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PHYSICAL AND CHEMICAL CHARACTERIZATION OF BIO-FUELS PRODUCED BY PYROLYSIS OF POSIDONIA OCEANICA SEA PLANT

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Ho sempre amato i fari, la storia che raccontano, la loro luce così chiara capace di guidare una nave anche durante la tempesta più violenta, la loro attesa paziente e ferma, il conforto silenzioso che infondono durante il passaggio.

*Siamo marinai e naufraghi e io non da meno dedico questo nuovo viaggio ai miei due fari più importanti… …**Mamma & Papà**… che hanno disegnato con me la mia rotta aspettando che giungessi in questa nuova isola.*

Abstract

The worldwide interest on renewable energies, arising mainly from the environmental constraint, is greatly increased in the last decade. Among different proposed alternatives, attention was addressed toward the employment of third generation biofuels derived from lignocellulosic and algal materials. The use of lignocellulosic biomasses are widely studied due to the low cost and high yield in products such as gas and bio-oil, but if compared to the terrestrial biomass, algal biomasses are considered a cheaper feedstock for production of chemicals and bio-fuels (bio-oil and bio-char). Pyrolysis is considered to be more economical for conversion of algal biomass into bio-fuels than thermal-acid or organic solvent extraction and transesterification methods, since it shows higher efficiency than other processes. Moreover, bio-oils can be upgraded by in-situ catalytic cracking to reduce its high acidity and oxygen content and increase the low heating value. Ni based catalyst have been often utilized in pyrolysis processes mainly due to its low cost rather than noble metals. Also the zeolites as HZSM-5 were found as one of effective catalysts for bio-oil upgrading process. These catalysts were effective to convert highly oxygenated compounds to hydrocarbons, thus Ni doping improves its hydrothermal stability and increases the yield of hydrocarbons. Furthermore, it was found that redox properties of ceria in Ni catalysts could promote both biomass/biofuel (i.e. biogas) conversion and deoxygenation reactions such as dehydration, decarboxylation and decarbonylation. Although, many papers are present in literature on catalytic biomass pyrolysis for bio-oil production, researches on effect of catalysts on pyrolysis process apply to sea plants are really scarce. Hence, main objective of this work was to investigate about the feasibility to produce high quality bio-oil from Mediterranean sea plant by pyrolysis process. Therefore, experiments using Posidonia Oceanica at 500 °C were explored with respect to biomass conversion and bio-products (bio-char, bio-oil and syngas) yields. Moreover bio-oil was studied in terms of oxygen and organic compounds content. Effect of different "home-made" Ni, Ce, HZSM-5 based catalysts on pyrolysis process was analyzed mainly in terms of bio-oil yield and bio-oil oxygen content. The highest bio oil yield (51.15 wt. %) and effect on deoxygenation (6.87 wt.%) was obtained at 500°C with CeO_2 catalyst but the best composition was showed in presence of Ni/HZSM-5 catalyst. Lower content of acids and oxygen in the bio-oil, higher hydrocarbons, combined with HHV show promise for production of high-quality bio-oil from Posidonia Oceanica via catalytic pyrolysis.

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INTRODUCTION

Since their discovery, fossil fuels have provided humans with an abundant and inexpensive energy source other than primarily biomass. However, there are now concerns over remaining fossil fuel reserves [1,2], and the combustion of fossil fuels is controversial with many claims that releasing sequestered carbon is causing global warming [3]. The atmospheric carbon dioxide concentration due to emissions from fossil fuel combustion increases by approximately 2% per year [2,4], and is expected to reach up to 550 ppm by 2050 [5]. Consequently, these global concerns are forcing us to rethink our current sources of energy. Some of the main issues are: climate change, fuel security and increasing and fluctuating costs [6]. Currently in a global context, fossil fuels make up the majority of our energy source with coal/peat, oil and natural gas accounting for 28.8%, 31.5% and 21.3% respectively [7]. Limiting the use of these energy sources is a key priority for most countries as a result of pledges to reduce greenhouse gas emissions [8]. Replacement sources of energy are necessary to replace the shortfall in fossil fuels, bio-energy is one such source [9]. The production of bio-energy is the result of converting organic matter into an energy carrier such as liquid fuel, gas, electricity and heat [10]. Therefore, the worldwide interest on renewable energies, arising mainly from the environmental constraint, is greatly increased in the last decade. Among proposed alternatives, attention was recently addressed toward the employment of biomass and biofuels (biogas, ethanol, glycerol, organic waste, etc. . .) [11-17] as a feedstock for energy production through gasification technology sector and alternative way to the classic technologies used to separate and to fix CO_2 [18-

21]. Targets to encourage the production of bio-energy have recently been implemented in many countries. The target for sustainable biofuel production for all European Union member states set by the European Commission is 10% of all transport fuels by 2020 [22]. Whilst hailed as a commendable aim when proposed, the target has led to the development of arable land for the production of 1st generation bio-energy crops (starchy crops) causing an increase in the cost of food crops [23]. Not only is there an impact on food prices, the true sustainability of biofuel produced from conventional 1st generation crops such as corn is in doubt [24]. Inefficient, expensive and environmentally damaging biofuel production cannot be considered a sustainable substitute for fossil fuels. Alternative 2nd generation (lingo-cellulosic crops) and 3rd generation (algal feedstock) substitutes are therefore being sought to replace fossil fuels [25]. The uses of lignocellulosic biomasses are widely studied due to the low cost and high yield in products such as gas and bio-oil; however, the terrestrial biomass show often lower yields if compared with algal biomasses (both micro- and macroalgae) [26,27]. Algae, therefore are considered as among the most potentially significant future sources of sustainable biofuels, nevertheless despite their obvious potential, there are no economically-viable commercial-scale quantities of fuel also due to the high water content [28–31]. Algae have a very different chemical composition from lignocellulosic feedstocks, since they contain significant amounts of lipids and proteins in addition to carbohydrates and are particularly poor in lignin. Furthermore, bio-oil obtained from algae is more stable it has lower O/C ratio and hence higher calorific value compared to lignocellulosic bio-oil [32-35].

Posidonia Oceanica is a seagrass widely distributed along coastlines of the Mediterranean sea, leaves residues that reaching the coasts and represent a significant economical, and hygienic problem in all coastal zones [36]. Thus the conversion of these residues into value-added products are required to deploy the created know how to the industry for the ultimate aim of waste utilization. Therefore, this biomass offers an abundant, renewable and low cost precursor for different uses (biofuel, activated carbon, etc…) [37,38]. There are several different biomass conversion processes that can yield high calorific value products and which utilize the complete organic content of algal biomass to make the process economically attractive[39-45]. The pyrolysis of biomass has drawn great attention in recent years. Pyrolysis is a processing technique that can be applied to achieve thermal decomposition of biomass in the absence of oxygen to derive renewable oil, gas and char[46]. Pyrolysis is a promising technology for conversion of algal biomass into liquid fuels mainly due to its low capital and operating cost advantages compared to competing technologies such as thermal-acidic or organic solvent extraction, transesterification, fermentation and gasification. The liquid fuel produced by pyrolysis is called bio-oil or pyrolysis oil. The bio-oils produced can potentially be used for direct combustion in energy generation, or can be upgraded further into liquid transport fuels and bio-chemicals. Despite this the pyrolysis oil has half the energy content of a petroleum based liquid fuel, a high oxygen content (45–50 wt%), low pH and a complex composition. In addition the pyrolysis oil is unstable and undergoes phase separation with time [47,48]. Therefore, several techniques such as hydrodeoxygenation, emulsification, steam reforming and catalytic cracking were used to upgrade the pyrolysis oils in recent years. Catalytic cracking pyrolysis, one of the pyrolysis techniques, has been widely used as a convenient method by many researchers for the direct conversion of biomass into high quality liquid bio-fuels. Catalytic pyrolysis involves two steps: biomass pyrolysis and catalytic conversion of pyrolysis vapors. Biomass is heated firstly and converted into pyrolysis vapors, non-condensable gases and bio-char. Then, the pyrolysis vapors are contacted with the surface of the catalyst on which the oxygen containing compounds can be converted into aliphatic and aromatics by deoxygenation reactions (decarboxylation, decarbonylation and aromatization)[49]. Moreover, these reactions lead to a bio-oils with lower H/C and O/C molar ratios.

In the last years, many types of catalysts including Ni and Mg-based materials and alumina sand have been utilized in pyrolysis and gasification studies[50,51]. Also, the effect of catalyst on conversion and distribution of the pyrolysis products has been studied [52-56]. To date, there have been few studies on the catalytic pyrolysis of algae, where zeolites were mainly the catalysts of choice [55,57]. The zeolites as HZSM-5 were found as one of effective catalysts for biomass pyrolysis and for vapor catalytic upgrading process [58]. Although traditional catalysts were effective to convert the highly oxygenated compounds to hydrocarbons, but many problems were encountered, such as low organic liquid yield, low selectivity, short lifetime, etc. [58]. Therefore, many metals, such as zinc, copper, cobalt, iron, molybdenum, magnesium, aluminum, gallium and cerium were tested to adjust the acidity of ZSM-5 catalysts to increase the yield of useful compounds in bio-oils [49,59-65]. However, the above metal modified catalysts were either expensive or unstable. Another cheap transition metal (nickel) was selected to modify HZSM-5 to upgrade pine sawdust bio-oil because it is considered to increase the yield of aromatic hydrocarbons and the hydrothermal stability of zeolite [66]. In some studies, addition of catalyst increased the liquid yields while in some others, it decreased the liquid yields[54,56]. In a recent study, alumina supported Ni-based catalysts were used in pyrolysis–gasification of Scenedesmus almeriensis biomass residue to produce H_2 rich gases [67]. The results indicated that Ni-based catalyst activated the cracking and reforming of biomass volatiles and tars released during pyrolysis at low temperatures. Catalytic pyrolysis of Chlorella vulgaris using HZSM-5 catalyst resulted in a bio-oil yield of 52.7 wt.% which contained alkanes and aromatic hydrocarbons [55]. Zeng et al. [52] studied the catalytic pyrolysis of natural algae from water blooms over silica-supported nickel phosphide to produce bio-oil. The results showed that catalytic pyrolysis could convert the algae to high quality bio-oil containing long-chained alkanes (59.4%) where the oxygen content was reduced from 41.7 wt.% in the algae to 8.0 wt.% in the bio-oil. Posidonia Oceanica is considered as a promising biomass for fuel production since it has intermediate features between algal feedstocks and those lignocellulosic. Experimental data on pyrolysis of Posidonia Oceanica, alone and mixed with waste vegetable oils, at different temperatures (400-600 °C) are reported by Zaoufouri et al [36] and Chiodo et al [38]. Results confirmed the feasibility to produce bio-fuels from local organic biomass and in particular was shown that the bio-oil yields increase with pyrolysis temperature getting the highest rate at 500 °C (> 50%). Pyrolysis behavior and kinetics of Nannochloropsis sp. was investigated by thermogravimetric analysis [68,69]. Nannochloropsis sp. was also pyrolyzed with different amount of HZSM-5 catalyst-to-material ratio (0/1, 0.2/1, 0.4/1, 0.6/1, 0.8/1 and 1/1 wt.%) in a fixed bed reactor. The produced bio-oils, mainly aromatic hydrocarbons, had lower oxygen content (19.5 wt.%) and higher heating-value (32.7 MJ/kg) than those obtained without catalyst (30.1 wt.% and 24.6 MJ/kg) [70]. Low cost and available source of Ni-based catalysts are important criteria for using these catalysts instead of noble metals [71]. It has been reported that Ni(8%)/Al_2O_3–CeO_2 catalyst has higher conversion and better stability compared to Ni(8%)/Al_2O_3 catalyst due to redox properties of ceria. CeO_2 enhances the water gas shift (WGS) reaction and the redox reversibility of active phase [72]. Ni promoted steam reforming reactions and retarded the rate of carbon deposition onto the catalyst surface [73]. Among various carriers (ZrO_2, CeO_2, $MgAl_2O_4$, Ce–ZrO_2), Ni/CeO_2–ZrO_2 showed the highest activity as well as high stability [72]. The cracking properties of Ni, Ce and HZSM-5 can be beneficial to the in-situ deoxygenation of algal bio-oils.

Aim of the work

Although, many papers are present in literature on catalytic biomass pyrolysis for bio-oil production, to the best of my knowledge, there are no works available in the literature on the behavior of Posidonia Oceanica using catalytic pyrolysis with Ni, ceria and HZSM-5 based catalysts. Accordingly, the aim of this work was to investigate about the feasibility to produce high quality, bio-oil as biofuels, from Mediterranean sea plant by catalytic pyrolysis process. Therefore, experiments using Posidonia Oceanica at 500 °C were explored with respect to biomass conversion and bio-products (bio-char, bio-oil and syngas) yields. Bio-oil was studied also in terms of oxygen and organic compounds content. Moreover, was investigated the effect of different "home-made" Ni, Ce, HZSM-5 catalysts on pyrolysis process in terms of conversion yield, products selectivity and bio-oils deoxygenation. The low acids and oxygen content and the high hydrocarbons content in the bio-oil, combined with HHV show promise for production of high-quality bio-oil from Posidonia Oceanica via catalytic pyrolysis.

Outline of the thesis

In the first chapter we will discuss of the main biomass classes (lignocellulosic and algal) and their possible applications as biofuels for energy purpose. Moreover, will also be introduced the main biomass conversion technologies into biofuels.

The second chapter will be dedicated at the pyrolysis process and to the pyrolysis products. Particularly will be highlighted the bio-oil's properties and the main catalysts used to bio-oil's catalytic upgrading.

The third chapter will be dedicated at the experimental part. Will be reported the biomass and catalyst preparation methods and all characterization techniques used to products analysis. In this chapter will also reported the descriptions of experimental plant and the pyrolysis tests carried out.

In the fourth chapter, dedicated at results and discussions will be described the effect of the catalyst on the pyrolysis products distribution and the obtained results will be discussed on the basis of used characterization techniques. In order to determine the best catalyst for bio-oil's upgrading more attention will be given to the comments on bio-oils properties.

Conclusions of the study are summarized in a final chapter, the fifth, where some recommendations for future research directions are also collected.

The thesis work was carried out at CNR-ITAE of Messina which for many years conducts its activities in the field of processes and energy technologies with high efficiency and low environmental impact for the direct production of energy from conventional and renewable fuels.

1. Chapter 1: Biomass and Conversion Technologies

1.1. Biomass

In the energy context biomass term is often used to mean plant based material, but can also apply to both animal and vegetable derived material. Biomass is a key building block of biofuels – it can be specially grown for electricity production or to produce heat in the energy context, as an alternative to fossil fuels. According to the United Nations Convention on Climate Change, biomass (UNFCCC, 2005) is a "non-fossilized and biodegradable organic material originating from plants, animals and microorganisms. This includes products, by-products, residues and waste from agriculture, forestry, as well as the organic fraction non-fossilized and biodegradable of the industrial and municipal waste [74].

The increasing interest for the biomass depends on the reason that it constitutes a renewable and clean energy source, useful to respect the international commitments for the reduction of greenhouse gas emissions. The main contribution that biomass offer for reducing the greenhouse effect, derives from their capacity to storage high amounts of CO_2, subtracted the atmosphere and immobilized for a long time inside the fibers that constitute it. In contrast, when a fossil fuel is burnt the CO_2 in the atmosphere increases as it takes hundreds of millions of years for the fossil fuel source to be replenished.

Biomass is a complex mixture of organic materials such as carbohydrates, fats, and proteins, along with small amounts of other atoms, including alkali, alkaline earth and heavy metals can also be found.

This type of feedstock contains stored energy from the sun. Plants absorb the sun's energy in a process called photosynthesis. When biomass is burned, the chemical energy in biomass is released as heat. Biomass can be burned directly or converted to liquid biofuels and biogas that are burned as fuels. Therefore, biomass suitable for energy transformation can be divided by origin sector in the following areas:

1. forestry and agro-forestry industry: residues of forestry operations or agroforestry activities, utilization of coppice forests, etc;
2. agricultural sector: crop residues from agricultural production and dedicated crops of lignocellulosic species, oil plants for oils extraction and their transformation into biodiesel, alcoligene plants for the production of bioethanol;
3. zootechnical sector: livestock waste for biogas production;
4. industrial sector: waste from wood and paper industries or wood products , as well as food industry residues;
5. Algal sector: algae and microalgae cultivated or gathered [75]. There are also many energy applications relating to this class of compounds. The main types of applications are thus:
    - Energy production (biopower);
    - Fuels production (biofuel);
    - Synthesis of products (bioproducts).

1.1.1. Lignocellulosic biomass composition

Lignocellulose is the fibrous material that makes up the cell walls of plants, the average chemical composition of consists of lignin (≈25-30%) and carbohydrates (≈75%), that is sugar molecules linked to form long polymer chains. The two main carbohydrates are cellulose (≈40%) and hemicellulose (≈25%). Cellulose is a natural linear polysaccharide with the general formula $(C_6H_{10}O_5)$ n, an average molecular weight of 300-500 u.m.a and a degree of polymerization which can range from 3000 up to 10.000 depending on the plant.

Cellulose is insoluble in water, train the supporting structure of all the biomasses present on earth and constitutes approximately 50% of the cell wall material. The cellulose molecules have with a basic unit a ring of β-D-glucopyranose. Each ring is rotated through 180° with respect to the next, therefore, the repetitive unit is formed by two contiguous rings united by means 1,4-β-glycosidic bonds, **Figure 1.1**.

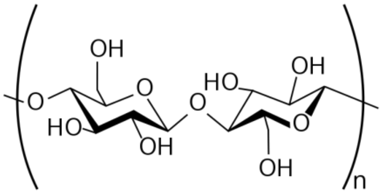


Figure 1.1: Molecular structure of cellulose

The stability of the structure is due to the rings to six carbon atoms, to the absence of double bonds and by the presence of intra- and intermolecular hydrogen bonds. The hydrogen bridges are formed by a hydrogen atom of an alcohol group partially bound to a second oxygen atom belonging to a polymer of a parallel fiber.

Hemicellulose is another constituent of the cell walls of a plant. While cellulose has a crystalline, strong structure that is resistant to hydrolysis, hemicellulose

has a random, amorphous structure with little strength; the molecular arrangement of a typical hemicellulose molecule, xylan is showed in **Figure 1.2.** It is a group of carbohydrates with a branched chain structure and a lower degree of polymerization (DP <100-200) and may be represented by the generic formula $(C_5H_8O_4)n$ [76].

