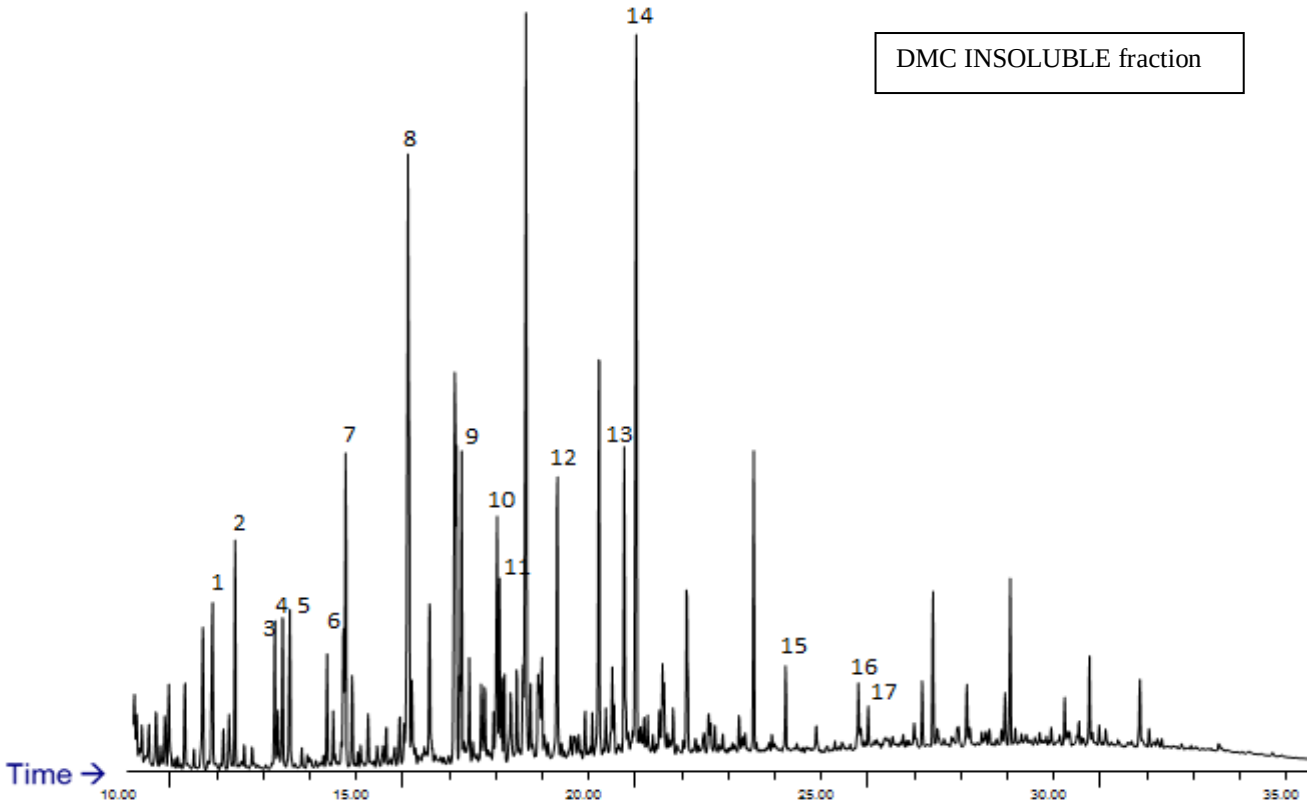


Figure 4.11: chromatogram of the most insoluble compounds in DMC.

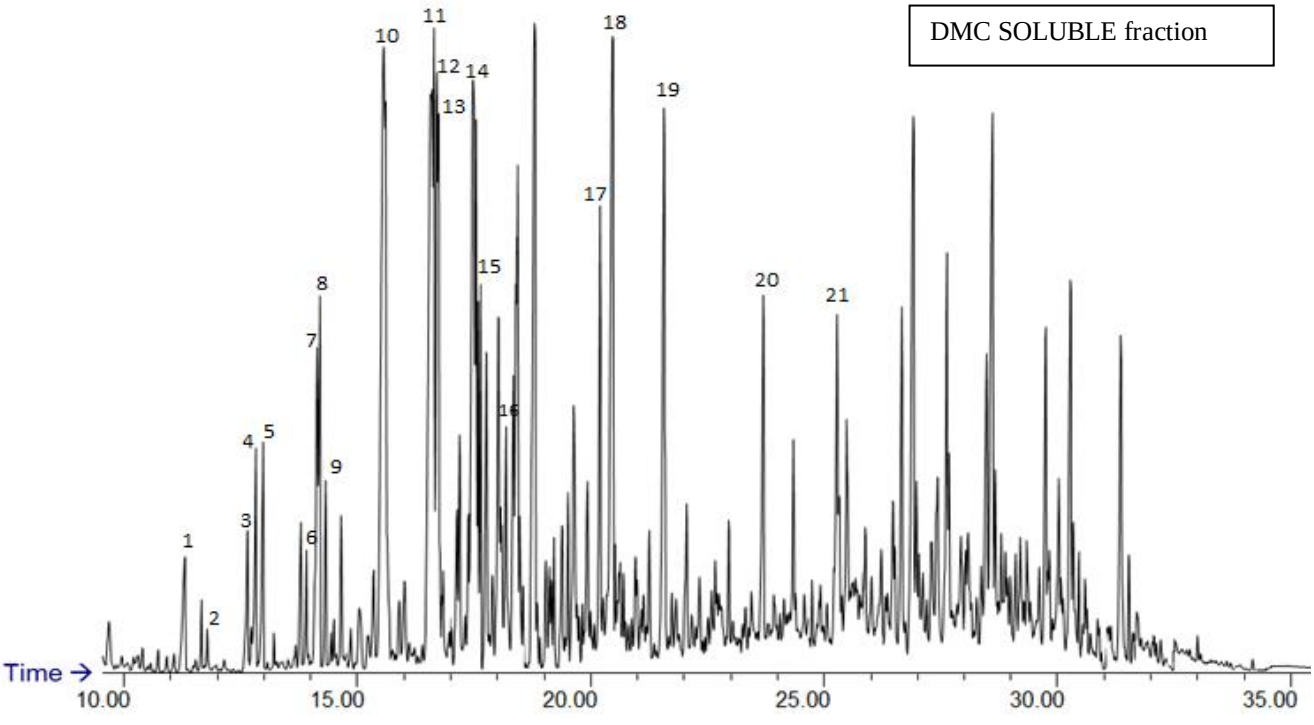


Figure 4.12: chromatogram of the most soluble compounds in DMC.

Table 4.16: relative abundance and retention time of the compounds both in soluble and insoluble phase.