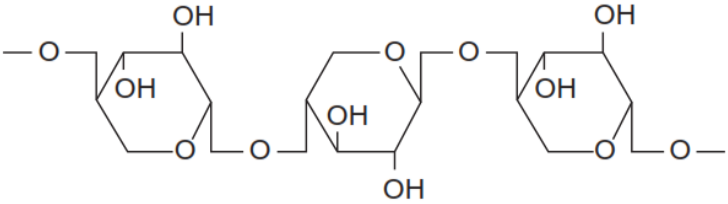


Figure 1.2: Molecular structure of a typical hemicellulose, xylan

There is significant variation in the composition and structure of hemicellulose among different biomass. Most hemicelluloses, however, contain some simple sugar residues like D-xylose (the most common), D-glucose, D-galactose, L-ababinose, D-glucurnoic acid, and D-mannose. Hemicellulose tends to yield more gases and less tar than cellulose [77]. It is soluble in weak alkaline solutions and is easily hydrolyzed by dilute acid or base. It constitutes about 20-30% of the dry weight of most wood.

Lignin is a complex highly branched polymer that consists of an irregular array of hydroxy and methoxy substituted phenylpropane units and is an integral part of the secondary cell wall of plants, **Figure 1.3** [78]. Lignin is the cementing agent for cellulose fibers holding adjacent cells together. The dominant monomeric units in the polymers are benzene rings. A typical hardwood contains about 18-25% by dry weight of lignin, while softwood contains 25-35%.

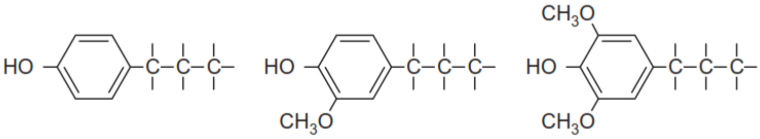


Figure 1.3: Some structural units of lignin

1.1.2. Algal biomass composition

The algal biomass presents a chemical composition similar to that lignocellulosic, in different percentages depending on the kinds of algae, in so far as are formed from proteins, carbohydrates and lipids. Microalgae are precisely unicellular photosynthetic organisms that utilize carbon dioxide and light energy to produce biomass. In addition to grow rapidly, they are able to retain in their structure large amounts of lipids. A fatty acid is constituted by a hydrophilic group and a carboxyl group attached to one end of a hydrophobic hydrocarbon chain. Fatty acids can be classified according to the length of the carbon chain and the presence of double bonds. This latter feature classifies them into saturated and unsaturated fatty acids. Triglycerides (also known as triacylglycerols) are an important part of vegetable oil, and are structurally neutral esters of glycerol formed by three fatty acids at medium or long chain. The lipids can be defined as molecules able to solubilize in organic solvents. The lipid composition of microalgae varies considerably from one species to another and might be comprised, in terms of dry biomass, within a range between 5 to 77% by weight. It was demonstrated that the lipid fraction is influenced by the life cycle of the alga, as well as by the culture conditions such as temperature, illumination intensity, ratio of light / dark cycle and aeration rate. Some microalgal species are known to have increased under oxygen deficiency conditions the lipid content from 10% to nearly 20% by weight. However, this increase of fatty cells is not always followed even by an increase of oil production [74].

1.1.3. Use of algae for energy purposes

The promise of sustainable energy production from algae has generated tremendous interest in recent years [79,80]. Algae are an attractive source of biomass energy since they do not compete with food crops and have higher energy yields per area than terrestrial crops. Petroleum shortages and the climate implications of combusting proven reserves have driven research and business ventures into algae-based fuels [81]. This attention stems from several of algae's seemingly desirable characteristics that set it apart from other biomass sources. The first of these is that algae tend to produce more biomass than terrestrial plants per unit area, and unlike terrestrial plants, they can be cultivated on otherwise marginal land using freshwater or saltwater [82]. A fast-growing aquatic alternative to conventional crops is appealing since most developed nations consume more energy than they could offset using slow growing terrestrial crops [83]. A second characteristic is that algae do not compete directly with food crops [81]. The United States ethanol boom of 2008 was one of many factors that contributed to a spike in corn prices worldwide, raising complex ethical issues that could be avoided by production of separate crops for food and fuel [84,85]. The third characteristic is that algae, by virtue of their fast growth rates and aquatic habitat, could be cultivated in systems designed for simultaneous biomass production, uptake of anthropogenic CO_2, and removal of certain water pollutants [86,87]. Although both algae and terrestrial photosynthetic organisms tend to grow faster in the presence of slightly elevated CO_2 and nutrient levels, these nutrients are more easily delivered to algae than to terrestrial plants. There has been steady interest in algae-to-energy systems over the past several decades and therefore, the third-generation biofuels development has now become a matter of crucial importance [74].

1.2. Biofuels

In the last two decades the increase in the means of transport has led to a substantial increase of energy consumption with obvious negative environmental effects. The combustion of fossil fuels causes an increase in CO_2 in the atmosphere by promoting the greenhouse effect. Among the possible solutions for the overall improvement of environmental impact there is the possibility to replace traditional fossil fuels with than that of origin "bio" [88]. In general, the term "biofuel" refers to a renewable fuel that is produced by fermentation of microorganisms or from the processing of vegetable extracts [89]. Most common are bioethanol, biomethanol and biodiesel that represent real substitutes for fossil fuels and that may replace fossil fuels and be utilized in the transport sector with significant environmental benefits. Indeed, biofuels are of biodegradable compounds with a high energy content, comparable to that of fossil hydrocarbons. The lower presence of oxygen in their composition allows a strong reduction of the gaseous pollutants (in particular carbon monoxide) in the atmosphere emissions of internal combustion engines that use them. In addition they have a very low sulfur content with a substantial reduction in sulfur dioxide emissions. Bioethanol and biomethanol are fuels that can be used instead of gasoline with a few changes to the car's ignition system; in Brazil from some years the bioethanol is used for urban mobility.

Among the fuels derived from crops the most promising is the biodiesel. This last one is a replacement alternative fuel to diesel fuel made from renewable sources such as vegetable oils and animal fats [90].

1.2.1. Classification of fuels by belonging categories

Biofuels have been classified into four categories:

- **First generation biofuels:** belong to this category bioethanol produced by fermentation of sugar and starchy crops such as sugar cane, sugar beet and corn, biodiesel obtained from oil plants (palm oil, rapeseed and soybean), the bio-ETBE (Ethyl Ter Butyl Ether from the bioethanol) and biogas. The main limitation in the application of the first-generation fuels is the conflict with food production.

- **Second generation biofuels:** they are based on the exploitation of lignocellulosic waste materials from forests and agriculture; these are raw materials with low cost of procurement but that especially not enter into competition with the food industry. Although the productive technology is not yet optimized, this category of biofuels is considered very promising because it is a concrete instrument for reducing the cost of biofuels production. These type of biofuels are currently penalized compared to those fossils because their production cannot be separated from the aid measures of the economic and tax incentive policies [91]. Belong to this category bioethanol from lignocellulosic raw materials bio-hydrogen, syngas, bio-oil, bio-methanol, the bio-dimethyl ether, bio-MTBE, bio-butanol, and synthetic diesel, obtained by Fischer-Tropsch reaction [92].
- **Third-generation biofuels:** are defined as an integration of second-generation biofuels for the gradual replacement of fossil fuels. These are based on the exploitation of specialty crops, such as microalgae cultures and seaweed, that do not compete with the food industry and the production of which does not require either farmland or expanses forest. The exploitation of microalgae crops with a high fat and sugar content allows to obtain biodiesel and bio-ethanol respectively.
- **Fourth-generation biofuels:** they include genetically modified microorganisms capable of capturing large amounts of CO_2 in such a way that they produce waste as a fuel. Nevertheless, the weak link of the chain is

represented by the CO_2 capture technology to be supplied at the microbes [90].

1.2.2. Classification of fuels for chemical constituents

Classification is an important means of assessing the properties of a fuel. Fuels belonging to a particular group have similar behavior irrespective of their type or origin. Thus, when a new biomass is considered for gasification or other thermochemical conversion, we can check its classification, and then from the known properties of a biomass of that group, we can infer its conversion potential.

There are different methods of classifying and ranking fuels using their chemical constituents as: atomic ratios, and the ternary diagram. All hydrocarbon fuels may be classified or ranked according to their atomic ratios, but the second classification is limited to lignocellulose biomass.

Atomic Ratio: Classification based on the atomic ratio helps us to understand the heating value of a fuel, among other things. When the hydrogen-to-carbon (H/C) ratio increases, the effective heating value of the fuel reduces. The atomic ratio is based on the hydrogen, oxygen, and carbon content of the fuel. **Figure 1.4** plots the atomic ratios (H/C) against (O/C) on a dry ash-free (daf) basis for all fuels, from carbon-rich anthracite to carbon-deficient woody biomass.

This plot, known as van Krevelen diagram, shows that biomass has much higher ratios of H/C and O/C than fossil fuel has. For a large range of biomass, the H/C ratio may be expressed as a linear function of the (O/C) ratio [93].

$$\left\lfloor \frac{H}{C} \right\rfloor = 1.4125 \left\lfloor \frac{O}{C} \right\rfloor + 0.5004$$

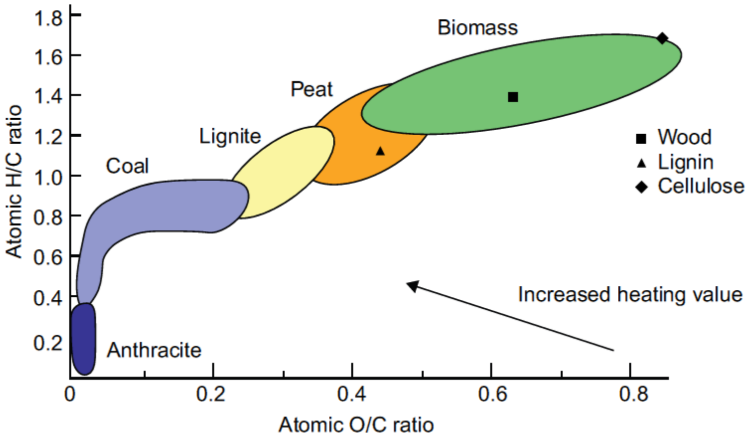


Figure 1.4: Classification of solid fuels by hydrogen/carbon and oxygen/carbon ratio

Fresh plant biomass like leaves has very low heating values because of its high H/C and O/C ratios. The atomic ratios of a fuel decrease as its geological age increases, which means that the older the fuel, the higher its energy content. Anthracite, for example, a fossil fuel geologically formed over millions of years, has a very high heating value. The lower H/C ratio of anthracite gives it a high heating value, but the carbon intensity or the CO_2 emission from its combustion is high.

Ternary diagram: The ternary diagram, **Figure 1.5,** is useful for representing biomass conversion processes. The three corners of the triangle represent pure carbon, oxygen, and hydrogen—i.e., 100% concentration. Points within the triangle represent ternary mixtures of these three substances. The side opposite to a corner with a pure component (C, O, or H) represents zero concentration of that component. For example, the horizontal base in **Figure 1.5** opposite to the hydrogen corner represents zero hydrogen—i.e., binary mixtures of C and O.

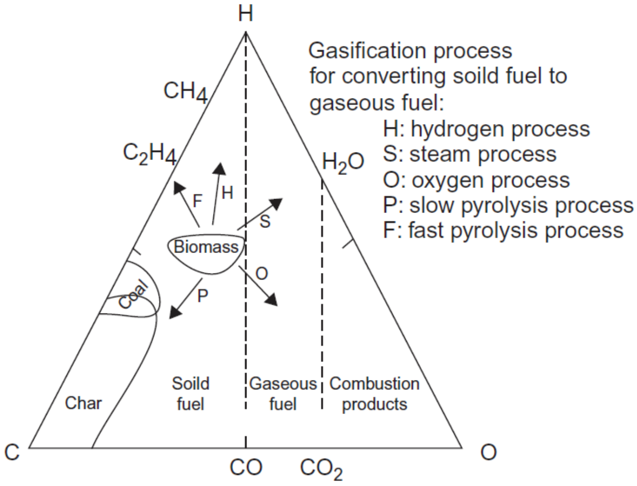


Figure 1.5: C–H–O ternary diagram of biomass showing the gasification process

A biomass fuel is closer to the hydrogen and oxygen corners compared to coal. This means that biomass contains more hydrogen and more oxygen than coal contains. Lignin would generally have lower oxygen and higher carbon compared to cellulose or hemicellulose. Peat is in the biomass region but toward the carbon corner, implying that it is like a high-carbon biomass. As mentioned earlier, the ternary diagram can depict the conversion process. For example, carbonization or slow pyrolysis moves the product toward carbon through the formation of solid char; fast pyrolysis moves it toward hydrogen and away from oxygen, which implies higher liquid product. Oxygen gasification moves the gas product toward the oxygen corner, while steam gasification takes the process away from the carbon corner. The hydrogenation process increases the hydrogen and thus moves the product toward hydrogen.

1.3. Conversion technologies

In this section, the technically viable conversion options for algal biomass and end-use of derived energy or energy carriers (liquid or gaseous fuels) are considered. The large-scale exploitation of biomass in industrialized countries requires the adoption of modern advanced technology, capable of enhancing the relatively expensive agroforestry resources in an efficient and economically acceptable way, as well as sustainable from an environmental point of view [94]. Although, there are basically two ways that can be used for the conversion of the biomass (thermal and biological), in Europe more attention is focused on thermochemical conversion processes such as pyrolysis and gasification [90]. The conversion of the algae is carried out by means of different processes normally used for conventional biomass, the choice of which depends largely on the type of biomass and from the purpose and use of the product. These technologies can be divided into two major categories: thermochemical conversion and biochemical conversion, **Figure 1.6**. The factors that influence the choice of the conversion process can be different: the type and amount of feedstock, economic and design aspects, type of energy produced [90,92].

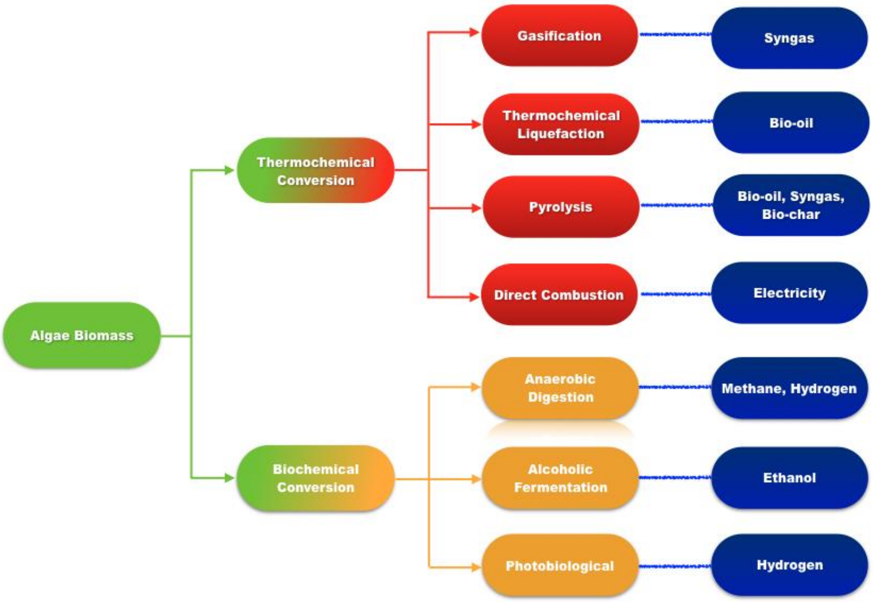


Figure 1.6: Algal biomass conversion technologies

1.3.1. Biochemical conversion

The biochemical process for energy conversion of biomass into other fuels includes alcoholic fermentation, anaerobic digestion and photobiological hydrogen production [95].

Alcoholic fermentation is the conversion of biomass materials which contain sugars, starch or cellulose into ethanol [94]. The biomass is ground down and the starch is converted to sugars which is then mixed with water and yeast and kept warm in large tanks called fermenters [96]. The yeast breaks down the sugar and converts it to ethanol [94]. A purification process (distillation) is required to remove the water and other impurities in the diluted alcohol product (10–15% ethanol). The concentrated ethanol (95% volume for one distillation) is drawn off and condensed into liquid form, which can be used as a supplement or substitute for petrol in cars [96]. The solid residue from the process can be used for cattle-feed or for gasification [94]. This helps offset feedstock costs which typically make up 55–80% of the final alcohol selling price. Starch based biomass like microalgae require additional processing before fermentation [96].

Anaerobic digestion (AD) is the conversion of organic wastes into a biogas, which consists of primarily methane (CH_4) and carbon dioxide, with traces of other gases such as hydrogen sulphide [97]. It involves the breakdown of organic matter to produce a gas with an energy content of about 20–40% of the lower heating value of the feedstock. Anaerobic digestion process is appropriate for high moisture content (80–90% moisture) organic wastes [94], which can be useful for wet algal biomass. The AD process occurs in three sequential stages of hydrolysis, fermentation and methanogenesis. In hydrolysis the complex compounds are broken down into soluble sugars. Then, fermentative bacteria convert these into alcohols, acetic acid, volatile fatty acids (VFAs), and a gas containing H_2 and CO_2, which is metabolised into primarily CH_4 (60–70%) and CO_2 (30–40%) by methanogens [98]. It has been estimated that the conversion of algal biomass into methane could recover as much energy as obtained from the extraction of cell lipids [99], while leaving a nutrient rich waste product that can be recycled into a new algal growth medium [100,101].

Microalgae can have a high proportion of proteins that result in low C/N ratios (ca. 10) which can affect the performance of the anaerobic digester. This problem may be resolved by co-digestion with a high C/N ratio product (e.g. waste paper).

The **photobiological process** is used to produce a natural molecule which hydrogen (H_2), which is a clean and efficient energy carrier [102]. Algae possess the necessary genetic, metabolic and enzymatic characteristics to photoproduce H_2 gas [103]. Under anaerobic conditions hydrogen is produced from eukaryotic algae either as an electron donor in the CO_2 fixation process or evolved in both light and dark [104]. During photosynthesis, algae convert water molecules into hydrogen ions (H^+) and oxygen; the hydrogen ions are then subsequently converted by hydrogenase enzymes into H_2 under anaerobic conditions [98]. Due to reversibility of the reaction, hydrogen is either produced or consumed by the simple conversion of protons to hydrogen [102]. Photosynthetic oxygen production causes rapid inhibition to the key enzyme, hydrogenase, and the photosynthetic hydrogen production process is impeded [98,105–108]. Consequently, algae cultures for hydrogen production must be subjected to anaerobic conditions.

There are two fundamental approaches for photosynthetic H_2 production from water. The first H_2 production process is a two stage photosynthesis process where photosynthetic oxygen production and H_2 gas generation are spatially separated [103]. Instead, the second approach involves the simultaneous production of photosynthetic oxygen and H_2 gas.

1.3.2. Thermochemical conversion

Organic components contained in biomass are converted to yield fuel products by different thermochemical conversion processes such as direct combustion, gasification, thermochemical liquefaction, and pyrolysis [109]. The thermo-chemical conversion processes have two basic approaches. The first is the gasification of biomass and its conversion to hydrocarbons. The second approach is to liquefy biomass directly by high-temperature pyrolysis, high-pressure liquefaction, ultra-pyrolysis, or supercritical extraction. These processes convert the waste biomass into energy rich useful products. Choice of conversion process depends upon the type and quantity of biomass feedstock, the desired form of the energy, i.e., end use requirements, environmental standards, economic conditions and project specific factors. Different thermo-chemical conversion processes include combustion, gasification, liquefaction, and pyrolysis. During current energy scenario, pyrolysis has received special attention as it can convert biomass directly into solid, liquid and gaseous products by thermal decomposition of biomass in the absence of oxygen. Pyrolysis offers efficient utilization of particular importance for agriculture countries with vastly available biomass by-products. In this thesis, the focus has been made on pyrolysis while other conventional processes have been briefly discussed as follows:

Combustion: The biomass is directly burnt in the presence of air to convert chemical energy stored in biomass into heat, mechanical power, or electricity, etc.[94,102,110]. It is possible to burn any type of biomass but in practice combustion is feasible only for biomass with moisture content of <50%. Combustion process has got many disadvantages. Biomass rarely arises naturally in an acceptable form of burning. In most of the cases it requires some pretreatment like drying, chopping, grinding, etc., which in turn is associated with financial costs and energy expenditure [92,111].

Liquefaction: Thermochemical liquefaction is a process that can be employed to convert wet material, as algal biomass, into liquid fuel [112]. Thermochemical liquefaction conditions are low-temperature (300–350 °C), high pressure (5–20 MPa) process, and a catalyst in the presence of hydrogen to yield bio-oil [110]. The process utilizes the high water activity in sub-critical conditions to decompose biomass materials down to shorter and smaller molecular materials with a higher energy density [112]. Reactors for thermochemical liquefaction and fuel-feed systems are complex and therefore expensive [94], but have advantages in their ability to convert wet biomass into energy [102]. The reactor effluent consists of three different phases: a water phase, a hydrophobic phase and a gas phase. By extraction the hydrophobic reaction product can further be separated into a solvent (e.g., acetone) soluble and a solvent insoluble part. The hydrophobic phase is considered the main reaction product and has considerably lower oxygen content than the feedstock. Various studies have investigated the thermochemical liquefaction applied at algal biomass as a feedstock. Dote et al. [113] used this process at 300°C on B. braunii to achieve a maximum yield of oil (64% dry weight basis) with a Higher Heating Value (HHV) of 56.0 MJ kg^{-1} [75,114].

Gasification: gasification involves the partial oxidation of biomass into a combustible gas mixture at high temperature (800-1000 °C) [102]. In the normal gasification process the biomass reacts with gasifying agents (oxygen and/or steam) to generate syngas, a mixture of CO, H_2, CO_2, CH_4 and short chain hydrocarbons such as ethane and ethylene [96]. Network of the main chemical reactions involved in the syngas production of the gasification process are reported in the **Table 1.1**.

Reaction	***Name***
Biomass + heat $\rightarrow$ gases + tar + char	Pyrolysis
Tars+$H_2O \rightarrow H_2 + CO + CO_2$ + hydrocarbons	Tars reforming
Hydrocarbons + $H_2O \rightarrow H_2 + CO + CO_2$	Hydrocarbons reforming
Reactions with water	
$C + H_2O \rightarrow CO + H_2$	Water gas
$C + 2H_2O \rightarrow CO_2 + 2H_2$	Water gas (secondary)
$2C + 2H_2O \rightarrow CO_2 + CH_4$	Carbon Gasification
$CH_4 + H_2O \rightarrow CO + 3H_2$	Methane reforming
Combustion of the char	
$2C+ ½ O_2 \rightarrow CO$	Carbon oxidation (I)
$C+ O_2 \rightarrow CO_2$	Carbon oxidation (II)
Reaction of Oxidation	
$CO + ½ O_2 \rightarrow CO_2$	Carbon monoxide oxidation
$H_2 + ½ O_2 \rightarrow H_2O$	Water production
$CH_4 + 2O_2 \rightarrow CO_2 + 2 H_2O$	Methane oxidation
$CO + H_2O \rightarrow CO_2 + H_2$	Water gas shift
Parallel reaction of syngas (back combinations)	
$C + CO_2 \rightarrow 2CO$	Boudouard reaction
$C + 2H_2 \rightarrow CH_4$	Carbon methanation
Methanation reactions	
$CO + 3H_2 \rightarrow CH_4 + H_2O$	
$2CO + 2H_2 \rightarrow CH_4 + CO_2$	

Table 1.1: Network of the main chemical reactions involved in the syngas production of the gasification process

These gases can be burnt in situ for the generation of energy or if the hydrogen content is particularly high, can be integrated in the oil conversion cycles in the refineries, such as the Fisher-Tropsch process or methanol synthesis. The key advantage of gasification as a biomass-to—energy pathway is that it can produce a syngas from a wide variety of potential feedstocks [102]. As regard the algae, Hirano et al. have gasified the Spirulina in a temperature range between 850 and 1000 °C to obtain a gas yield of 64% [115]. A higher gas yield (69.7 %) has been obtained from Hanaoka et al. by gasification of Sargassum Horneri with a mixture of CO_2/O_2 in a downdraft fixed bed reactor at 900 °C [116].

Pyrolysis: pyrolysis is a thermochemical conversion process and is found to be best suited for conversion of biomass to liquid fuel.

The pyrolysis typically refers to a process by which the biomass is thermally degraded to bio-oil syngas and bio-char at medium to high temperature (350-700 °C) in total absence of oxygen. The pyrolysis process may be represented by a generic reaction such as:

$$\mathbf{C_nH_mO_p\ (Biomass) \rightarrow \Sigma_{liquid}\, C_xH_yO_z + \Sigma_{gas} C_aH_bO_c + H_2O + C\ (bio\text{-}char)}$$

For biomass-to-liquid fuel conversion, it is deemed to have the potential for large scale production of biofuels that could replace petroleum based liquid fuel [117]. Compared to other conversion technologies, research on pyrolysis of algal biomass is quite extensive and has achieved reliable and promising outcomes that could lead to commercial exploitation [118].

2. Chapter 2: Pyrolysis process and bio-oils upgrading

2.1. Pyrolysis process

Pyrolysis process is commonly used for conventional biomass, the choice of this methodology is complex and depends on a range of different factors, which include the nature and form of the biomass feed and the desired final product composition. Pyrolysis involves rapid heating of biomass or other feed in the absence of air or oxygen at a maximum temperature, known as the pyrolysis temperature, and holding it there for a specified time to produce non-condensable gases, solid char, and liquid product. The liquid product is of primary interest in pyrolysis, **Figure 2.1**.

The initial product of pyrolysis is made of condensable gases and solid char. The condensable gas may break down further into non-condensable gases (CO, CO_2, H_2, and CH_4), liquid, and char, **Figure 2.2**. This decomposition occurs partly through gas-phase homogeneous reactions and partly through gas solid-phase heterogeneous thermal reactions. In gas-phase reactions, the condensable vapor is cracked into smaller molecules of non-condensable permanent gases such as CO and CO_2.

As mentioned earlier, pyrolysis involves a breakdown of large complex molecules into several smaller molecules. Its product is classified into three principal types:

- Liquid (tars, heavier hydrocarbons and water);
- Solid (mostly char or carbon);
- Gas (e.g., H_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6).

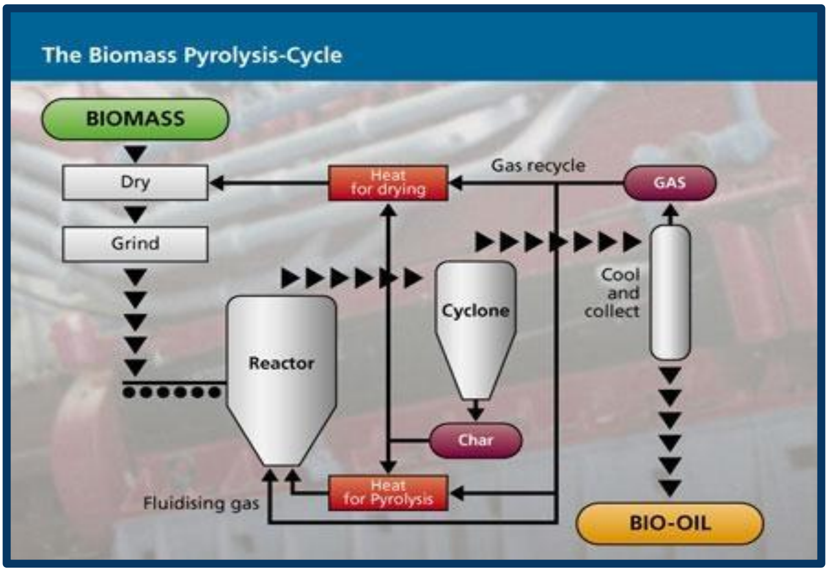


Figure 2.1: Pyrolysis process

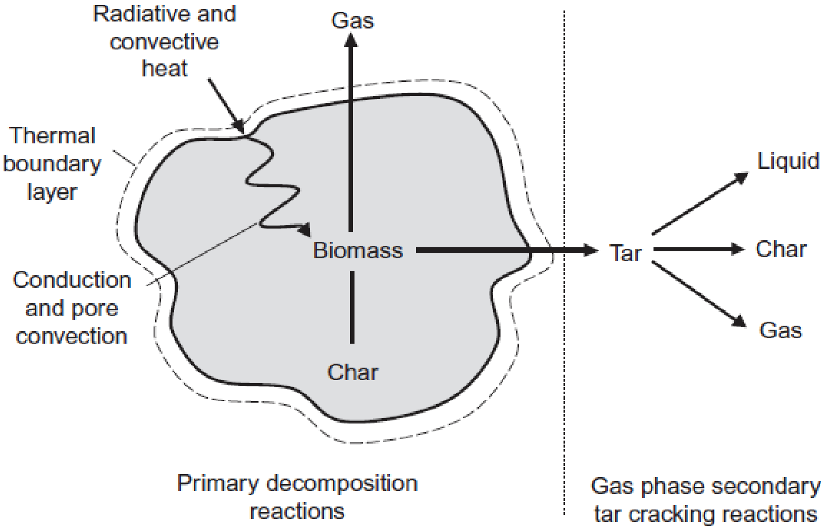


Figure 2.2: Pyrolysis process in a biomass particle and separation in three main products

The composition of pyrolysis products change depending with temperature because different reactions can be triggered, as reported in **Table 2.1**.

At low temperatures (T <350 °C) occurs the evaporation of the water inside into biomass and the free radicals formation. A increase in temperatures produces polysaccharides bonds breaking with a consequent formation of oligosaccharides mixture.

Conditions	Process	Products
T < 350°C	free radicals formation, H_2O elimination and depolymerization	carbonyl and carboxyl groups formation
350°C < T < 450°C	glycosidic bond breaking	levoglucosan, anhydrides and oligosaccharides mixture
T > 450°C	Dehydration, and rearrangement of sugar units	carbonyl compounds formation, such as acetaldehyde and acrolein
T > 500°C	mixture of all processes listed above	mixture of all products listed above
Condensation	unsaturated condensed products unified with char	highly reactive char containing residual free radicals trapped

Table 2.1: Pyrolysis reactions at different temperatures

Moreover at these temperatures the molecules present in the liquid and solid residue are broken down to produce smaller molecules that enrich the gaseous fraction. Finally, at temperatures above 500 °C the condensation of unsaturated products occurs and these are fixed in the char, previously produces, forming a highly reactive residue containing free radical. The pattern reported in **Figure 2.3** show with more details the steps that occur from the starting biomass until complete decomposition. The Biomass after removing the moisture present inside its particles can be subjected at two types of pyrolysis:

Primary pyrolysis produces fragmentation and rearrangement of molecules that form the biomass. While, **secondary pyrolysis** leads at final products by reforming, cracking, oxidation, dehydration and polymerization reactions.

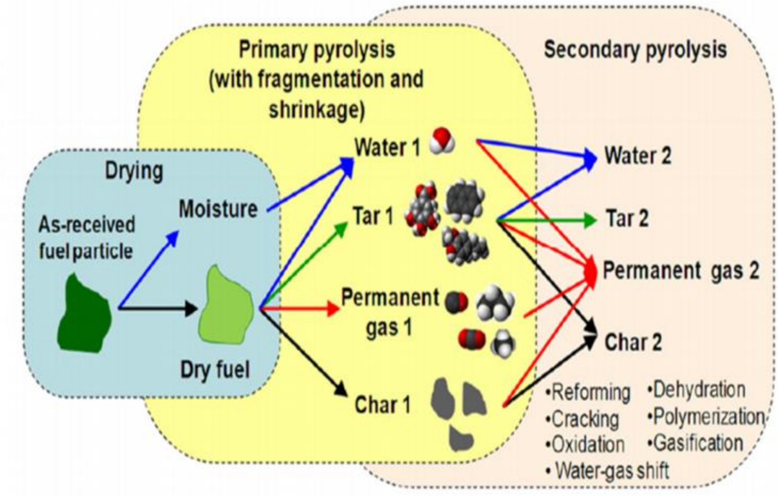


Figure 2.3: Reaction pathway of pyrolysis process

The relative proportion of each products resulting from the process is controlled by varying the pyrolysis operating conditions, in particular the temperature, heating rate and residence time [119]. Therefore, depending on the operating conditions, the pyrolysis process can be divided into three subgroups: slow, fast and flash pyrolysis[120]. The operating condition of these three type of pyrolysis are reported in **Table 2.2** [121].

Process	Operative conditions	Products Yield (%)		
		Oil	Char	Gas
Slow pyrolysis	Low temperatures (400°C), very long residence time (over 30 min)	30	35	**35**
Fast pyrolysis	Moderate temperatures (500°C) and residence time (about 10-20 sec)	50	20	**30**
Flash pyrolysis	Moderate temperatures (500 °C), low residence time (about 1 sec)	75	2	13

Table 2.2: Operating condition of different kind of pyrolysis

2.1.1. *Pyrolysis types: Slow, fast, flash*

Slow Pyrolysis: The pyrolysis of biomass undertaken with a heating rate of approximately 0.1 and 1 °C/sec is classified as a slow pyrolysis process [122-123]. Here, the biomass is heated to 400–500 °C with reaction vessel residence times for the resulting vapors being of the order over 30 minutes, something that facilitates secondary reactions between low molecular weight (volatile) components and gives rise to high charcoal contents and lower liquid yields [124]. This methodology is suitable for a diverse range of feedstocks including waste wood and food, and even sewage sludge [125]. The solid residue (or biochar) produced during the pyrolysis process can be used as an agricultural fertilizer (something that provides a good example of a carbon sequestration cycle) or can be used to produce energy through co-combustion in thermal power plants [126].

Fast pyrolysis: In order to increase the yield of the desirable liquid fraction (i.e., bio-oil) biomass pyrolysis must be achieved extremely rapidly to help minimize the occurrence of secondary thermochemical reactions [127], which favor the formation of solid char residues. Consequently, fast pyrolysis processes have been developed. To achieve reliably high bio-oil yields using this type of protocol, the following precautions must be employed to maximize heat and mass transfer, which limit undesirable lower temperature side reactions [128]: (i) very high heating and heat transfer rates (usually requiring use of a finely ground feed); (ii) a carefully controlled pyrolysis reaction temperature, often in the range of 425–600 °C; (iii) short vapor residence times (typically <2 s); and (iv) rapid cooling and water quenching of the pyrolysis vapors and aerosols (solid particles suspended in a gaseous stream) to achieve good separation of water-soluble/-insoluble components. Furthermore, feeds with high initial moisture content are unsuitable for fast pyrolysis since the rapid generation of water vapor brings about a detrimental reduction in reactor temperature.

However, when optimum conditions are achieved, fast pyrolysis processes can consistently produce 60-75 wt.% bio-oil, 15–25 wt.% of solid char, and 10–20 wt.% of non-condensable gases, depending on the particular feedstock used [130].

Flash pyrolysis: Flash pyrolysis (sometimes called very fast pyrolysis), characterized by rapid heating rates (>1000 °C/s) and high reaction temperatures (900–1300 °C), has been shown to afford high yields of bio-oil with low resulting water content and conversion efficiencies of up to 70% [130,131]. The residence times used are even shorter than those of fast pyrolysis, typically less than 0.5 s. To obtain such high heating and heat transfer rates, the biomass feedstock particle size must be as small as is practically possible, usually around 105–250 μm (60–140 mesh size) [132]. Flash pyrolysis is of following types:

(a) *Flash hydro-pyrolysis*: Hydro-pyrolysis is flash pyrolysis done in hydrogen atmosphere. It is carried out at a pressure up to 20 Mpa [133].

(b) *Rapid thermal process*: It is a particular heat transfer process with very short heat residence times (between 30 ms and 1.5 s). It is done at temperatures between 400 and heating eliminates the side reactions whereby giving products with comparable viscosity to diesel oil [134].

(c) *Solar flash pyrolysis*: Concentrated solar radiation can be used to perform flash pyrolysis. The solar energy can be obtained through devices like solar towers, dish connectors, solar furnaces, etc. [135].

(d) *Vacuum flash pyrolysis*: In this process, pyrolysis is done under vacuum. It limits the secondary decomposition reactions, which in turn gives high oil yield and low gas yield.

2.1.2. *Pyrolysis products: bio-oil, bio-char, bio-gas*

As discussed, pyrolysis processes can convert biomass directly into solid (biochar), liquid (bio-oil), and gaseous products (bio-gas), each of which have their own commercial merits. The relative proportions and chemical composition of these fractions are intimately linked to the reaction conditions, the type of reactor, and the feedstock used. In general, to maximize the yield of liquid products, small particle size, low temperatures, high heating rates, and short gas residence times are required. In contrast, greatest char production is achieved when pyrolysis is undertaken using low temperatures, low heating rates, and intermediate residence times, while fuel gas (e.g., mixtures of methane, acetylene, short chain hydrocarbons, syngas, etc.) yields may be maximized using higher temperatures, low heating rates, and gas residence times of the order of hours to days [136].

Biogas: In particular the precise composition of the gaseous products (biogas) obtained from biomass pyrolysis can be complex. Typically, the biogas fraction comprises various proportions of H_2, CO, CO_2, CH_4, N_2, nitrogen oxides and nitrogen compounds such as HCN and NH_3. Additionally, biogas may also contain minor amounts of light hydrocarbons traces as C_2H_6, C_2H_4, C_3H_8, C_3H_6, and C_4H_{10} which come from the cracking of heavy molecules [137]. It is not currently economical to use this non condensable gas for synthetic gas production due to the low energy density and dilution from the fluidising gas if N_2 is used. The gaseous product formation occurs during primary and secondary cracking reactions [138,139]. **Table 2.3** provides detailed data on the biogas formation at different pyrolysis temperatures [138,140]; the data indicates that CO_2 is mainly produced during primary reactions while CO is mainly produced during secondary reactions, especially through secondary reactions of low molecular weight compounds, thus the CO concentration can give an indication of the degree of secondary reactions. Increasing the pyrolysis temperature above 500 °C increases volatile cracking reactions to produce higher portions of CO, H_2, and CH_4 in the biogas, overall increasing the gas's lower heating value (LHV) but lowering the bio-oil's LHV [140-142].