DMC INSOLUBLE FRACTION				DMC SOLUBLE FRACTION			
N.	**Compounds**	**R.T.**	**Relative Abondance (%)**	**N.**	**Compounds**	**R.T.**	**Relative Abondance (%)**
1	Phenol	10.807	1,32	1	Phenol	10.857	0,34
2	Acetic acid	11.296	1,26	2	Acetic acid	11.339	0,07
3	o - cresol	12.150	0,86	3	o - cresol	12.201	0,29
4	m - cresol	12.319	0,96	4	m - cresol	12.377	0,40
5	p - cresol	12.474	1,13	5	p - cresol	12.535	0,43
6	4-ethylguaiacol	13.632	0,88	6	Ethylphenol	13.462	0,20
7	Guaiacol	13.680	1,63	7	Dimethylphenol	13.690	0,73
8	4-methyl-guaiacol	15.024	5,73	8	Guaiacol	13.749	0,54
9	2-ethylguaiacol	16.180	2,22	9	Dimethylguaiacol	13.874	0,32
10	2-(2-hydroxyethyl)phenol	16.944	1,78	10	Pyrocatechol	15.115	3,43
11	4-(hydroxymethyl)phenol	16.997	0,97	11	4-ethylguaiacol	16.191	0,89
12	4-(2-E-propenil)guaiacol	18.242	2,08	12	Catechol	16.256	1,01
13	Mannosan	19.687	2,22	13	Methylcatecol	16.291	0,90
14	Levoglucosan	19.768	0,26	14	3,4-dimethyl-1,2-dihydroxy-benzene	17.031	2,03
15	Palmitic acid	23.169	0,65	15	Eugenol	17.136	0,42
16	Oleic acid	24.738	0,72	16	E-isoeugenol	17.737	0,65
17	Stearic acid	24.950	0,43	17	Mannosan	19.751	1,03
				18	Levoglucosan	20.021	2,50
				19	Vanillyl-propanol	21.118	1,80
				20	Palmitic acid	23.245	1,09
				21	Oleic acid	24.823	1,26

Table 4.16 shows how aromatic compounds tend to remain more in the insoluble phase. With regard to anhydrosugars we can see how mannosan is more present in the insoluble phase while levoglucosan is more concentrated in the soluble phase.

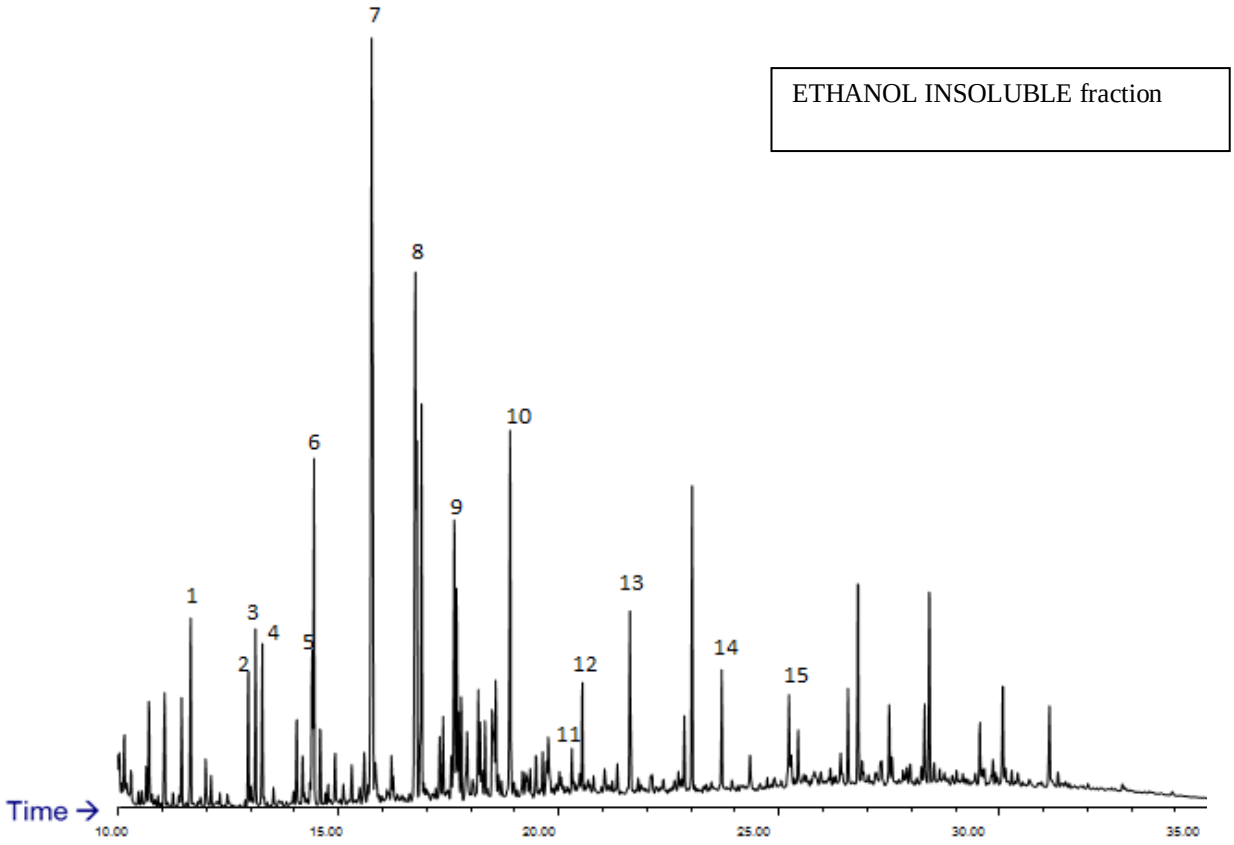


Figure 4.13: chromatogram of the most insoluble compounds in Ethanol.