	Primary gas [138]	Secondary gas [138]	Temp. of maximum evolution (°C) [140]
CO_2 (wt%)	53	9	350
CO (wt%)	36	63	350
Hydrocarbons (wt%)	6.7	27	425
H_2 (wt%)	0.8	1.4	700-750
LHV (MJ/nm^3)	11	20	

Table 2.3: Gas evolution from primary and secondary reactions during pyrolysis

Bio-Char: Char is the solid residue (carbon-rich, fine-grained, porous substance) remaining at the end of the pyrolysis process (often called bio-char when derived from biomass), which is made up of varying ratios of a highly carbonaceous material (sometimes referred to as charcoal) and ash, which comprises various inorganic residues.

The definition adopted by the International Biochar Initiative (IBI) furthermore specifies the need for purposeful application of this material to soil for both agricultural and environmental gains [143]. This fact distinguishes biochar from charcoal, which is used as a fuel for heat, as an adsorbent material, or as a reducing agent in metallurgical processes [144]. Char yield and its characteristics are influenced by the pyrolysis temperature, heating rate, reaction pressure, and biomass properties [141,145]. Primary chars produced at low pyrolysis temperatures or low heating rates are unstable and can undergo secondary reactions to form a stable char and additional volatiles [146]. Char produced at low temperatures exhibits a higher oxygen and hydrogen content than char produced at higher temperatures [141].

The char typically accounts for about 15–25 wt.% of the products and equates to around 25% of the total energy available from the biomass feed [147]; the carbon content of the char is often around 50 wt.% of the total carbon content of that found in the original feedstock.

These solid residues can be utilized in various industrial applications that include [li8]: (i) as a solid fuel in boilers; (ii) the production of activated carbon; (iii) as a reactive feed for further gasification processes for the production of hydrogen-rich syngas (CO, CO_2, H_2) by thermal cracking; (iv) soil improvers/fertilizers (v) as a carbon feedstock for the manufacture of carbon nanotubes. The interesting properties of biochar that makes it attractive as a soil amendment is its porous structure, which is believed responsible for improved water retention and increased soil surface area [143]. Furthermore, the addition of biochar to soil has been associated with an increase of the nutrient use efficiency, either through nutrients contained in biochar or through physicochemical processes that allow better utilization of soil-inherent or fertilizer-derived nutrients [143]. In addition to the above-mentioned potentially beneficial effects, a key property of biochar is its apparent biological and chemical stability. In fact, studies of charcoal from natural fire and ancient anthropogenic activity indicate millennial-scale stability [148,149]. This property can allow biochar to act as a carbon sink [143].

According to the above-explained considerations, the conversion of biomass to long-term stable soil carbon species can result in a long-term carbon sink, as the biomass removes atmospheric carbon dioxide through photosynthesis [150]. For this reason, the use of biochar can imply a net removal of carbon from the atmosphere [144]. Furthermore, three complementary goals can be achieved by using biochar applications for environmental management: soil improvement (from both productivity and pollution points of view), waste valorization (if waste biomass is used for this purpose), and energy production (if energy is captured during the biochar production process). In light of this, the production of biochar from agricultural residues and/or forest biomass appears to be a very promising alternative to integrate carbon sequestration measures and renewable energy generation into conventional agricultural production [150].

Bio-Oil: The liquid fraction, commonly known as bio-oil is as a dark colored, free-flowing, but viscous fluid; depending on the initial feedstock and the exact details of the pyrolysis protocol employed, the color can be almost black through dark red-brown to dark green [128]. In general, a typical bio-oil is made up of a complex mixture of oxygen-containing organic compounds (with an oxygen content of ~30–40 wt.%) and tars (benzenes, toluene, naphthalenes), together with an appreciable amount of water, around 10-30 wt.%, which originates both directly from moisture present in the biomass feed and from the dehydration of chemicals as they decompose [41,151]. Notably, pyrolysis-derived bio-oils can contain up to 400 different organic compounds, depending on the precise nature of the pyrolysis process and the particular biomass feedstock [129]. Generally, however, the organic products can be divided into five main categories: anhydrous sugars, furan ring derivatives, low molecular weight compounds (e.g., formic acid, ethanol, acetone), phenols, and other aromatics. Understanding the exact chemical composition and physical properties of bio-oils is important since insight is given into both their stability and suitability for downstream upgrading and subsequent application [147]. For example, due to their high oxygen content, bio-oils are generally viscous, often miscible with water, corrosive, unstable (due to the presence of high levels of unsaturation), and have a density, typically 1150–1300 kg/m^3, that is much higher than that of petroleum-derived from fossil-based crude oils. The density of bio-oils with a low water content is higher, approximately 1200–1300 kg/m^3 [152-154]. Most problematically, the high oxygen content of bio-oils renders them incompatible with today's fossil fuel-based refinery processes, which can tolerate feeds with ~7% oxygen [155]. Viscosity is an important consideration in the application of many fuels and, in the case of bio-oil, this parameter can vary from as low as 25 m^2/s to as high as 1000 m^2/s (measured at 40 °C), depending on the chemical nature of the feedstock, the water content, the amount of volatile species present, and the extent to which reactive components within the bio-oil polymerize over time (aging) [156,157]. Furthermore, bio-oil produced by fast biomass pyrolysis has a heating value (the amount of heat produced from the complete combustion of a specific amount of bio-oil) of only about 16 MJ/kg, compared with 43 MJ/kg for typical fossil diesel [158]. **Table 2.4** lists typical bio-oil properties; the properties for heavy fossil oil are also given for a comparison. Consequently, these oils are corrosive toward common construction materials, such as carbon steel and aluminum and can affect some sealing materials [127]. Together, these factors clearly necessitate that bio-oil be upgraded prior to utilization as a drop-in transportation fuel replacement.

Property	Pyrolysis oil [3,161]	Heavy fossil oil [3]	Effect on the quality in terms of fuel use
HHV ($MJkg^{-1}$)	14-20	40	Larger volumes required [162]
H_2O content (wt%)	15-30	0.1	Lowers the heating value, viscosity, density and ignition rate [159, 163]
pH	2.5	-	Corrosive to pipes and vessels: compounding at elevated temperatures [159, 163]
Solids(wt%)	0.2-1	1	May enhance bio-oil aging, corrosion and equipment blockages [163]
Inorganics	0-0.2	0.1	High temperature corrosion, hard deposits, and bio-oil aging [159, 164]
Viscosity	40-100	180	High pressure drop which increases equipment costs, leakages and ruptures [163]
Density (kgL^{-1})[138]	1.2	0.85	Higher density can cause pumping issues [162]
O_2 content (wt%)	30-48		Immiscible with petroleum based fuels [159]
Safety (flammable class)	3	3	Potentially harmful [160]

Table 2.4: Properties of bio-oil and their effect on the quality

Given some of the problems with bio-oils discussed above, it is desirable that any upgrading process would deliver a product with lower amounts of water and oxygen, as well as decreased acidity, viscosity, and an increased higher heating value (HHV). Consequently, to achieve these targets, bio-oil can be upgraded in a number of ways; physically, chemically, and catalytically, with minimal use of expensive hydrogen [165]. The chemistry of bio-oils reactions and catalytically upgrading way will be extensively discussed in the next paragraphs.

2.2. *Bio-oil's compounds*

The chemistry of compounds in bio-oil and their interactions must be understood in order to predict fuel characteristics and to be able to implement biomass pretreating techniques, bio-oil upgrading, and final refining of the upgraded bio-oil. Bio-oil can contain around 400 compounds produced through hydrolysis, dehydration, isomerisation, dehydrogenation, aromatization, retrocondensation, and charring reactions [3]. Due to the variety and complexity of bio-oils, it is necessary to group compounds into major chemical groups such as water, organic acids, aldehydes, ketones, furans, sugars, alcohols, phenols, esters, light oxygenates and hydrocarbons [166]. Based on the mass of components in the bio-oil, approximately one third is phenols, one third is neutral components, and rest is a mix of organic acids, aldehydes, ketones, esters, and water [167,168]. The light oxygenates, sugars, organic acids, alcohols, and furans originate from cellulose and hemicellulose. Secondary reactions of oxygenates, sugars, and furans probably produces esters, organic acids, alcohols, ketones, and aldehydes [3]. The significant organics produced during pyrolysis are listed below:

- Organic acids: Acetic acid is the major organic acid, formed mainly from acetyl braches of hemicellulose [139, 168]. Acetic acid is also produced during the secondary reactions of volatiles, such as the dehydration of an aldehyde alcohol to a ketone and then rehydration to an acidic product [169]. Smaller quantities of formic, lactic, and oxalic acid are formed mainly during the secondary reactions.

- Anhydrosugars: Levoglucosan (anhydroglucose, 1,6-anhydro-β-D-glucopyranose) is the main anhydrosugars formed. It is a primary product, which is probably formed by a mechanism involving intramolecular condensation and sequential depolymerisation of glycosidic units [3]. The yields can be up to 20 wt% if biomass is pretreated to reduce the inorganic and hemicellulose content [3,163,170], as levoglucosan is stable at pyrolysis conditions when no catalyst is present [171,172]. In the presence of catalysts, levoglucosan can breakdown to substituted furans and pyran derivatives [158]. Levoglucosan is not suitable as a fuel, as combustion at 527 °C will not cause vaporisation [166], but it can be used as a building block for producing other compounds. Hydrolysis of levoglucosan gives glucose, this can be converted to fructose, then hydroxymethylfurfural (HMF), which is a precursor to 2,5-dimethylfuran (DMF): potential biofuel [173,174].
- Light oxygenates: Normally in pyrolysis, the system can be set to produce either high yields of levoglucosan or light oxygenates. Production of light oxygenates is thought to occur during sequential decomposition of levoglucosan or through parallel reactions [170]. Higher temperatures, longer residence times, or the presence of catalysts (such as fructose, inorganics, chloride, and zinc chloride) enhance hydroxyacetaldehyde (glycolaldehyde), 1-hydroxy-2-propanone, hydroxyacetone, and 5-hydroxymethly-furfural formation over levoglucosan [163,169,171,172].

- Polycyclic aromatic hydrocarbons (PAHs): Aromatic compounds can be formed through secondary and tertiary cracking reactions. These involve pyrolysis of alkanes to produce alkenes which are subsequently aromatised through Diels-Alder type reactions to form a single ring aromatic compound that can further react to form PAHs [175]. The concentration of PAHs increases with the pyrolysis operating temperature [176,177]. They are normally not detectable below 500 °C and only become significant in the tar fraction above 700 °C. Examples of PAHs include naphthalene, phenanthrene, and fluorene and their alkylated substituents.
- Phenols: These are produced primarily from lignin during pyrolysis. Phenolic compounds are produced between pyrolysis temperatures of 200-350 °C, following radical C-O and C-C bond cleavage [178]. As phenols are potentially high value compounds, different methods have been used to separate or extract phenols from bio-oil including alkaline extraction; partition into different solvents or adsorption on different packed materials; liquid chromatography; and steam distillation [178].
- Oligomeric compounds: Also defined as pyrolytic lignin, and can make up 20-30 wt% of the bio-oil. This high molecular weight fraction cannot be vaporised and rapidly forms tar, then eventually char when heated to over 100 °C [180]. Pyrolytic lignin can be produced during the secondary reactions or sudden entrainments of small wood polymers as aerosol, before they have time to full depolymerise [180]. Their molecular weight is normally between 650-1300 $gmol^{-1}$; therefore increases the bio-oil's viscosity.
- Alcohols: Methanol is the primary alcohol formed during pyrolysis from the cleavage of methyl branches and from

the breakdown of methyl esters and/or ethers. The addition of 5% methanol to bio-oil can reduce the viscosity by 35% via partial oxidation reactions [159,168], and reducing polymeric interactions.

- Furans: 5-hydroxmethyl furfural (5-HMF) can be produced during pyrolysis of hemicellulose. Alternatively, a glucose monomer from cellulose can be converted to a five membered structure via a ring opening step [172]. This has the potential to be upgraded to 2,5-dimethylfuran (DMF) through triple dehydration, which is a potential biofuel [181].

Short residence times and rapid quenching during pyrolysis means that vapours do not reach thermodynamic equilibrium; therefore they may react during storage until thermodynamic stability is obtained [159]. The bio-oil's viscosity is often used as a measure for stability [138,182,183], as it tends to increase upon storage or upon heating through polymerization, condensation, esterification, and polycondensation reactions. A homogeneous bio-oil can separate into layers during storage as low molecular weight compounds (such as water and alcohols) are released during polymerization reactions [183]. If bio-oil separates into two phases, the heavy bottom phase undergoes polymerization and condensation reactions during storage, increasing the bio-oil's viscosity [183]. It is important to understand potential reactions in bio-oil to be able to enhance desirable ones and prevent undesirable ones. Possible reactions are listed in **Table 2.5**, from which it can be seen that the carbonyl compounds (especially aldehydes) are highly active in bio-oil and can lead to polymerization reactions [184]. Inorganics and/or organic acid catalysts are required for many reactions. Other reactions possible are methoxy (R-O-CH3) compounds being polymerization precursors [185], and pyrolytic lignin reacting with other pyrolytic lignin or other compounds (especially carbonyl compounds).

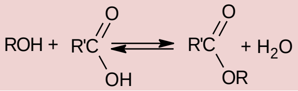
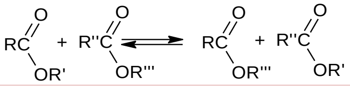
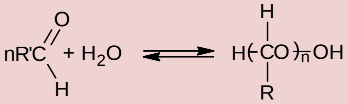
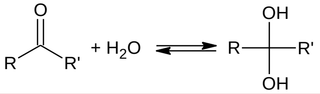
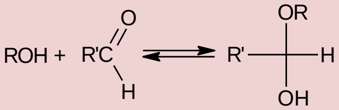
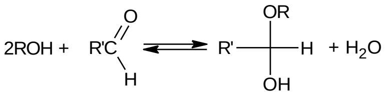
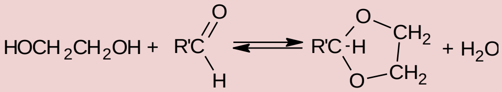
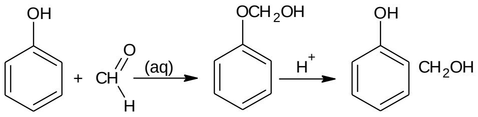
Reaction	**Reactants**	**Products**
Esterification 	Alcohols, organic acids	Esters, water
Trans-esterification 	Esters	Esters
Homo-polymerisation 	Aldehydes, furfurals	Polyacetal oligomers and polymers
Hydration 	Aldehydes or ketones, water	Hydrates (glycol)
Hemiacetal formation 	Aldehyde, alcohols	Hemiacetals
Acetalisation 	Aldehyde, alcohols	Aldehydes, alcohols, or a cyclic diether
Trans-acetalisation 	Aldehyde, alcohols	Aldehydes, alcohols
Phenols 	Phenols, aldehydes	hemiformal
Polymerisation	Phenols, aldehydes	Novolak resins, water
Condensation	Furan derivatives	Furan polymers
Olefinic condensation	Unsaturated compounds	Polyolefins
Oxidation	Air, alcohols, aldehydes	Carboxylic acids, hydroperoxides, alkylperoxides
Decarboxylation	Carboxylic acids	Mono-acids, carbon dioxide

Table 2.5: Possible reactions in bio-oil [3,186]

2.2.1. *Bio-oil upgrading*

Crude bio-oil cannot be used directly in a diesel combustion engine [138]. This implies that upgrading and subsequent refining steps are required to improve the bio-oil's quality and stability before its commercial use as a liquid fuel [184]. The multi-scale structure and complex composition of biomass make fundamental predictions of bio-oil properties challenging [172], thus it is hard to define the general severity of upgrading required. An obstacle for the bio-oil upgrading is the bio-oil's instability, leading to coke formation on the upgrading catalysts. Carbonyl compounds (aldehydes, ketones, carboxylic acids, and esters), inorganics, char, and pyrolytic lignin are thought to be responsible for many of the polycondensation reactions that cause bio-oil aging [163, 184, 185]. Hydrocarbons and alcohols are traditionally acceptable compounds for fuels. Levoglucosan is desirable as alternative products are non-condensable gases and small oxygenated compounds. Phenols are also desirable due to the high commercial value if extracted [185].

For all this reasons pyrolysis bio-oils cannot be used directly as fuels due to their high oxygen content, corrosive nature, high acidity and viscosity, and relative instability. Accordingly, prior to their use as fuels these bio-oils must be improved by applying physical or chemical, moreover the catalytic way does not require costly pre-upgrading techniques as condensation and revaporization. Biomass pyrolysis in the presence of a catalyst, in situ, is considered as one of the options to overcome the problem characteristics of bio-oil mentioned above. Selective removal by decarboxylation of carboxylic acids (formic, acetic acids) will decrease the acidity of bio-oil. Selective deoxygenation of organic fractions (aldehydes and ketones, unsaturates, etc.) that undergo easy condensation/oligomerization reaction can help in the stabilization of the oil. Indeed, many times the final product is evaluated by its O/C ratio and H/C ratio, with low O/C and high

H/C ratios indicating a higher quality liquid product. These ratios are particularly important if the bio-oil is to be used as a substitute for demanding petrochemical applications such as transportation fuels that need a clean, homogenous fuel stream [46].

The methodologies that can be used for the directly introduction of a catalyst into pyrolysis reactor system are various and depend from nature of the employed reactor. The simplest method involves in physically mixing the catalyst with the starting biomass [186,187]. Alternatively, another ex situ approach consist in to while away the gaseous pyrolysis products over a catalyst directly placed upon exiting the reactor. The kind of catalyst and the reactions involved in catalytic pyrolysis process will be discussed in the next paragraph.

2.3. *Catalytic upgrading*

For bio-oil upgrading many chemical routes including cracking, decarboxylation, decarbonylation and hydrodeoxygenation can be extensively used to improve the quality of bio-oils [188-192]. A high oxygen content and the active oxygenates such as acids, ketones, and aldehydes in bio-oil are mainly responsible for the adverse attributes of bio-oils [192]. Thus the role of a catalyst in catalytic pyrolysis is to promote the removal of most of the oxygen in selective ways and convert the active species to stable and useful components in bio-oil. A scheme of the most representative catalytic upgrading reactions is shown in **Figure 2.4**. Deoxygenation by full *decarboxylation* is the best route to make fuel precursors from bio-oil, because paraffin is produced and expensive hydrogen is not required. Decarboxylation of bio-oil has been tried over zeolites, yielding an aromatic product with a too low yield and excessive coke formation.

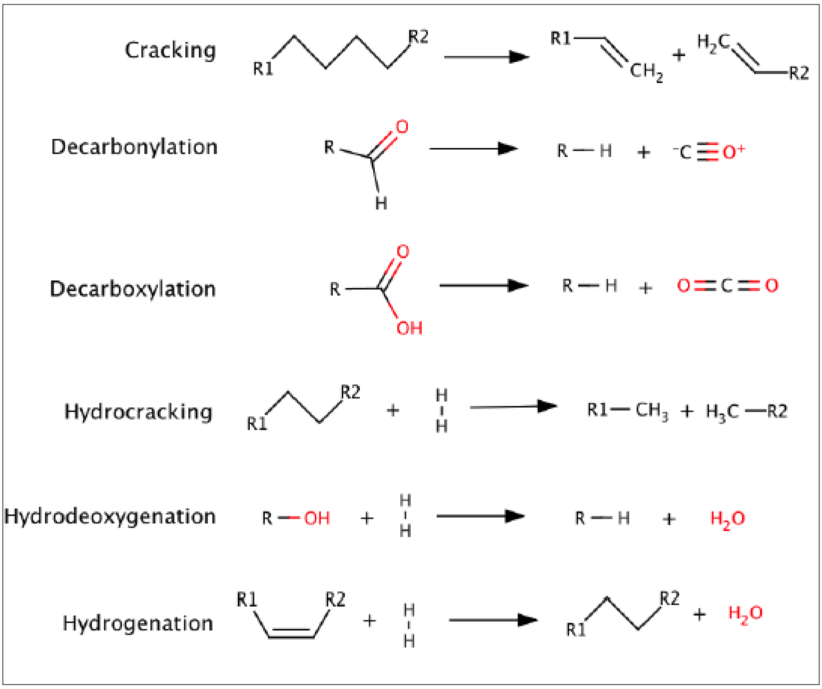


Figure 2.4: Representative catalytic upgrading reactions

Selective decarboxylation of organic acids makes the bio-oil less acidic and corrosive. If acids can be removed selectively as CO_2, it would also improve the energy content of the resultant bio-oil. Removal of oxygen as CO_2, as against water, retains hydrogen content and hence the higher energy content of the bio-oil. The actual oxygen removal by only decarboxylation of the acids is, however, not sufficient and this makes this process not optimal for the goals to be achieved.

Hydrodeoxygenation (HDO) is a hydrogenolysis process that removes oxygen from a feedstock. Carbon-oxygen bonds are cleaved with hydrogen in the presence of a catalyst producing CO_2 and H_2O and partially eliminating oxygen from the final product. This type of reaction can be achieved through sulfide/oxide and transition metal catalysts through a combination of chemisorption, proton donation, and desorption. The catalyst reactivity relies on the number and strength of both Lewis acid and Brønsted acid sites on the catalyst/support system. Supports affect both the acidity and reactivity of the catalyst compound. Ideally, they should be stable and have a low affinity for carbon formation and a high affinity for activation of oxy-compounds [193]. HDO produces a quality, energy dense, non-corrosive, naphtha-like product, which can be further upgraded to other chemicals [163]. HDO also has the advantage of easy separation of water and benefits to turbines from the separation of alkali metals from the hydrocarbon product when oxygen levels are reduced to less than 2%. However, it has the major disadvantage of consuming large quantities of high-pressure H_2, 600–1000 L/kg bio-oil, thus increasing costs [163].

Another upgrading process is the *catalytic cracking* of pyrolysis vapors. Indeed, The heavy organics that formed from re-polymerization or fragmentation can also be converted to low molecular-weight products by cracking. The catalytic cracking chemistry of pyrolysis vapors involves conventional reactions, such as protolytic cracking (cleavage of C–C bonds), hydrogen transfer, isomerization, and aromatic side-chain scission, as well as deoxygenation reactions, such as dehydration, decarboxylation, and decarbonylation [193-195]. Dehydration occurs on acid sites and leads to the formation of water and a dehydrated product. Decarboxylation and decarbonylation result in the formation of CO_2 and CO. Repeated dehydration and hydrogen transfer of polyols allows the production of olefins, paraffins, and coke [196]. Aromatics are formed by Diels–Alder and condensation reactions of olefins and dehydrated species [196]. The conceptually complete deoxygenation reaction of pyrolysis vapors predicts a maximum oil yield of 42 wt% [193]. Hydrocarbons are formed in catalytic cracking with Zeolite. For this process can be used different kind of catalysts such as zeolite or metal oxides (nickel and cerium catalysts).

2.3.1. *Zeolite cracking*

Zeolites are complex, three-dimensional porous structures with varying elemental compositions that exhibit catalytic activity in up to 50% of their volume. Cracking and dehydration are the main reactions seen. Adsorption of the oxy-compound occurs on an acid site. This is followed by either decomposition or bimolecular monomer dehydration, as determined by pore size [193]. As with sulfide/oxide and transition metal catalysts, the acidity of the zeolite affects the reactivity and yields, with high acidity leading to a higher affinity for C and water formation [197].

In HZSM-5, one of the most widely used zeolites, acidity is linked to the Si/Al ratio, with a low ratio indicating high acidity. Pore blockage from polymerization and polycondensation reactions causes deactivation of the catalyst. The protonated form of ZSM-5 (H-ZSM-5) can be obtained by thermal decomposition of ammoniated form of ZSM-5. The conditions applied for deammoniation (temperature, heating rate, and period) will affect the acidity of ZSM-5. Zeolites should have correct pore size and Bronsted acidic sites to promote desired reactions while minimizing carbon formation [193]. A possible mechanism for dehydration of hydroxyl containing compounds (i.e., carbohydrates) on an aluminosilicate zeolite is given in **Figure 2.5** [193].

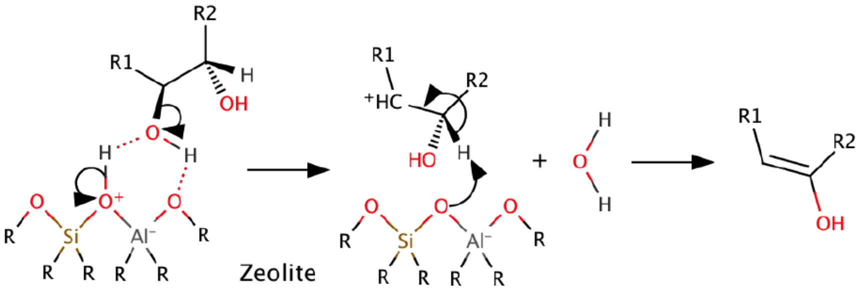


Figure 2.5: Aluminosilicate zeolite dehydration of model compound

Zeolites produce aromatics at atmospheric pressures without H_2 requirements. In presence of acid zeolites, some of light organics are deoxygenated and cracked.

Deoxygenation of light organics (esters, ketones, alcohols, ethers, and phenols) on acid catalysts involve decarbonylation, decarboxylation and dehydration which produce hydrocarbons, water, and carbon oxides. Cracking will give various carbon fragments which undergo oligomerization to produce mixture of C2-C6 olefins. These olefins undergo a series of aromatization reactions to produce benzene followed by alkylation and isomerization to produce varios aromatic hydrocarbons. Aromatization involes cyclization and hydrogen or hydride transfer. The final product generally has a low heating value. This is due both to its low H/C ratio and high O/C ratio as compared to HDO oils [111,193]. Research is generally conducted at temperatures from 350 to 600 °C. For HZSM-5, yields are in the 15% range with predictions of 23% [163]. A disadvantage of these catalysts is an excessive C production and therefore catalyst coking is a problem.

2.3.2. Mineral Catalyst

The minerals can be described as homogeneous solids that have a precise, but generally not fixed, chemical composition and an ordered atomic arrangement [198]. The catalysts belonging to this class they can be used as it is or after having undergone a heat treatment. In general, the minerals are relatively cheap compared to synthetic catalysts. Here are the main minerals used in catalytic reforming of tar. The calcined rocks are constituted by oxides of alkaline - earth metals (CaO, MgO) that belong to the second group of the periodic table (beryllium, magnesium, calcium, strontium, barium, radio) and generally comprise calcite, magnesite and calcined dolomite. The non-calcined forms of such materials are called respectively limestone ($CaCO_3$), magnesium carbonate

($MgCO_3$) and dolomite ($CaCO_3$, $MgCO_3$). These materials exhibit catalytic activity in the tar reduction when calcined. The calcination is a heat treatment which causes the loss of carbon dioxide contained in the mineral when this is heated. The catalytic activity of the calcined rocks is linked to various factors such as the pore size, surface area, and the content of alkali metals (K, Na). I factors that cause the catalytic deactivation of the calcined rocks are related to the formation of coke and the partial pressure of CO_2. The formation of coke causes the deactivation of the calcined rocks, for "pore mouth blockage" [199]. The partial pressure of CO_2 instead causes the deactivation of the catalyst when its value is greater than the value of the equilibrium partial pressure of CO_2 to the calcination temperature. Studies conducted on the pyrolysis of cellulose and biomass have shown that these oxides of alkali metals favor the formation of char during the thermochemical conversion. A lower conversion of char increases the percentage of ash. Among the calcined rocks, dolomite is very interesting because very economical and with the significant reduction in tar capabilities [200].

Dolomite is a calcium magnesium compound whose overall chemical formula $CaMg(CO_3)_2$ with a content of 20% of MgO, ~ 30% CaO and ~ 45% by weight of CO_2, with a small amount of mineral impurities. The dolomites in their original form are not suitable as catalysts, therefore must undergo a calcination process during which the carbonate is decomposed into CaO and MgO thus eliminating CO_2. The total calcination of dolomite occurs at temperatures between 800 and 900 °C. These temperatures restrict the use of dolomite as catalyst. Calcined dolomite also loses its status as a catalyst for conversion of tars under conditions in which the partial pressure of CO_2 is greater than the equilibrium decomposition pressure of dolomite; this feature should be considered in pressurized gasification processes. At high partial pressure of CO_2, the calcination of dolomite takes place in two steps:

$$CaMg(CO_3)_2 \uparrow 780\text{-}800\ °C \rightarrow CaCO_3 + MgO + CO_2$$
$$\uparrow 880\text{-}900\ °C \rightarrow 2CO_2 + MgO + CaO$$

At low partial pressure of CO2 (<200 Torr) calcination occurs in one step:

$$CaMg(CO_3)_2 \uparrow 700\ °C \rightarrow MgO + CaO + 2CO_2$$

In literature we can found that the primary tars converted to gases increases markedly with temperature. Various research groups have conducted extensive studies examining the loss of effectiveness of calcined dolomite in the conversion of tar and other non-metallic oxides catalysts. In general, studies have shown that dolomite is an effective catalyst for reforming tar [201,202]. Another mineral used for its catalytic activity and which can be an alternative to dolomite is olivine. This mineral, very abundant in the earth crust, contains magnesium oxide, iron oxide and silicon. Its general formula is (MG1-xFex) 2 SiO_4, with an iron content (x) that can vary depending on its origin, but remains practically close to 0.1 for most of the olivine.

2.3.3. *Metal oxides*

Metal oxides, particularly transition metal oxides, have been widely used as heterogeneous catalysts in various reaction [203,204]. Generally, metal oxides possess either redox properties due to their multivalent nature and/or certain acid–base properties which could potentially catalyze the thermal decomposition of lignocellulose and/or the reaction of pyrolysis intermediates to for more stable products [203-205]. Various metal oxides, including MgO, NiO, Al_2O_3, ZrO_2, TiO_2, MnO_2, CeO_2, Fe_2O_3, and their mixtures, have been tested as catalysts for catalytic pyrolysis. Acidic metal oxides such as Al_2O_3, SiO_2, and SiO_2–Al_2O_3 have been investigated as catalysts in pyrolysis [206-210]. Addition of acidic metal oxides led to the decrease of liquid yield and increase of gas and solid yields [206]. The presence of acidic metal oxides also changes the composition of bio-oil. For Al_2O_3-catalyzed pyrolysis, there were many more aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAH) in the organic products. SiO_2 with weak acidity and medium porosity was active in removing oxygenated compounds such as acids, ketones, and aldehydes and in inhibiting coke and polycyclic aromatic compound formation [208]. Furthermore classic basic and acidic metal oxides, transition metal oxides such as NiO, tetragonal ZrO_2, ZnO, TiO_2, Fe_2O_3, CeO_2, MnO_2, and binary transition metal oxides such as ZrO_2/TiO_2, Mn_2O_3–CeO_2, and ZrO_2–CeO_2 have also been investigated in catalytic pyrolysis of biomass [59,206,211-214].

TiO_2, Fe_2O_3, NiO, and ZnO catalysts can decrease the liquid and organic product yields and increase the gas, water, and solid products yields [59]. Particularly, CO_2 yield increased in the presence of NiO and ZrO_2/TiO_2. And the simultaneous increase of CO_2 and H_2 in gas products indicates the increase of CO_2 yield over NiO is more likely due to the steam reforming [206]. In a recent study, alumina supported Ni-based catalysts were used in pyrolysis of *Shenedesmus almeriensis* biomass residue to produce H_2 rich gases [67]. The results indicated that Ni-based catalyst activated the cracking and reforming of biomass volatiles and tars released during pyrolysis at low temperatures. Low cost and available source of Ni-based catalyst are important criteria for using these catalysts instead of noble metals [71]. It has been reported that Ni(8%)/Al_2O_3-CeO_2 catalysts has higher conversion and better stability compared to Ni(8%)/Al_2O_3 catalyst due to redox properties of ceria. CeO_2 enhances the water gas shift (WGS) reaction and the redox reversibility of active phase [72]. Ceria-zirconia solid solution promoted the cracking of C-C bonds converting more acetic acid compared to the use of only ZrO_2. Besides, the addition of Ni improved both conversion and selectivity of hydrogen [53]. Ni promoted steam reforming reactions and retarded the rate of carbon deposition above the catalyst surface [73]. Among various carrier, Ni/CeO_2 showed the highest activity as well as high stability [72]. The cracking properties of Ni and ceria can be beneficial to the in-situ deoxygenation of bio-oils.

3. Chapter 3: Experimental section

3.1. Feedstock pre-treatment

Posidonia Oceanica samples were collected from the costs of Sicily region (Italy). First, the samples were washing with distilled water, successively, Posidonia Oc. was air-dried (at 110 °C for 12 h), shredded and sieved into a size range of 16-25 mesh. Samples were conserved an oven at 100°C.

3.2. Catalyst preparation and characterization

Catalysts were prepared by impregnation (incipient wetness) using γ-Al_2O_3 AKZO-NOBEL 001-3P (SA (BET) 260 m^2 g^{-1}), ZSM-5 ALFA AESAR (SA (BET) 400 m^2 g^{-1}) (30:1 molar ratio) and CeO_2 Sigma Aldrich (SA (BET): 27 m^2 g^{-1}) as supports. Ni(5%)/CeO_2, Ni(21%)/Al_2O_3, Ni(5%)/HZSM-5 were prepared using an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich) as precursor. Ni(5%)Ce(5%)/HZSM-5 was prepared using an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich) and $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar) as precursors. Dolomite ($MgCa(CO_3)_2$) a mineral catalyst was purchased from Minerali Industriali S.r.l.. All catalysts were dried at 110°C for 3h and then calcinated at 600°C for 3h before use. Catalysts were pressed at 400 bar, crushed and sieved and the 16–25 mesh fraction was used for the catalytic tests.

The surface area, pore volume and average pore size of the prepared catalysts were analyzed by N_2 adsorption method at −195.8 °C using Micromeritics ASAP 2020 instrument. The catalyst samples were outgassed overnight at 180 °C. The surface area and pore size distribution of the samples were calculated by using the standard Brunauer–Emmett–Teller (BET) equation and the Barret-Joyner-Halenda (BJH) method, respectively. The crystalline phases of the catalysts were identified by powder X-ray diffraction using Philips X'Pert X-ray diffractometer, operating with Cu/Kα radiation (wavelength = 1.5406 Å, 40 kV, 30 mA). Data were collected over the angular range 5–80 degrees in 2θ under atmospheric pressure. The peak profiles of the (2 2 0) reflection in the face-centered cubic (fcc) structure were obtained using the Marquardt algorithm. Instrumental broadening was determined using a standard platinum sample.

3.3. Proximate and ultimate analysis

Each sample of biomass was characterized by proximate, ultimate analyses and HHV (higher heating value) value and results are reported in **Table 3.1**.

Posidonia Oceanica		
Proximate analysis (wt%)	Ash	14,02
	Moisture	12,67
	V.M. 525°C	60,95
	F.C.	12,36
Ultimate analysis (wt%)[a]	C	40,29
	H	5,96
	N	1,12
	S	0,29
	O[b]	25,65
H/C atom ratio		1,40
O/C atom ratio		0,64
HHV (MJ/kg)		16,20
Protein (wt%)		7,03

a. As received b. By difference

Table 3.1: Physical-chemical properties of the Posidonia Oceanica feedstock

Proximate analysis included measurement of moisture content, volatile matter, fixed carbon and ash. The moisture content measurement were performed on biomass samples, dried in a convection oven at 110 °C until constant weight was recorded. The volatile matter content was determined by measuring weight loss after heating biomass samples to 575 °C in an alumina crucible under N_2 atmosphere. The ash content was measured by heating samples at 575±25 °C for 24 h to constant weight in a muffle furnace and the fixed carbon fraction was calculated by subtracting the percentages of volatile matter, moisture content and ash from 100%. Elemental analysis was performed on biomass samples, bio-oil and bio-char using CHNS-O Elemental Analyzer (Thermo Fisher Scientific, Flash EA 1112). Based on the elemental composition and according to literature [215,216], High Heating Values (HHV) of biomass, bio-chars and bio-oils were calculated with following equations:

$$\mathbf{HHV(OLS)=}\ 1.87(C)^2 - 144(C) - 2802(H) + 63.8(C*H) + 129(N) + 20147 \qquad \text{eq. 1}$$

$$\mathbf{HHV(PLS)=}\ 5.22(C)^2 - 319(C) - 1647(H) + 38.6(C*H) + 133(N) + 21028 \qquad \text{eq. 2}$$

$$\mathbf{HHV=}3.55(C)^2 - 232(C) - 2230(H) + 51.2(C*H) + 131(N) + 20600 \qquad \text{eq. 3}$$

HHV of biomass and bio-char samples were calculated with an average of ordinary least-squares regression (OLS, eq. 1) and a partial least-squares regression (PLS, eq. 2) methods. Differently HHV bio-oil samples were calculated with equation 3.