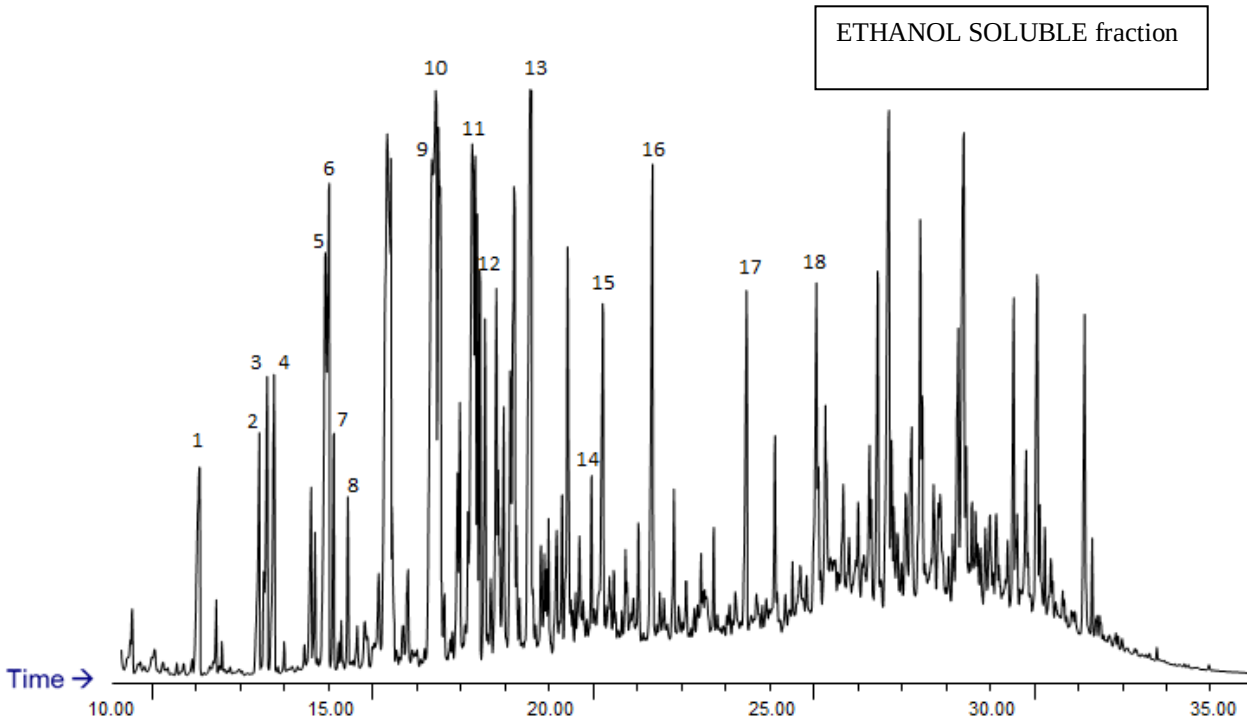


Figure 4.14: chromatogram of the most soluble compounds in Ethanol.

Table 4.17: relative abundance and retention time of the compounds both in soluble and insoluble phase.

ETHANOL INSOLUBLE FRACTION					ETHANOL SOLUBLE FRACTION			
N.	**Compounds**	**R.T.**	**Relative Abondance (%)**		**N.**	**Compounds**	**R.T.**	**Relative Abondance (%)**
1	Phenol	10.795	1,49		1	Phenol	10.866	0,85
2	o - cresol	12.138	1,08		2	o - cresol	12.223	0,63
3	m - cresol	12.305	1,27		3	m - cresol	12.401	0,69
4	p - cresol	12.463	1,27		4	p - cresol	12.560	0,81
5	3,5 - dimethylphenol	13.624	1,37		5	3,5-dimethylphenol	13.719	1,46
6	Guaiacol	13.669	2,32		6	Guaiacol	13.801	1,28
7	4 - methyl - guaiacol	15.014	9,60		7	Ethylphenol	13.909	0,48
8	3 - methyl - 1,2 - dihydroxy - benzene	16.030	7,43		8	dimethylphenol	14.230	0,35
9	3,4-dimethyl-1,2-dihydroxy-benzene	16.175	3,31		9	3 - methyl - 1,2 - dihydroxy - benzene	16.134	2,28
10	Eugenol	18.238	2,92		10	4 - ethyl - guaiacol	16.222	2,28
11	Mannosan	19.765	0,17		11	3,4-dimethyl-1,2-dihydroxy-benzene	17.047	2,26
12	Levoglucosan	19.919	0,93		12	Eugenol	17.160	0,63
13	Vanillyl-propanol	21.029	1,88		13	Z - isoeugenol	18.374	2,74
14	Palmitic acid	23.168	1,16		14	Mannosan	19.745	0,48
15	Oleic acid	24.737	1,12		15	Levoglucosan	20.002	1,46
					16	Vanillyl - propanol	21.122	1,58
					17	Palmitic acid	23.254	1,14
					18	Olei acid	24.833	1,36

Table 4.17 shows a situation similar to the previous one, with the aromatic compounds mostly present in the insoluble phase, but as regards the anhydrosugars it can be noted that Mannosan divides more in the soluble phase while Levoglucosan is present in very similar concentrations in both fractions.

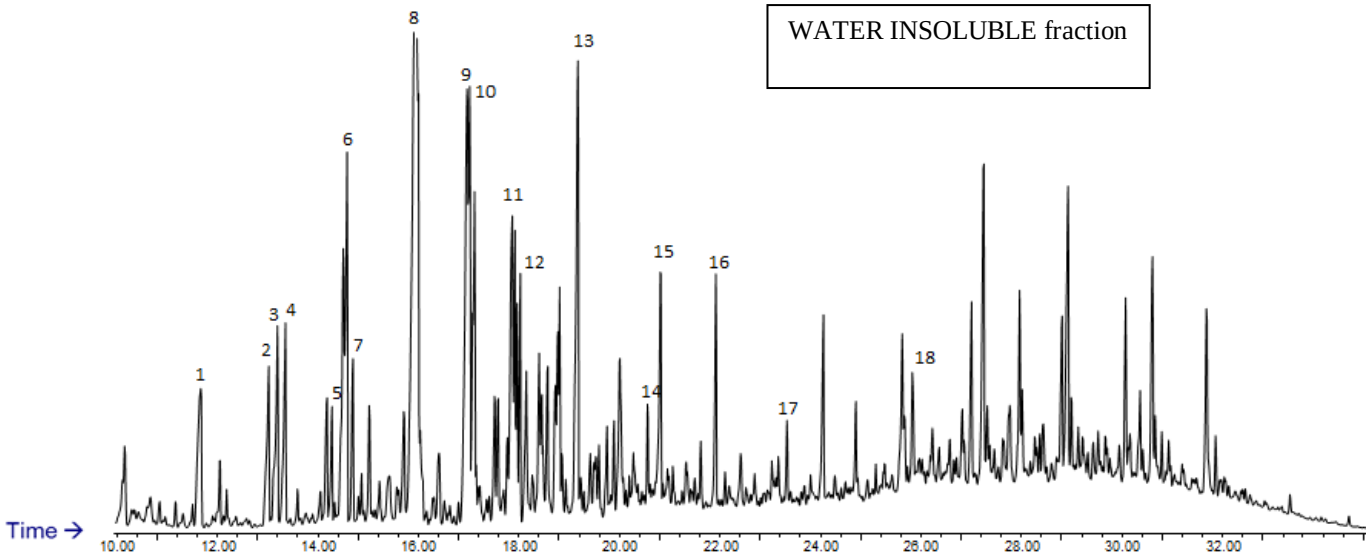


Figure 4.15: chromatogram of the most insoluble compounds in water.

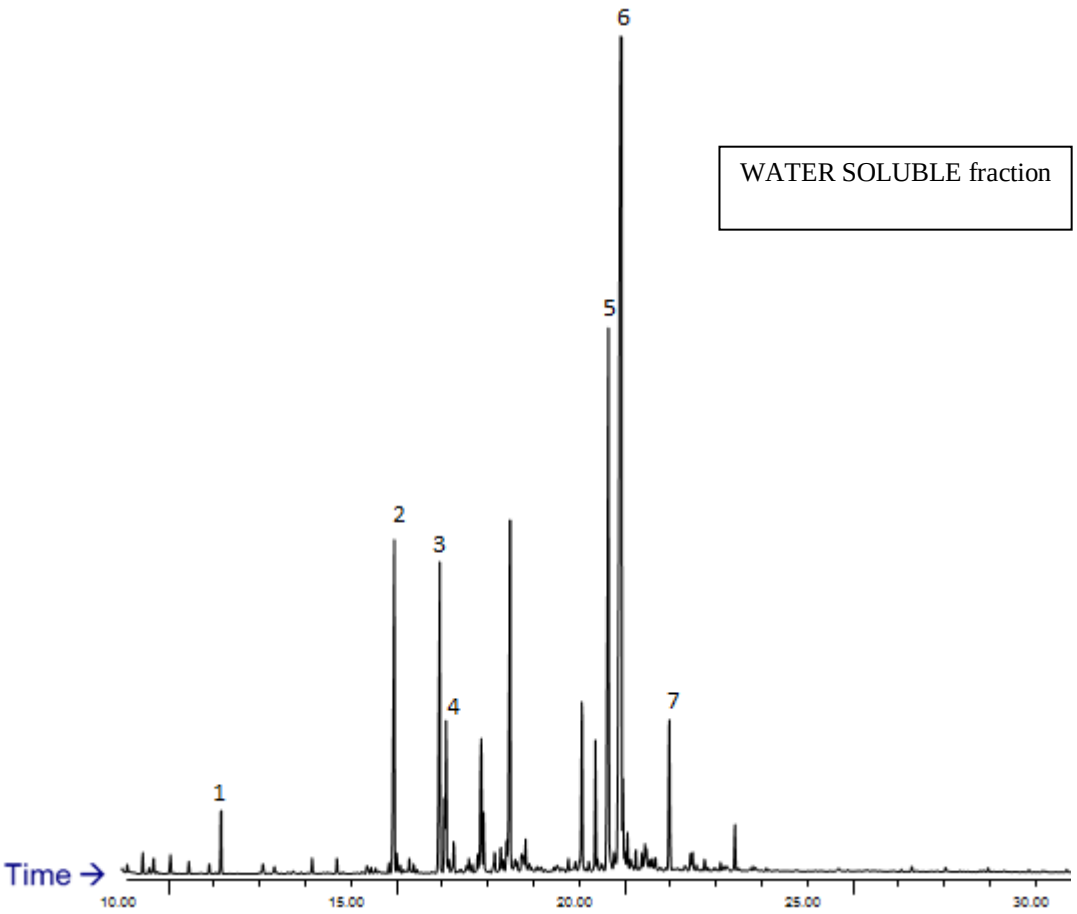


Figure 4.16: chromatogram of the most soluble compounds in water.

Table 4.18: relative abundance and retention time of the compounds both in soluble and insoluble phase.

WATER INSOLUBLE FRACTION					WATER SOLUBLE FRACTION			
N.	**Compounds**	**R.T.**	**Relative Abondance (%)**		**N.**	**Compounds**	**R.T.**	**Relative Abondance (%)**
1	Phenol	10.851	0,89		1	2 - hydroxy - acetic acid	11.278	0,80
2	o - cresol	12.202	0,76		2	1,2 - dihydroxy - benzene	15.050	5,06
3	m - cresol	12.379	0,88		3	3 - methyl - 1,2 - dihydroxy - benzene	16.041	4,53
4	p - cresol	12.536	0,86		4	1,3 - dihydroxy - benzene	16.145	0,97
5	3,5 - dimethylphenol	13.461	0,41		5	1,6 - anhydro - D - mannopyranose	19.717	9,20
6	Guaiacol	13.762	1,20		6	Levoglucosan	19.993	25,98
7	Ethylphenol	13.878	0,59		7	Vanillyl - propanol	21.046	2,49
8	1,3 - dihydroxy - benzene	15.104	4,39					
9	3 - methyl - 1,2 - dihydroxy - benzen	16.110	2,52					
10	4 - ethyl - guaiacol	16.159	1,23					
11	Eugenol	17.106	0,52					
12	Acetovanillone	17.168	0,65					
13	E-isoeugenolo	18.319	2,29					
14	1,6 - anhydro - D - mannopyranose	19.712	0,42					
15	Levoglucosan	19.969	1,29					
16	Vanillyl- propanol	21.072	0,96					
17	Palmitic acid	23.218	0,94					
18	Stearic acid	24.998	0,80					

In Table 4.18 it is easy to see that only a small part of the compounds is present in the soluble phase. Among these, anhydro sugars are the ones that most compose the chromatogram, reaching 35% of the total areas. Considering the chemical composition of the pyrolytic lignin, and according to its extremely low water solubility, this fraction, being not suitable for biological processing (e.g. anaerobic digestion) was envisaged for possible applications for the synthesis of bio based materials or, possibly, liquid fuels.

ANAEROBIC DIGESTION OF THE AQUEOUS PHASE OF BIO-OIL

Aqueous phase of bio-oil (AP) consists in a water solution with low amount of dissolved compounds. According to chemical properties of AP, anaerobic digestion was tested, in presence of biochar, for the obtainment of additional biogas from this portion of pyrolysis product. Since no significant quantities of compounds of chemical interest were detected, an UASB (*upflow anaerobic sludge blanket reactor*, figures 4.17), filled with 10% of biochar co-produced by pyrolysis, was developed to convert its organic component into biomethane.

An anaerobic digester (100 ml) was inoculated with digestate from sewage sludge, daily fed with other digestate and admixed with 10 g of finely grinded biochar, so as to create a support material for the enhancement of pyrolysis product digestion, as verified from numerous studies carried out on pyrolysis liquids (Mumme et al., 2014; Torri and Fabbri, 2014). The AP in pure form was gradually added to the reactor. Initially the reactor was given an organic load equal to 0.25 gCOD L^{-1} d^{-1} corresponding to 1 g L^{-1} g^{-1} of pyrolysis liquid, obtaining a production of methane equal to or higher than the theoretical yield (probably due to the biodegradation of a portion of the biochar).