Protein fraction was estimated based on the nitrogen content (wt.%) of the biomass using a nitrogen factor (NF=6.25) [217]. Protein fraction of all biomass samples was calculated as follows:

Wt.% protein = N wt.% * NF

3.4. Feedstock and products analysis

3.4.1. Thermogravimetric analysis (TGA)

Thermo-decomposition of Posidonia Oceanica under pyrolysis has been investigated by thermo-gravimetric analysis (TGA) and derivative thermo-gravimetric (DTG) measurements. TG-pyrolysis using N_2 as carrier gas was used to determine the moisture content, volatile matter and fixed carbon and to compare/confirm with the results obtained by ASTM standards. These techniques measure the amount and rate of change in the weight of material as a function of temperature. The temperature at the peak (the minimum or maximum) of the DTG curve represents the thermal decomposition of the samples. If the peak of the DTG occurs at a low temperature, the reaction can occur easily, and the height of the DTG curve identifies the capability to release volatile matter from a reaction during the pyrolysis process. Experiments were carried out by feeding the feedstock samples to a thermogravimetric analyzer (Netzsch Thermische Analyse TASC 414/2). The samples, weighing approximately 10 mg, were heated from 25 to 800 °C with a constant heating rate of 10 °C/min under N_2 and then the temperature was decreased to 600 °C to determine the fixed carbon and ash contents under air atmosphere. The loss of weight between 25 and 105°C was used to calculate the moisture content of the samples. The volatile content of the raw material was determined from the weight loss between 105 and 600°C as primary volatiles and 600 and 800°C as secondary volatiles. The ash content of the sample was determined from the amount of solid remaining at the end of the combustion step. Fixed carbon was calculated by subtracting the ash content from the solids remaining at the end of run. The TGA and DTG plots of all samples are shown in **Figure 3.1**.

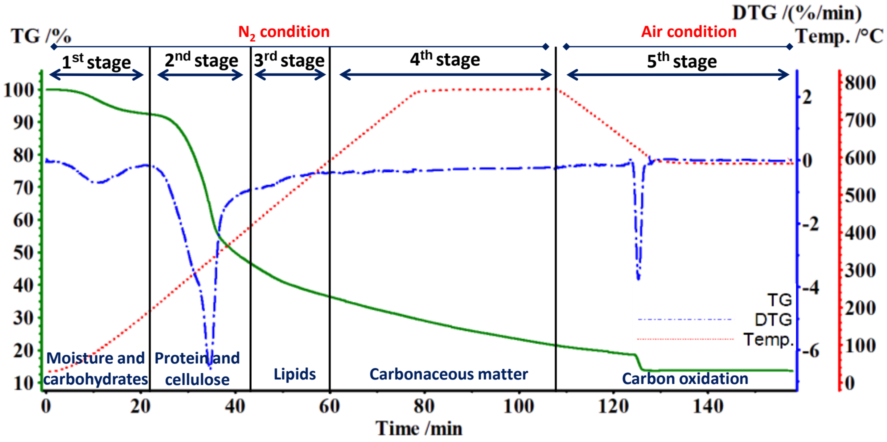


Figure 3.1: TGA and DTG curves of Posidonia Oceanica

3.4.2. *X-ray diffraction (XRD) analysis*

The crystalline phases of Posidonia Oceanica feedstock and bio-chars samples obtained from pyrolysis process were identified by powder X-ray diffraction using Philips X'Pert X-ray diffractometer, operating with Cu/Kα radiation (wavelength = 1.5406 Å, 40 kV, 30 mA). Data were collected over the angular range 5–80 degrees in 2θ under atmospheric pressure. The peak profiles of the (2 2 0) reflection in the face-centered cubic (fcc) structure were obtained using the Marquardt algorithm. Instrumental broadening was determined using a standard platinum sample.

3.4.3. *X-ray fluorescence (XRF) analysis and pH measurements*

Bio-char's mineral content obtained by non -catalytic pyrolysis was measured by X-ray fluorescence (XRF) spectrophotometer (Innov-X Systems Alpha 4000) equipped with a rhodium target X-ray tube and a 4 kW generator. Dry char (4 g) was mixed with X-ray pellet mix powder (1.5 g) and boric acid (1 g) for 2 min in a puck grinder, and then pressed into a pellet under vacuum to 25 tons pressure for 15 s.

For the pH measurements an Orion pH meter (Thermos Scientific) was used; in particular, bio-char to deionized water ratio (1:10 wt.:wt) was used to form a homogeneous suspension, and the pH was determined after 1 h of equilibration.

3.4.4. Bio-oil water contents and Gas chromatograph - mass spectrometry (GC-MS) analysis

Water contents of oils obtained by non-catalytic pyrolysis process were determined by Karl-Fischer Volumetric Titrator.

Bio-oils and aqueous samples were extracted with dichloromethane (1:1, v/v) and, extracts were semi-quantitative quantitative analyzed by gas chromatography coupled with mass selective detector (GC-MSD), performed on an Agilent 7890A-5975C instrument using a DB-WAXETR Agilent Technologies (30m X 0.25mm X 0.25 μm) [230]. GC and the injector temperatures were the same during analysis. Helium was used as the carrier gas at a flow rate of 3.0 ml/min. 1 μL samples was injected with a split ratio of 1:20. The GC oven temperature program was as follows: start at 40 °C; hold for 10 min, raise from 40 °C to 200 °C at a heating rate of 5 °C/min; hold for 15 min, raise to 240 °C at a heating rate of 10 °C/min; hold for 15 min, raise to 260 °C at a heating rate of 10 °C/min; hold at the final temperature for 10 min. The end of column was directly introduced into the ion source of a mass selective detector of Agilent 5975C series with operating conditions of transfer line at 270 °C, ion source at 250 °C and electron energy of 70 eV. Mass spectral library databases provided by NIST05a.L was used to identify the chemical constituents.

3.4.5. Coke analysis

The amount of coke deposited on each catalyst was determined by the weight change during combustion using a thermogravimetric analyzer (Netzsch Thermische Analyse TASC

414/2). The burning of coke was carried out. 20 mg of sample in the alumina crucible were heated from 25 °C to the final temperature of 900 °C at a rate of 10 °C/min under a 70 mL/min air atmosphere.

3.5. Experimental plant

As shown in **Figure 3.2 a**, the schematic diagram of the experimental plant for pyrolysis of Posidonia Oceanica mainly consisted of carrier gas system, reactor unit, bio-oil collectors and GC monitor as major setups.

The accurate regulation and measurement of gas flow is performed by flow electronic meters, type "Mass Flow Controllers", ASM-AFC 25.50 model.

The details of fixed-bed reactor were presented in **Figure 3.2 b**, the reactor is made of preheat zone (80 mm in length) and pyrolysis zone (100 mm in length); this last is a high temperature resistant stainless steel pipe (length: 300 mm; internal diameter: 16 mm) with a shrinking point at the bottom. The reactor was placed into an electric furnace of 1.0 kW whose temperature was leaded by a controller driven by one thermocouple (K type) located in an internal wall within the same. Additional thermocouple (K type) was placed at the center of the biomass bed to measure temperature inside the reactor. The heating apparatus was calibrated is such a way that all temperature measuring points have the same constant temperature.

Bio-oils are collected in three cold traps maintained at -78 °C (liquid nitrogen and ethyl acetate mixture) and placed immediately next the reactor outlet stream. Gas chromatography technique is used for analysis of gas and liquid products. In particular, gases are analyzed with a GC 7890A (Agilent Technologies) with three column (molecular sieves SA, Porapack Q, Hayesep) connected at two detectors; one to thermoconductivity (TCD) and the other to flame ionization (FID). Instead, the liquid product is analyzed with gas chromatography coupled with mass selective detector (GC-MSD), performed on an Agilent Technologies 7890A-5975C instrument using a DB-WAXETR (30m X 0.25mm X 0.25 μm) column.

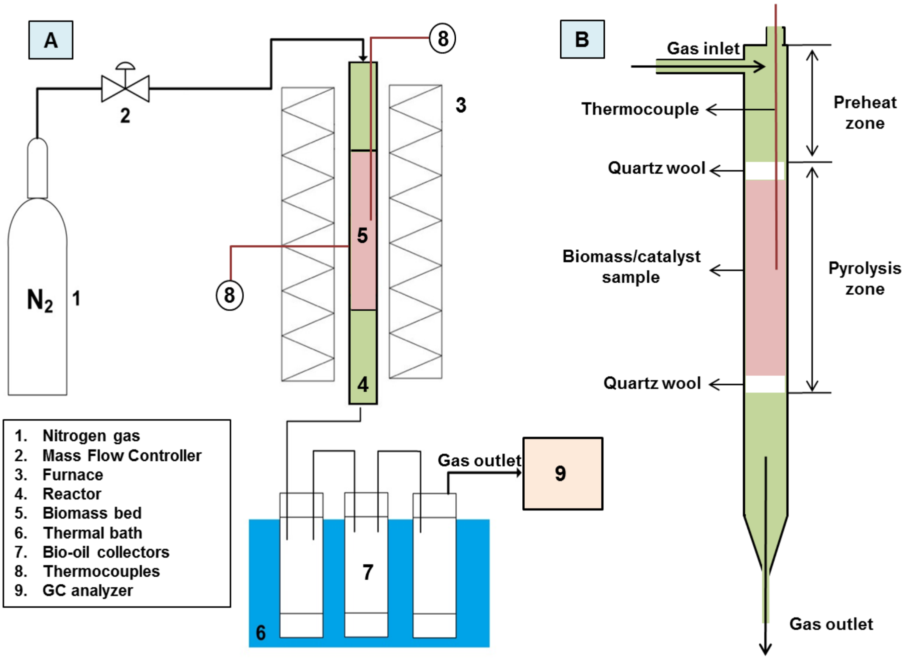


Figure 3.2: a) Scheme of lab-scale pyrolysis plant; b) details of the fixed-bed reactor

3.6. Pyrolysis experiments

3.6.1. Preliminary experiments

Before of catalytic pyrolysis proofs have been conducted preliminary tests for evaluate the best process conditions in term of conversion and bio-oil yield. These tests were carried out changing whenever only a single operative parameter in order to identify optimal test conditions.

Considered parameters were: sweeping gas flow rate, heating rate and reaction temperature.

Measures at different sweeping gas flow rates: residence time of pyrolysis vapors is an important factor to determine the secondary reactions possibility, as thermal cracking, polymerization and condensation. The residence time is principally determined from flow rate. Nitrogen flow facilitates volatiles component removal from the hot zone to than the cold, so as to maximize the yield of the liquid fraction [218]. Studies have shown that in green-blue algae pyrolysis at 500°C an increasing the nitrogen flow rate until at 100 cc/min leads at an increment of bio-oil yield from 20.36% at 54.97%. Instead, the bio-char and bio-gas yields are decreased from 27.47% to 23.97% and from 54.97% to 20.47% respectively. In the present work was studied the flow rate in a range between 30-120 cc/min of nitrogen.

Measures at different heating rates: another important factor that affect the pyrolysis products yield is heating rate of the biomass. Various studies have demonstrated that an increase of heating rate involve in an enhancement of bio-oil yield. Demiral et al have demonstrated that the bio-oil yield increases from 45% to 57% with an increments of heating rate from 50°C/min to 250°C/min [219]. In this particular case, the studies were performed in a range of heating rate among 10-80°C/min.

Measures at different reaction temperatures: pyrolysis temperature is the most important parameter for distribution of the product yields. Indeed, the change of products yield reflects the temperature capacities on the biomass decomposition [220]. Tests were carried out at four different temperatures: 400, 500, 600 and 700°C respectively.

The catalytic proofs were conducted in the best operating conditions find at the end of preliminary tests.

3.6.2. *Catalytic experiments*

Experiments were performed in a stainless steel fixed-bed reactor (height: 30 cm; diameter: 1.6 cm) under nitrogen flow (50 ml/min) as a carrier gas that flowed from the top of reactor to the bottom. Measurements were carried out at atmospheric pressure and 500 °C of temperature but before each pyrolysis test, the reaction system was purged by N_2 for 30 min to swap out air to obtain an inert condition.

In a typical run, 3 grams of dried Posidonia Oceanica (70%)/catalyst (30%) mixture was put inside the reactor. An external electric furnace with temperature controlled was used to heat the reactor at 60°C/min. The reactor was kept at desired temperature for 60 min. Outlet gas stream was condensed in three cold traps (-78°C) and the liquid product (bio-oil) was extracted with dichloromethane (CH_2Cl_2), then the solvent was evaporated at 40 °C using a rotary evaporator and the bio-oils weighted. The solid residue (bio-char) remained in the reactor was successively recovered and weighted. The amount of gaseous products was calculated by subtracting the solid and liquid yields from the amount of initial raw algae (3g).

The following equations were used to calculate the conversion and product distribution (yields) of pyrolysis experiments:

$$\textbf{Conversion (\%)} = [(W_0\,(1-M) - W_{char}\,(1-A-M))/W_0\,(1-M)]*100 \qquad \text{eq.4}$$

$$\mathbf{Y_{char}\ (\%)} = ((W_{char} - W_0A)\,/\,W_0\,(1-A-M))*100 \qquad \text{eq. 5}$$

$$\mathbf{Y_{oil}\ (\%)} = (W_{oil}\,/\,W_0\,(1-A-M))*100 \qquad \text{eq. 6}$$

$$\mathbf{Y_{gas}\ (\%)} = (1 - Y_{oil} - Y_{char})*100\% \qquad \text{eq. 7}$$

Where W_{char} is the weight of char obtained during experiments, W_0 is the initial weight of the biomass, W_{oil} is the weight of oil obtained from experiments, A is the ash content, and M is the moisture content in the biomass (wt%, dry basis) [221].

4. Chapter 4: Results and Discussions

4.1. Raw materials characterization: EA, TGA, XRD

Before performing the pyrolysis experiments, ultimate and proximate analysis of Posidonia Oceanica were performed to determinate the composition and evaluate the potential for production of bio-oil. The results are given below. Ultimate analysis; carbon: 40.29%, hydrogen: 5.96%, nitrogen:1.12%, sulfur 0.29%, oxygen: 25.65%, higher heating value (MJ/kg): 16.20. Proximate analysis; moisture: 12.67%, ash: 14.02%, volatile matter: 60.95% and fixed carbon: 12.36%. Low amount of proteins (7.03 wt%) and lipids (7 wt%) were recorded meaning this biomass not ideal for biodiesel production, but suitable for pyrolysis process. Furthermore, Posidonia Oc. has relatively high carbon content (40.3 wt%) and makes it a suitable for biofuel production. However the high ash rate (14.02 wt%) detected could promote char formation since inorganic elements in the ash are known to catalyze the formation of char during pyrolysis [217, 222-223].

Before performing the actual experimental study, thermogravimetric (TGA) and DTG analysis were used to estimate the thermal behavior of Posidonia Oceanica, **Figura 3.1**.

The pyrolysis diagram can be divided in three steps: i) dehydration T<110°, ii) devolatilisation (200-600 °C), iii) stabilization and decomposition of the carbonaceous matter (600-800 °C). In particular, five main stages can be observed; the first, at T<150 °C, is related to superficial moisture and carbohydrates decompositions; the second and third, between 200-600°C, correspond at protein (270-300°C), cellulose (325°C) and lipids (450°C) devolatilisation [32,35,230]; in the fourth, among 600-800°C occurs the formation and stabilization of carbonaceous matter.

Finally, fixed carbon and ash content in the starting biomass were calculated in the last stage (air atmosphere) by oxidation of the solid residue remaining at 800°C (about 26%). Moreover, the TGA/DTG curve shows that the initial decomposition temperature and the maximum weight loss rate of Posidonia Oc. are lower than the lignocellulosic biomasses. This is due to the different chemical composition of Posidonia Oceanica and in particular at his very low lignin content respect at woody biomasses [230]. XRD diffraction patterns of the fresh biomass is showed in **Figure 4.1**. The XRD pattern highlights the intermediate behavior of Posidonia Oceanica sea plant. In particular are present the main peaks at approximately 16° and 22° (corresponding to the 101 and 002 crystal plane) associated with the crystalline region of cellulose and generally attributed to carbon solids with a long-terms structural order [224]. Moreover, the XRD spectrum of Posidonia Oc. showed a peak of greatest intensity at 29.3°; this peak, corresponding to the calcite, represents a typical characteristic of the algal biomass [225].

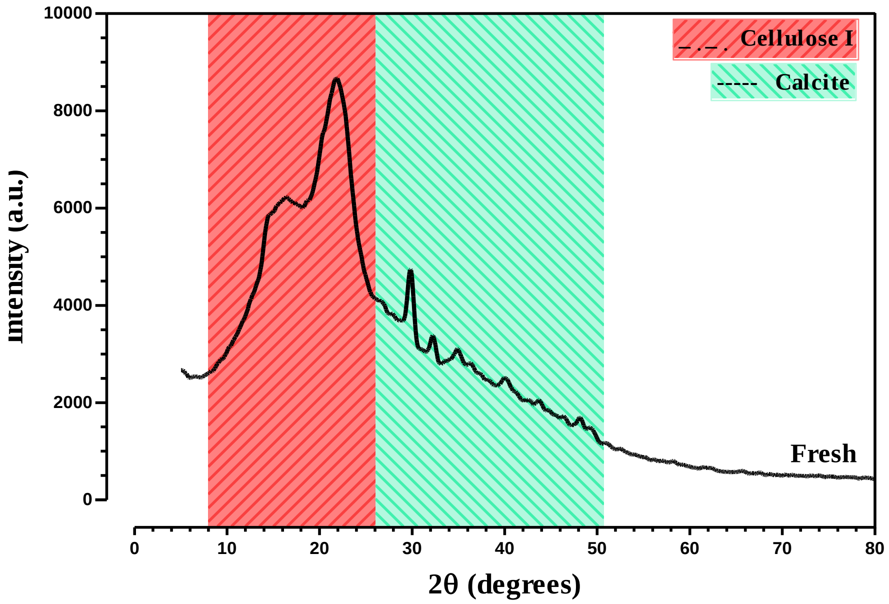


Figure 4.1: X-ray diffraction result for the Posidonia Oceanica biomass

4.2. Catalysts characterization: BET, XRD

Table 4.1 presents the physical properties of the prepared catalysts and supports that were evaluated using N_2 adsorption isotherms at 77 K. The total pore volume, specific surface area (SBET) and average pore diameter of Al_2O_3, CeO_2, HZSM-5 supports were evaluated. Addition of metal oxide influenced the catalyst properties, surface area and pore volume were decreased while average pore size was increased slightly. This properties is clearly visible for the following catalyst couples, Al_2O_3 - Ni/Al_2O_3 and CeO_2 - Ni/CeO_2 indeed, surface area of the doped catalyst decreased from 260.02 to 59.57 m^2/g and 27 to 8.50 m^2/g respectively.