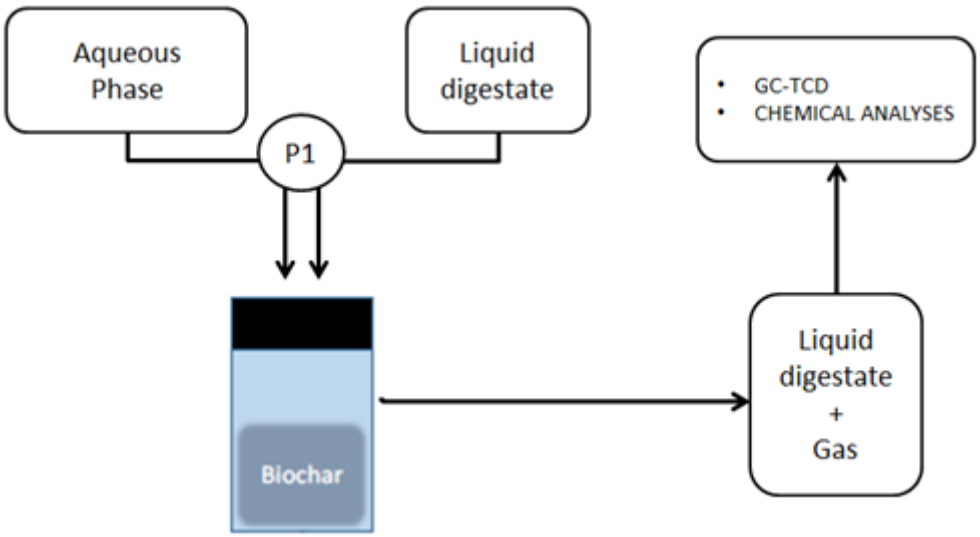


Figure 4.17: scheme of the experimental system used for anaerobic digestion.

Subsequently, the organic load was raised up to values of 2.5 gCOD L^{-1} d^{-1} and, following phenomena of slight intoxication (contemporaneous with a lowering of pH) reported to a value of 1.25 gCOD L^{-1} d^{-1} which proved to be sustainable in the long term. In the final phase of the study, the yield of biomethane was equal to 40% of the theoretical yield, with an additional production equal to 20% of VFA (volatile fatty acids).

The chemical analysis of the aqueous phase before and after the digestion (figure 4.18) showed that there is an effective degradation of the pyrolytic compounds (mainly levoglucosan) present in the fraction, confirming the general biodegradability of the pyrolysis products even in the presence of the aforementioned toxicity phenomena (limiting the volumetric conversion rate).

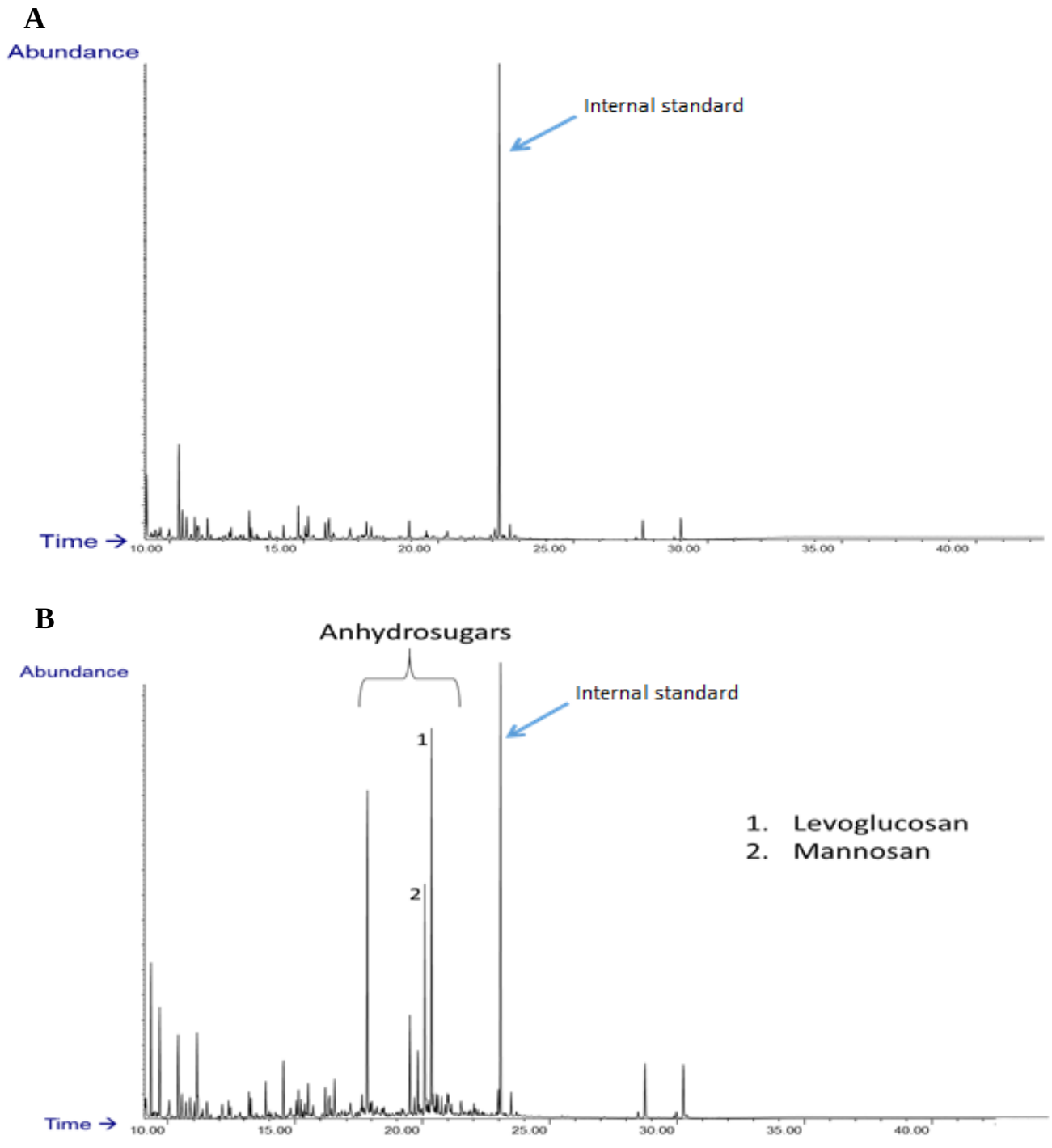


Figure 4.18: shows two chromatograms of the AP. (A) displays the composition of the AP of the bio-oil at 5% concentration (1.25 gcod l^{-1} d^{-1}) before the anaerobic digestion. (B) shows the composition of the AP of the bio-oil at 5% concentration (1.25 gcod l^{-1} d^{-1}) after the digestion carried out by the microorganisms.

In conclusion, it was therefore considered 1.25 gCOD L^{-1} d^{-1} (5 $g_{aqueous\ phase}$ L^{-1} d^{-1}) the maximum conversion rate for the aqueous phase and a normal yield of methane equal to 60% (40 + 20) of the theoretical biomethanation potential (figure 4.19).

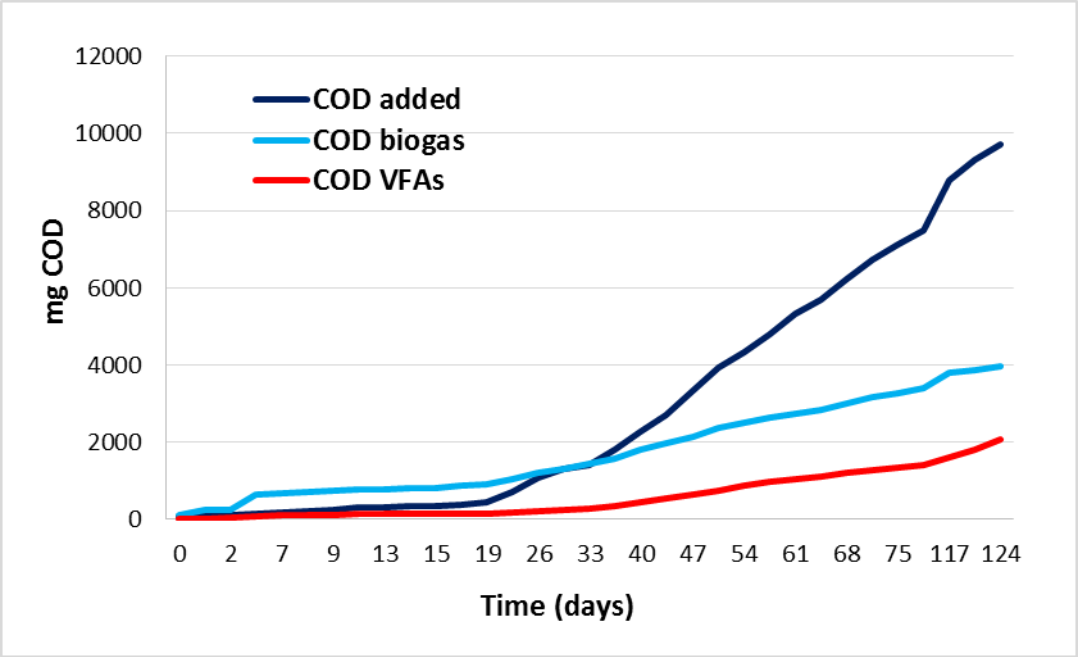


Figure 4.19: trend of the production of methane and VFA in the continuous conversion system fed with the AP resulting from the pyrolysis of wood.

CARBON BALANCE OF AP DIGESTION

The analysis of the total organic carbon allows us to verify how the incoming carbon has been distributed in the various products. In table 4.19 it is possible to see the carbon concentrations of the aqueous phase of the bio oil, of the bacterial inoculum and finally the digested liquid at the exit of the reactor.

Table 4.19: carbon concentrations in the samples analyzed.

	Carbon content (g/L)	RSD (%)
Aqueous phase bio-oil	103	1.98
Digestate from sewage sludge	1.02	0.84
Digested liquid on exit	3.04	1.35

6.2 g of added carbon, composed of the aqueous phase of the bio-oil and the digestate, were calculated. After the anaerobic digestion carried out by the microorganisms, a value of 3.6 g of carbon in the outlet liquid was found, corresponding to 56.7% of the total incoming, composed for 11.2% by VFA and for 45.5% by compounds not degraded.

The carbon converted into biogas is about 17% of the total, corresponding at 1.05 g. The loss of carbon detected at the exit of the reactor (about 1.6 mg) is probably attributed to the ability of the biochar to sequester CO_2, especially in the early phases of the experiment, where the output of a biogas was particularly rich in CH_4 and poor in CO_2 (figure 4.20).