Catalyst	Surface area (m^2/g)	Pore size (Å)	Pore volume (cm^3/g)
Al_2O_3	260.02	37.44	0.129
Ni/Al_2O_3	59.57	37.56	0.120
CeO_2	27.00	38.01	0.154
Ni/CeO_2	8.50	39.20	0.132
HZSM-5	498.93	42.21	0.253
Ni/HZSM-5	385.88	44.34	0.217
NiCe/HZSM-5	263.86	45.86	0.208
Dolomite	32.09	146.2	0.116

Table 4.1: The physical properties of the catalysts

Also for the zeolite catalysts the impregnation with Ni and/or Ce transition metals reduced the surface area and pore volume respect at HZSM-5 alone. This could be due to pore blocking by metal species dispersed in the channels or by the presence of metal oxide aggregates. The X-ray diffraction patterns of the prepared catalysts are shown in **Figure 4.2**. XRD patterns of Ni/CeO_2 catalyst exhibit peaks at 2θ scale= 28.5°, 33.10°, 47.60°, 56.39°, 59.13°, 69.51°, and 79.10° attributed to the cubic cerium (IV) oxide crystal phase, instead the peaks of the cubic nickel(II) oxide at 2θ scale= 37.20°, 43.18°, 62.90°, 75.22°,79.40°.

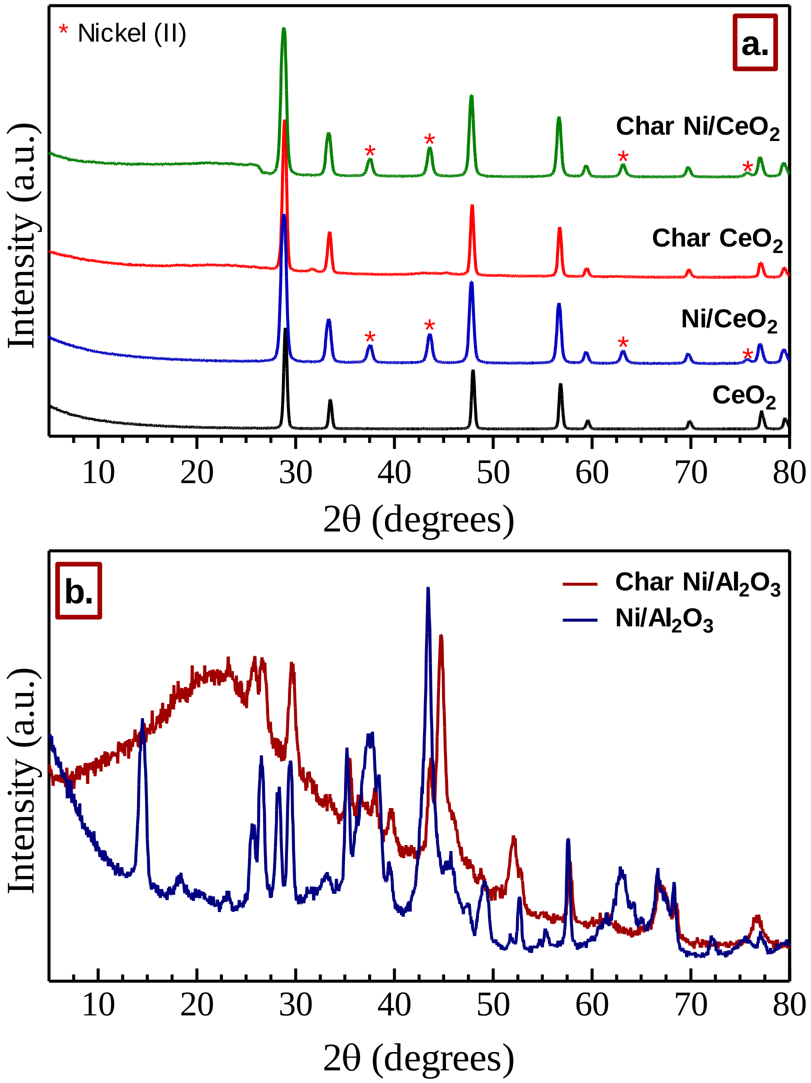


Figure 4.2: X-ray diffraction patterns of (a) CeO_2 and Ni/CeO_2, (b) Ni/Al_2O_3

Dolomite ($MgCa(CO_3)_2$) is a natural mineral catalyst composed mainly by magnesium and calcium carbonates. For this reason shows peaks of both compounds and in the specific case those of magnesium oxide at 2θ scale= 37.00°, 43.00°, 62.30°, and 78.50° and those of calcium carbonate at 2θ scale=26°, 29°, 41.18°, 50.98°. The XRD patterns of the fresh and used zeolite catalysts are shown in **Figure 4.3**.

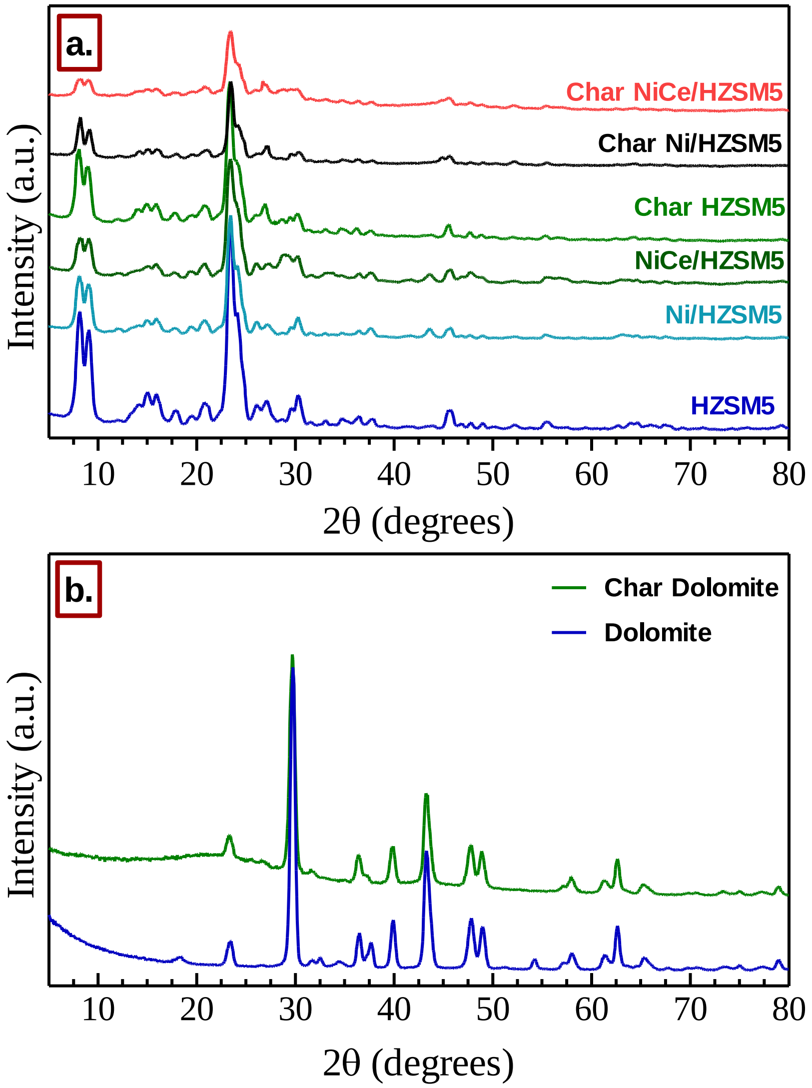


Figure 4.3: X-ray diffraction patterns of (a) HZSM-5, Ni/HZSM-5 and NiCe/HZSM-5, (b) Dolomite

The similarity of the XRD patterns between fresh HZSM-5 and other zeolite catalysts indicates that the framework of HZSM-5 was still kept after loading Ni and Ce or after reaction, because the presences of typical peaks of HZSM-5 (23-24°) are still maintained [226]. However, the intensities of diffraction peaks of used catalysts is changed compared to fresh catalysts, and this is due to the distortion of the zeolite lattice caused by the deposition of carbonaceous materials within zeolite pores [227]. The Ni and Ce peaks are not visible in the patterns, this is due to the low metal loading but also to the high crystallinity of the zeolite. These results were consistent with those previously reported in literature [228-230].

4.3. Pyrolysis experiments

4.3.1. Preliminary tests: effect of temperature, flow rate and heating rate

To evaluate the best process conditions preliminary tests have been conducted. Therefore, in order to identify the optimal testing conditions has been changed one operating parameter at a time. As previously mentioned, the parameters evaluated have been sweeping gas flow rate, heating rate and reaction temperature. The effect of this parameters on bio-oil yield are reported in **Figure 4.4**. The data were obtained from the experimental runs at different temperatures ranging from 400 °C to 700 °C, with heating rates of 10 to 80 °C/min and a sweeping gas flow rate of 30 to 120 cc/min. It can be seen that temperature has a positive effect both on conversion than on liquid product yield. According to results, when temperature is increased from 400 to 500 °C, liquid product yield increases from 43.61% to 50.07% at a heating rate of 60°C/min. So, the highest liquid product yield was obtained at 500 °C. Beyond 500 °C, even though the conversion has increased steadily, the liquid yields have decreased until 20.5 % at 700 °C. According to literature, temperature is the most important parameter on product yields [231-235]. Tests carried out at 500°C and a different heating rate, to 10 at 80°C/min have highlighted that the best condition was 60°C/min. Indeed, increasing the heating rate the bio-oil yield is increased by 25.3% at about 50%. Regarding the tests conducted at different sweeping gas flow rate, by 30 to 120 cc/min of nitrogen can be observed that the bio-oil yield not affected by the variation of the gas flow rate.

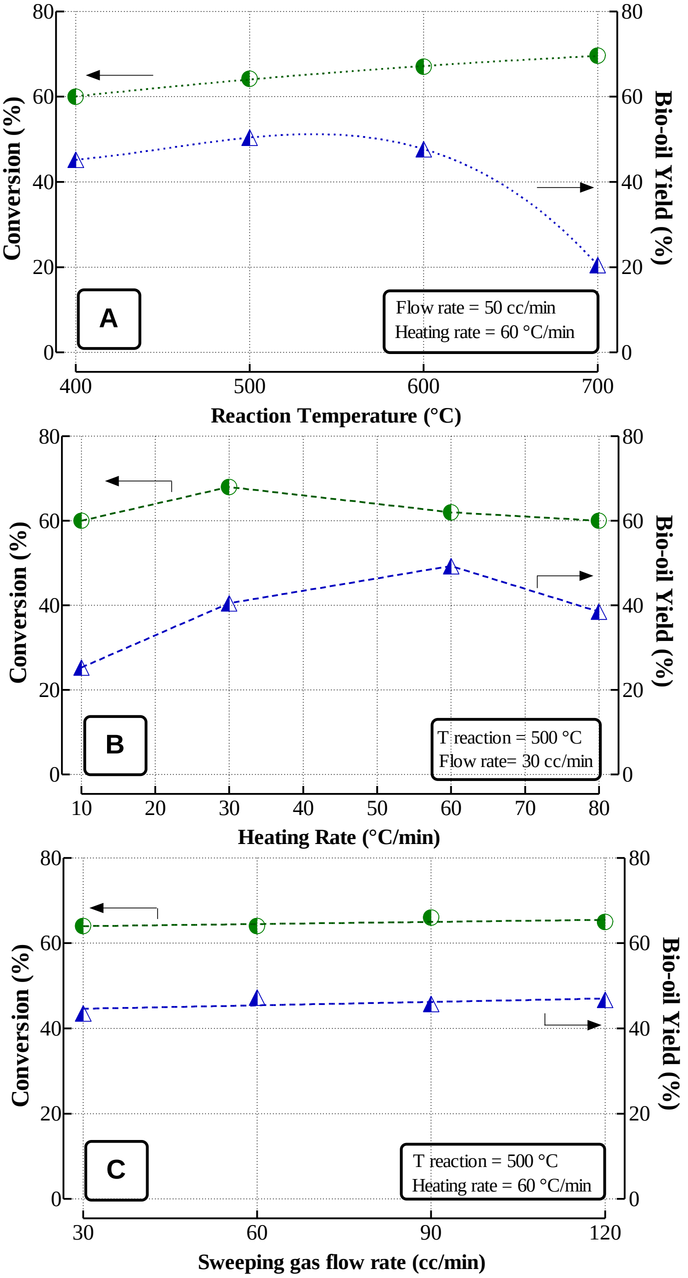


Figure 4.4: The effect of pyrolysis parameters on bio-oil yield; a) reaction temperature, b) heating rate, c) sweeping gas flow rate

Therefore, the best parameter conditions have been identified to Posidonia Oceanica pyrolysis in a temperature of 500°C, heating rate of 60°C/min and sweeping gas flow rate of 50 cc/min. All tests have been conducted according to the previously identified parameters.

4.3.2. Effect of temperature on products distribution

It is of general acceptance that temperature can add synergic effect on the liquid yields because of the extended fragmentation of biomass with increasing temperature. Temperatures lower than 400 °C are not enough for conversion, whereas temperatures higher than 600 °C would lead to formation of excessive gas. This is due to secondary decomposition reactions and formation of gas at very high temperatures. Also, presence of free radicals at high concentrations would lead to the formation of char as they recombine at high temperatures [231,236-240]. The conversion (bio-oil + gas yields) and distribution of products obtained by pyrolysis of Posidonia Oceanica without and with 30% catalyst are given in **Table 4.2**. The overall conversion and gas yields increased sharply according to the temperature increase, while biochar yields decreased at runs with and without catalysts. When temperature was increased from 400 to 600 °C, the conversion was increased from 60.15% to 70.21% in the non-catalytic tests and from 66.01% (dolomite) to 80.81% (Ni/HZSM-5) in the catalytic tests. At 600 °C, gas formation is favoured by secondary decomposition reactions and bio-oil yield decreased. The highest liquid yields were obtained at 500 °C, particularly the highest liquid yield (51.15 wt%) was produced with CeO_2 catalyst. The lowest bio-char yield (19.19%) was obtained with Ni/HZSM-5, this is due to greater activity of the catalyst on gasification of char by secondary reactions.

T °C	Pyrolysis test	Conversion % (Total volatiles)	Bio-char Yield %	Bio-oil Yield %	Gas Yield %
400	**No Catalyst**	60.15	39.85	45.03	15.12
500		63.37	36.63	47.74	15.62
600		70.21	29.79	40.54	29.67
500	**CeO_2**	79.07	20.93	51.15	27.91
500	**Ni/CeO_2**	78.53	21.47	49.74	28.79
500	**HZSM-5**	76.37	23.63	48.74	27.62
500	**Ni/HZSM-5**	80.81	19.19	48.72	32.10
500	**NiCe/HZSM-5**	78.44	21.56	50.66	27.77
500	**Ni/Al_2O_3**	66.37	33.63	48.72	17.66
500	**Dolomite**	66.01	33.99	41.38	24.62

Table 4.2: Conversion and products distribution obtained by pyrolysis of Posidonia Oceanica with and without catalyst

4.3.3. *Effect of catalyst on products distribution*

In situ catalytic pyrolysis can be used to deoxygenate the bio-oil during its production effectively converting biomass into bio-fuels and chemical precursors [241]. In general, oxygen represents about 30% of the algal biomass. In the presence of catalyst, volatiles released from pyrolysis are subjected to dehydration, decarboxylation, dehydrogenation, cracking and decarbonylation, which results in the production of desired products, namely hydrocarbons, furans, phenols, etc. When we look at the effect of catalysts used in this study, we see that they have exhibited different effects on product yields, **Table 4.2**. All catalysts have increased the conversions of Posidonia Oceanica compared to non-catalytic runs, with Ni/HZSM-5 and CeO_2 being the most effective. The highest conversion of 80.81% was obtained with Ni/HZSM-5. As for Posidonia Oceanica alumina based catalyst had negative effect and decreased the conversion and gas yield, while CeO_2 and zeolite supported catalysts increased the conversion. This can be related to the catalysts acidity and propensity for dehydration reaction with formation of charred species. On the other hand, the effects of catalysts on bio-oil yields were less marked compared to the effects of conversion. CeO_2 (51.15wt.%), NiCe/HZSM-5 (50.66 wt.%) and Ni/CeO_2 (49.74 wt.%) were the most effective catalysts and have increased the bio-oil yields of Posidonia Oceanica compared to non-catalytic ones (47.74 wt.%). This can be related to the cracking activity of Ni and synergic effect of Ni-Ce catalysts, where CeO_2 increases the stability, dispersion of Ni and carbon suppression [242]. TGA of the spent (coked) catalysts was carried out in pure air to evaluate the amount of coke formed on catalysts, **Table 4.3**.

Catalytic bio-chars	**Absorbed water**	**Char decomposition**	**Coke combustion**
	25-100 °C	100-600 °C	600-900 °C
CeO_2	0.68	35.29	1.33
Ni/CeO_2	0.81	26.31	1.15
HZSM-5	1.71	37.52	2.82
Ni/HZSM-5	1.81	25.75	2.01
NiCe/HZSM-5	1.36	26.98	0.14
Ni/Al_2O_3	1.77	34.60	4.05
Dolomite	1.1	36.46	5.57

Table 4.3: Coke amount on the pyrolysis catalysts

Initial mass loss between 25 and 100°C was associated to release of absorbed water. The second mass loss between 100 and 600°C was associated to decomposition of the char, while the third (final) mass loss between 600 and 900°C was associated to coke combustion. NiCe/HZSM-5 had the lowest amount of coke (0.14 wt. %) while dolomite had the highest (5.57 wt.%). This is in agreement with the pyrolysis mass balance, **Table 4.2**, which shows their catalytic activities in terms of total volatiles. Oxygen affinity of Ce improved the activity of Ni catalyst in terms of coke suppression. Adsorbed O species in presence of Ce and Ni , due to lattice O and redox properties of Ce forms gas species such as CO_2 and CO instead of coke deposition [243]. Therefore, can be observed as the presence of nickel in the following couples of catalysts, Ni/CeO_2 - CeO_2 and Ni/HZSM5 - HZSM5 leads to a lower carbon content, 1.15 vs 1.33 wt. % and 2.01 vs 2.82 wt. % respectively. Differently, the presence of the Ni has not worked for the Ni / Al_2O_3 catalyst, this was presumably due to the presence of the alumina which does not seem to be active for the purposes of the pyrolysis process.

4.4. Characterization of pyrolysis products by EA, TGA, XRD, XRF and GC-MS analysis

4.4.1. Bio-char

Aromaticity in bio-char structure is studied by Van Krevelen plot. In fact, a decrease in H/C and O/C atomic ratios is indication of development in aromatic structure in bio-char due to removing of hydrogen and oxygen from parent material by pyrolysis [92]. Fig. 3 shows the Van Krevelen diagram for fresh biomass used in this study and the corresponding bio-chars produced at different pyrolysis temperatures and during the catalytic tests, **Figure 4.5**. Increasing the pyrolysis temperature (from 400 to 600 °C) decreased both atomic ratios for bio-chars of Posidonia Oceanica indicating that structural transformations induce a carbonization process [224]. Bibliography results [224,244-245] proposed the combined use of H/C and O/C ratios as tool to assess the bio-char stability with threshold values of $H/C < 0.6$ and O/C ratio < 0.4; these values were observed for all biochars obtained by experimental tests.

XRD diffraction patterns of the no catalytic bio-chars obtained from temperature tests are showed in **Figure 4.6**.