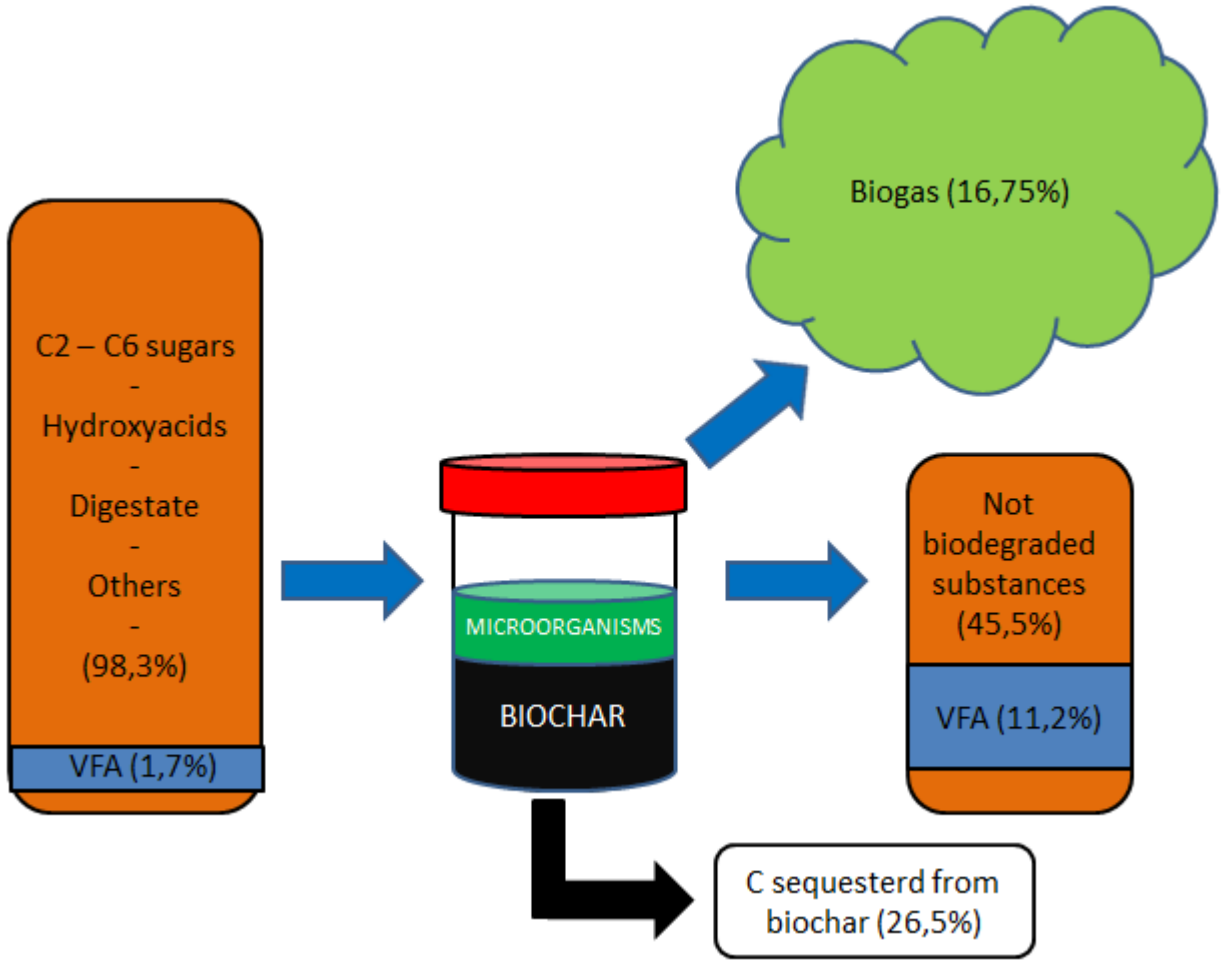


Figure 4.20: carbon inputs and outputs during the digestion of the AP of the bío-oil.

The necessary functional elements have been identified and sized, along with the operating returns and the typical capital costs. The figure 4.21 shows the process diagram for the conversion of wood biomass (e.g. pruning) into biochar and renewable electric energy.

The process involves drying the incoming material. Considering the low density of the material, the drying can be carried out through a very simplified static system, consisting of a large external square (also used as a storage area for incoming material) fluxed with the hot exhaust gases of the cogenerator and heated by a hot water circuit (also obtained from the cogenerator) [3], [5]. The dried material is then mechanically transferred to the pyrolyser [1] heated to 350°C in the initial part and 500°C in the final part through the fumes deriving from the combustion of a portion of the generated Pyrobiogas (the final gaseous product) [4].

The pyrolysis determines the production of biochar (subsequently cooled to 120°C and stored for sale) and of vapor phase pyrolysis products, subsequently cooled to 90°C. After cooling, it has the partial condensation of a pyrolysis liquid, consisting of an aqueous phase and a high-density organic phase. The aqueous phase, together with the aerosol not condensed during cooling, are administered to the digester [2], while the organic phase (made of pyrolytic lignin) could be used as a binder (e.g. binder for pellets) or in the synthesis of biobased polymers (e.g. liquid wood). In this phase, the excess pyrolysis water, together with the bacterial component of the digestate formed, is sent to a small sludge dryer [6] which allows the recirculation at the head of the process [7].

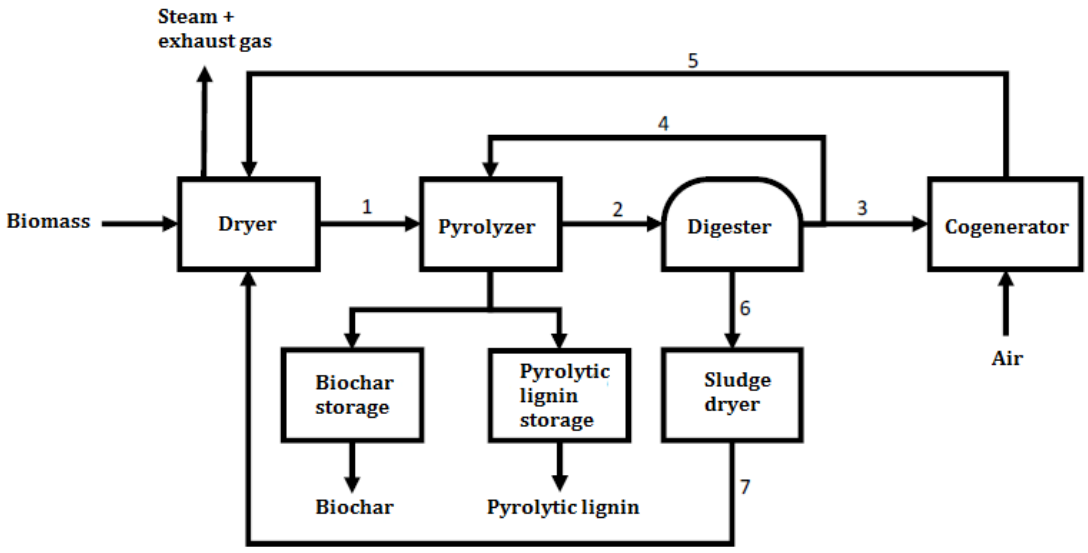


Figure 4.21: process scheme

From the functional point of view, the plant turns out to be energetically self-sufficient (table 4.20), with the generation of electricity, low temperature heat (< 100 °C), biochar and pyrolytic lignin. These two secondary products, despite being relatively new products, may hopefully have relevant markets (Pratt and Moran, 2010; Leach et al., 2012; Czernik and Bridgwater, 2004).

Considering the final price values obtainable in agricultural applications, and considering the possible assessment of biochar as a carbon storage material (which could be subsidized in the future), part of the benefit of the plant is therefore represented by the co-production of biochar. As far as pyrolytic lignin is concerned, although potentially a high value material, as it can be used for the synthesis of polymers, it is necessary to identify consolidated applications or to foresee their use as a low cost binder for wood pellets. This application would still have a significant value (> € 300/ton), and given the relatively low yield, the supply would not easily be able to saturate the demand.

Table 4.20: characteristic elements, sizing and energy parameters of the elements of a Py-AD plant, powered by pruning, capable of handling 50,000 tons of material per year

	Size (m^3)	Area (m^2)	Thermal watts (average)	Temperature (°C)	Electric watts (average)
Dryer	11.4	11.4	-1,372,332	90	0
Pyrolyser	3	6	206,191	350	-3995
Digester	4021	1340	398,065	40	-20103
Cogenerator	38.5	15	2,488,896	120	1626119
Biochar storage	200	67	181,427	100	-1949
Pyrolytic lignin storage	14.4	4.8	14,208	80	0
Sludge dryer	2.3	2.3	-453,965	90	-1348
Accessory structures and connections		289			
Total	4291	1446	1,462,490		1,598,723

Table 4.21: fixed costs and operational expense (OPEX) of a 50,000 tons/year biomass plant (40% humidity) assuming intermediate values for biomass (absence of tariff income), biochar and pyrolytic lignin

	Capital cost (€)		Quantity	Unit value	OPEX (€)
Dryer	259'878	Biomass (ton)	-50,000	0	-
Pyrolyser	2'631'581	Elect. En. (MWh el)	14,005	75	1'050'361
Digester	1'862'661	Heat (MWh th)	12,811	35	448'399
Cogenerator	794'104	Biochar (ton)	14,633	70	1'024'306
Biochar storage	35'137	Pyrolytic lignin (ton)	1,054	700	737'977
Pyrolytic lignin storage	5'905	Transports (ton)	15,687	-6	-94'123
Sludge storage	1'045'461	Personnel	-26,280	24	-630'720
Accessory structures and connections	995'209	Maintenance	7629938	-0.05	-381'497
Total	7'629'938			**Total**	2'154'703

Considering the fixed and operating costs shown in table 4.21, it is possible to outline different scenarios depending on the selling price of the products (biochar, electricity and pyrolytic lignin) and the possible presence of an entry tariff. Scenarios 1 to 4 assume the absence of a transfer fee for pruning, which are therefore considered biomass. In this case, being the biomass starting matrix, the solid product of the process, according to the law can be considered biochar, for which a value ranging between 70 and 10 €/ton has been assumed. Scenario 5 shows instead the situation that is created if the pruning is considered waste, and therefore characterized by a transfer fee (table 4.22). In this case it would not be possible to use the biochar in the agricultural field and for this it has been assumed a value of about 10 € / ton, equivalent to an energy use as a substitute for the coal fossil. All scenarios, excluding scenario 4 (pessimistic without incentives and no application of biochar in agriculture) produce a return on investment of less than 5 years. If the biochar produced by the plant is not characterized by a significant value (and therefore using it as a substitute for fossil coal) and electricity is sold at the current market price (no incentive or self-consumption), the time to return the investment would be 7 years (figure 4.22).

Table 4.22: economic values characteristic of the 5 reference scenarios used to evaluate the economic performance of the plant.

	Entry fee (€/ton)	Electric energy (€/ton)	Biochar (€/ton)	Pyrolytic lignin (€/ton)
(1) Normal scenario	0	75	70	700
(2) Partly incentivized scenario or self-consumption of electricity	0	120	70	700
(3) Partly incentivized or self-consumption scenario electricity, low value of co-products	0	120	10	300
(4) Pessimistic scenario	0	75	10	300
(5) Pruning = waste scenario	20	120	5	300

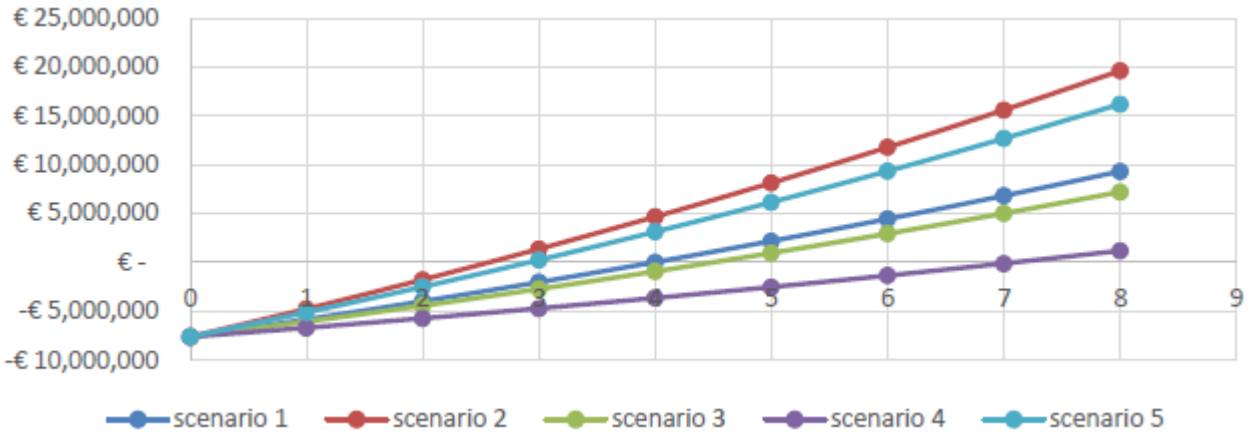


Figure 4.22: calculation of the time to return the investment for a plant of 50,000 tons / year of pruning. An interest rate of 8% per year is assumed.

CHAPTER 5: CONCLUSIONS

The Py-AD system, in the light of the studies carried out, has proven to be a valid technology which, by combining two technologies for the treatment and enhancement of organic material (pyrolysis and anaerobic digestion), has led to the formation of a mixture of pyrolysis products able to be digested without the occurrence of toxicity phenomena, although unfortunately this did not remain free from some critical issues.

Examining the results obtained, and considering the normative certainties, the production of biomethane starting from an integrated pyrolysis-digestion process is technically not feasible with the technologies tested in the present study. The main problems encountered are:

- Presence of small hydrocarbons (C_nH_{2n+2}, compounds analogous to LPG) in the obtained biogas. Their presence, while enriching the calorific value of the gas, could cause problems in the upgrading phase with certain separation systems.

- Residual quantity of carbon monoxide and hydrogen. The content of carbon monoxide, although reduced (around 0.1 - 1% in the final phase of the study), is not low enough to allow a possible upgrading of biogas to biomethane. The phenomenon is probably due to the stop-and-go of the plant and its small size that determine a significant diffusion of gas with the backflow phenomenon. With the plant in question it is not reasonably possible to further decrease (and in a stable way) the content of carbon monoxide and hydrogen below 1%.

- Difficult regulatory framework for a process that includes pyrolysis and digestion (in the case of biomethane legislation).

- Insufficient heat at low and high temperature able to feed the pyrolysis process and the drying of the starting material (characterized by moisture content between 30% and 60%).

Despite this, the gas produced by the Py-AD process, although not suitable for the production of biomethane, is substantially a mixture with characteristics very close to some natural gas, without condensable contaminants, with a higher calorific value than that found in biogas and a reduced hydrogen content; therefore, although it cannot be considered a biogas in all respects, it is characterized by a calorific value (per unit of volume) higher than that of a conventional biogas. In terms of the equivalent biomethane produced (or MWh ton^{-1}) the plant yield would be close to 160

Nm^3 ton^{-1} (1.8 MWh ton^{-1}), equal to 40% of the calorific value of the material; a very interesting datum from the point of view of conversion effectiveness.

Another critical point is the high content of PAHs detected in the biochar produced by the Py-AD system, this is probably due to the "stop & go" to which the system has often been subjected, where, each time the pyrolyser is turned on, the fumes derived from pyrolysis, once in contact with the cold products outlet tube, condense to impregnate the biochar and increasing the final content of PAHs. So, keeping the system always operational without repeated ignitions should improve the biochar produced from the point of view of the pollutant content.

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