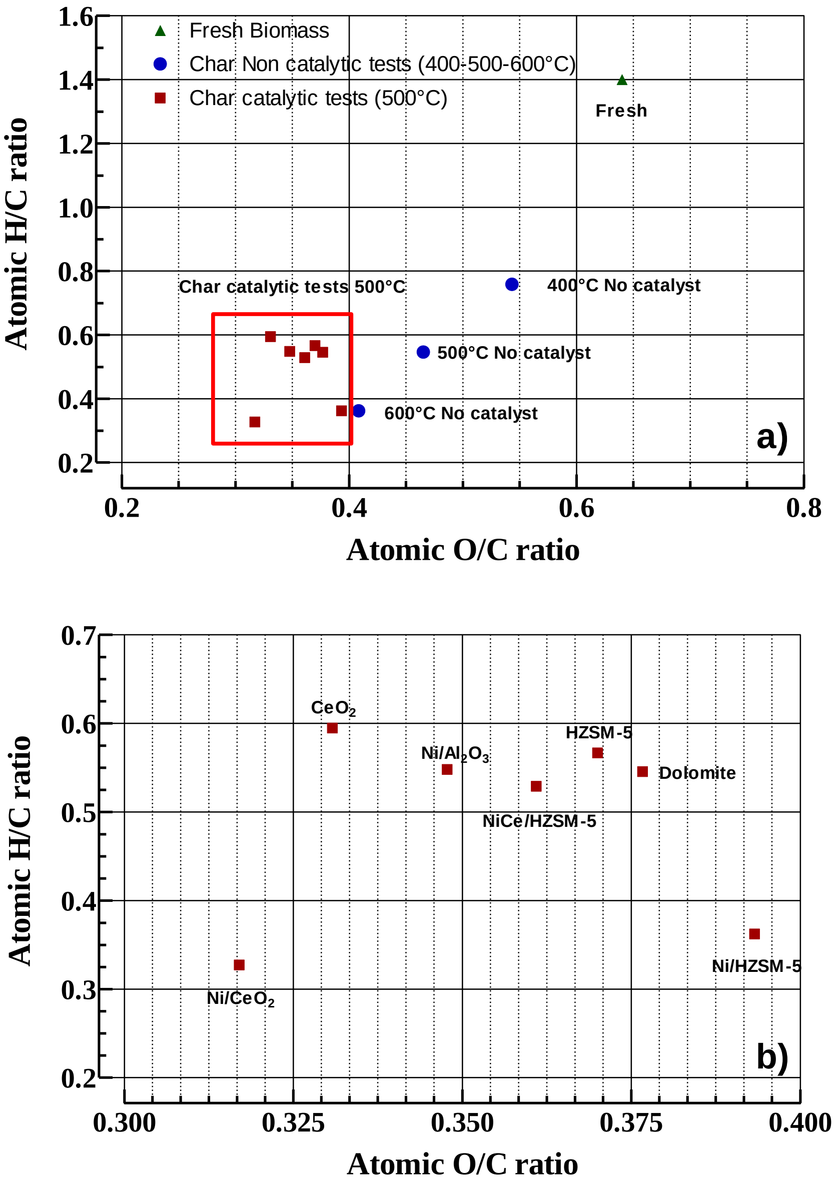


Figure 4.5: a) Van Krevelen plot for biomass precursor and bio-chars; b) Enlargement of the plot corresponding to catalytic bio-chars

It was found that the X-ray diffraction peaks, for the Posidonia Oceanica bio-chars were characterized by a broad band instead of cellulose signals (with the pyrolysis temperatures) indicating a destruction of biomass structure and a highly disordered structure [224,244,248] in agreement with the results of thermo-gravimetric analysis. The fraction of disordered carbon includes both the presence of amorphous carbon and aliphatic side chains.

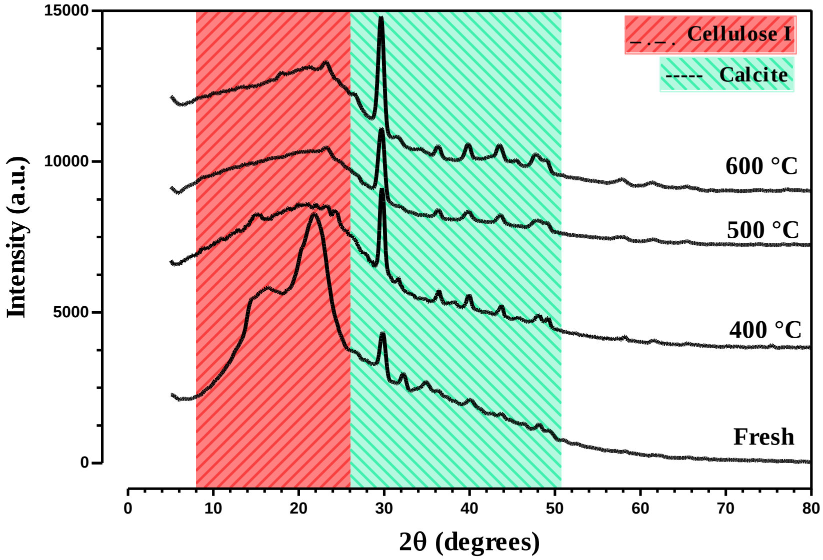


Figure 4.6: X-ray diffraction results for no catalytic bio-chars

The HHVs and elemental analyses of the bio-chars are reported in **Table 4.4**. This table shows that bio-chars have higher carbon content (62-66 wt.%) than the original raw material (40 wt.%) and accordingly have also high HHVs when compared with that of the raw material. As shown in **Table 4.4**, the higher heating values of bio-chars were higher than 22-24 MJ/kg, in comparison with the low HHV (16.20 MJ/kg) of the raw material. Moreover, all bio-chars had high ash and nitrogen contents which make them suitable for utilization as soil amendment after separation from the catalyst [222]. **Table 4.4**, also lists pH of bio-chars obtained by pyrolysis. As highlighted, the pH of algal bio-chars resulted alkaline and this results to be useful for the neutralization of acidic soils improving the coil quality and increasing the productivity of crops [247].

Elemental analysis[a]	**No catalyst**			**CeO_2**	**Ni/CeO_2**	**HZSM-5**
	400°C	500°C	600°C	500°C	500°C	500°C
Carbon	57.00	62.15	68.50	66.22	65.97	63.93
Hydrogen	3.40	2.85	2.08	2.26	2.84	2.72
Nitrogen	0.80	0.53	0.70	1.75	2.47	1.28
Sulfur	0.85	0.81	0.80	0.58	0.86	0.56
Oxygen[b]	37.95	33.66	27.92	29.18	27.86	31.51
H/C molar ratio	0.76	0.55	0.36	0.59	0.33	0.57
O/C molar ratio	0.54	0.41	0.41	0.33	0.32	0.37
HHV (MJ/kg)	21.37	22.69	24.13	23.28	24.34	23.30
pH	9.94	10.75	10.89	12.19	11.26	9.5

Elemental analysis[a]	**Ni/HZSM-5**	**NiCe/HZSM-5**	**Ni/Al_2O_3**	**Dolomite**
	500°C	500°C	500°C	500°C
Carbon	62.68	64.03	64.48	63.65
Hydrogen	2.56	2.59	3.24	2.49
Nitrogen	1.30	1.97	1.93	1.67
Sulfur	0.62	0.62	0.48	0.25
Oxygen[b]	32.84	30.79	29.87	31.94
H/C molar ratio	0.36	0.53	0.55	0.55
O/C molar ratio	0.39	0.36	0.35	0.38
HHV (MJ/kg)	22.70	23.28	24.15	23.04
pH	10.05	10.4	11.19	11.72

a. On dry ash free basis b. By difference

Table 4.4: Results of elemental analysis of the bio-chars obtained from Posidonia Oceanica

This property is also due to presence of inorganic elements contained in the bio-chars. The inorganic elements contained in non-catalytic bio-char obtained at 500°C are reported in **Table 4.5**.

Mineral elements (wt%)		**Other metals (ppm)**	
K	0.33	Cu	44
Mg	3.87	Zn	125
Ca	21.80	V	43
Fe	0.77	Ni	37
P	0.52		

Table 4.5: Content of minerals present in the biochar obtained at 500 °C

4.4.2. Bio-oils (oxygen content and GC-MS family distribution)

Bio-oil produced, at 500 °C, by algal pyrolysis was analyzed as described in the chapter 2.2, and results are reported in **Tables 4.6**. In particular, from **Table 4.6** it is possible to see that the water content of bio-oil from Posidonia Oceanica was about 12.68 wt.%, resulting higher than that of fossil fuel oil (about 0.1 wt%) [248].

Physico-chemical properties of bio-oil at 500°C				
pH		4.05		
Density (kg/m3)		1250		
Water content (wt%)		12.68		
		Elemental analysis[a]		
	No catalyst	**CeO_2**	**Ni/CeO_2**	**HZSM-5**
Carbon	60.40	83.67	81.31	75.46
Hydrogen	7.00	6.95	6.12	6.90
Nitrogen	1.60	2.07	3.40	1.62
Sulfur	1.10	0.43	0.74	0.50
Oxygen[b]	**29.90**	**6.87**	**8.43**	**15.52**
H/C molar ratio	1.03	0.59	0.61	0.72
O/C molar ratio	0.37	0.06	0.08	0.15
HHV (MJ/kg)	26.08	40.60	37.48	34.79
	Ni/HZSM5	**NiCe/HZSM5**	**Ni/Al_2O_3**	**Dolomite**
Carbon	77.03	80.96	65.95	62.07
Hydrogen	6.74	6.81	6.97	6.64
Nitrogen	2.91	2.52	2.25	1.59
Sulfur	0.77	0.93	0.44	0.74
Oxygen[b]	**12.54**	**8.77**	**24.39**	**28.95**
H/C molar ratio	0.67	0.62	0.89	0.99
O/C molar ratio	0.12	0.08	0.28	0.35
HHV (MJ/kg)	35.74	38.46	29.03	26.39

a. On dry ash free basis   b. By difference

Table 4.6: Physical-chemical properties and elemental analysis of the bio-oils obtained at 500°C

The nitrogen content in all bio-oils is low respect at another type of algal biomass [230]. Indeed, from a fuel quality point of view, nitrogen originated from chlorophyll and proteins present in the starting biomass is detrimental in biofuels due to the formation of

NO_x during its combustion. This clearly indicates that the starting composition of the biomass significantly affects on the quality of the bio-oil. The HHVs and elemental analyses of the bio-oils are reported in **Table 4.6**. This table shows that bio-oils have higher carbon content (60-83 wt.%) than the original raw material (40 wt.%) and accordingly have also a high HHV when compared with that of the raw material. As shown in **Table 4.6**, the higher heating values of bio-oils were higher than 26-40 MJ/kg, in comparison with the low higher heating value (16.20 MJ/kg) of the raw material. Overall, all bio-oils have suffered deoxygenation. The oxygen content of the obtained bio-oils is reported in **Figure 4.7**, the decrease of this value respect to non-catalytic bio-oil can be attributed to the oxygen remove (as CO, CO_2 and H_2O) by deoxygenation reactions.

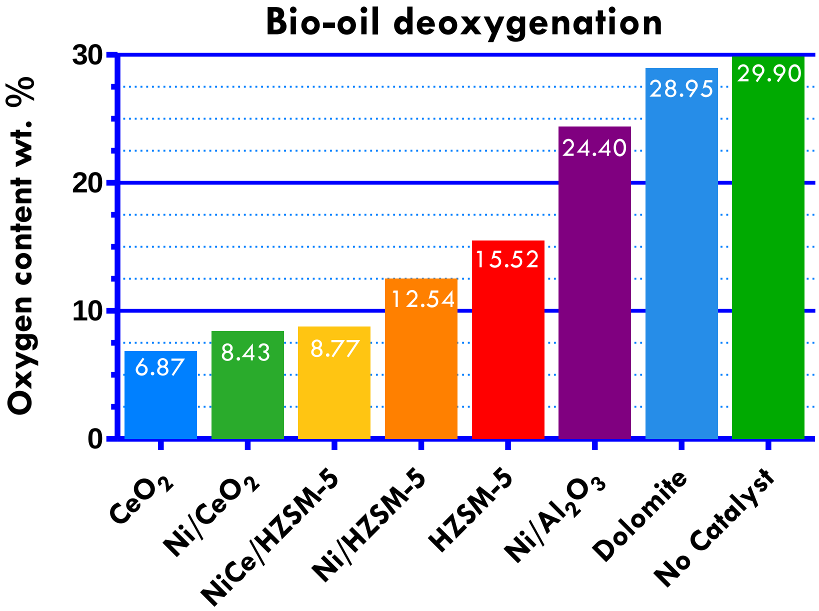


Figure 4.7: Oxygen content of bio-oils obtained by non-catalytic and catalytic tests

The bio-oils oxygen level was decreased from 25.66 wt.% in the starting biomass to 6-8 wt.% with CeO_2, Ni/CeO_2 and

NiCe/HZSM-5 catalysts. In terms of energy content, the most effective catalysts in improving the bio-oil quality were CeO_2, Ni/CeO_2 and NiCe/HZSM-5 which increased the HHVs of bio-oils, up to 40.60, 37.48 and 38.46 MJ/kg respectively, compared to non-catalytic test (26.08 MJ/kg). These results indicates the higher deoxygenation power of ceria and Ni-Ce/Zeolite catalysts.

Deoxygenation is consistent with elemental analyses (**Table 4.6**), which show low O_2 content, and also with the GC-MS analysis. Indeed, GC-MS analysis was carried out in order to determine the main products and verify the improvement by deoxygenation of the Posidonia Oceanica bio-oils. The list of the compounds identified by GC-MS are given in **Table 4.7**.

Compound Name	*No Catalyst*	*CeO_2*	*Ni/ CeO_2*	*HZSM*	**Ni/ HZSM**	**NiCe/ HZSM**	**Ni Al_2O_3**	**Dolomite**
Carboxylic acids								
2-Hexenoic acid, 3,4,4-trimethyl-5-oxo-,						0.091		
2-Propenoic acid	0.030	0.025	0.032	0.018	0.036	0.092	0.033	0.053
2-Propenoic acid, 1-methylundecyl ester								0.066
Acetic acid	17.702	9.491	10.241	12.535	10.451	11.34	26.498	27.135
Acetic acid, [(aminocarbonyl)amino]oxo-		0.054	0.021				0.113	0.088
Acetic acid, anhydride with formic acid		0.032				0.045		
Acetic acid, hydrazide					0.012			0.049
Benzoic acid, 3-hydroxy-			0.016	0.028		0.054	0.048	0.128
Dodecanoic acid, 3-hydroxy-			0.021			0.033	0.017	0.066
Ethanimidic acid, ethyl ester		0.052			0.026			
Oxalic acid		0.053	0.160	0.128	0.018	0.231	0.059	0.083
Propanoic acid	0.773	0.297	0.269	0.676	0.401	0.650	1.041	0.971
Propanoic acid, 2-hydroxy-, hydrazide	0.496	0.178						
Total %	**19.00**	**10.18**	**10.76**	**13.39**	**10.94**	**12.50**	**27.81**	**28.64**
Alcohols and Phenols								
1,3-Benzenediol, 4-ethyl-		0.050				0.461		
1,4:3,6-Dianhydro-à-d-glucopyranose	1.602	0.101	4.955	0.174	0.019	1.037	6.339	3.410
1,6-Anhydro-2,4-dideoxy-á-D-ribo-hexopyranose			0.095	0.096		0.020	0.126	0.038
1H-Indenol		1.950			0.433			
2,3-Anhydro-d-mannosan		0.066						
2-Cyclohexen-1-ol	0.015							
2-Hydroxy-gamma-butyrolactone							6.180	
3,4-Anhydro-d-galactosan			0.105				0.106	0.038
Anhydro-d-mannosan	0.015							
beta-D-Glucopyranose			0.159	0.175		0.056	0.100	0.088
Diglycidyl ether			5.523	2.739		1.371	6.180	3.656
DL-Arabinose			0.168	0.072	0.044	0.114	0.106	0.082
Levoglucosan			0.100	0.095	0.094	0.098	0.085	0.208
Maltol	0.014				1.396	3.255		
Methyl Alcohol	5.076	7.566	0.256	0.055		0.061		0.155
Phenol	15.166	35.780	32.028	26.222	29.770	30.357	11.822	15.838

Phenol, 2,4-dimethyl-, acetate			0.126					0.072
Phenol, 2,5-dimethyl-				2.454				
Phenol, 2,6-dimethoxy-4-(2-propenyl)-			0.461					0.042
Phenol, 2-ethyl-		0.113			0.854			
Phenol, 2-methoxy-					1.950			
Phenol, 2-methyl-		2.744	2.114		1.992	2.578		0.776
Phenol, 3,4-dimethoxy-					1.027			
Phenol, 3-ethyl-					1.033			
Phenol, 3-methyl-	0.572	1.806			1.675	2.749	0.680	
Phenol, 4-methyl-		3.084	3.311	0.086	3.363	4.016	0.069	0.124
Total %	**22.46**	**53.26**	**49.40**	**40.28**	**43.65**	**44.10**	**31.79**	**24.53**
Aldehydes and Ketones								
1-Hydroxy-2-butanone	0.981							
1,3-Cyclopentanedione, 2,4-dimethyl-	0.033					0.028		0.105
1,3-Dioxolane, 4,5-diethenyl-2,2-dimethy								0.229
1,3-Methanopentalene, 1,2,3,5-tetrahydro					0.188			
2,3-Butanedione	0.540							
2,4-Dimethoxyphenol						0.022		
2-Butenal, (E)-	0.013		0.157					
2-Cyclopenten-1-one	2.450	0.386			0.221			
2-Cyclopenten-1-one, 2-hydroxy-	1.471	0.014	0.155		0.960			
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	2.334	0.478	0.296	0.056	0.148	0.853	1.042	1.824
2-Cyclopenten-1-one, 2-methyl-	0.862	0.021	0.194		0.151	0.034		0.223
2-Cyclopenten-1-one, 3,4-dimethyl-	0.038	0.045	0.406	0.001			0.070	0.134
2-Cyclopenten-1-one, 3-methyl-	0.026							
2-Cyclopentene-1,4-dione	0.030							
2-Hydroxy-gamma-butyrolactone		0.011						3.656
2-Pentanone, 4-hydroxy-4-methyl-						0.022		
2-Propanone, 1-(acetyloxy)-	3.190	0.801						
2-Propanone, 1-hydroxy-	26.307	6.475	8.781	2.516	2.971	3.283	36.351	37.667
Cyclopentanone	0.085							
Ethanone, 1-(2-furanyl)-	1.054							
Ethanone, 1-(2-methyl-1-cyclopenten-1-yl						0.056		
Furyl hydroxymethyl ketone	0.766							
Methyl vinyl ketone	0.713							
Phenol, 3,4-dimethyl-, acetate						1.393		
Total %	**40.89**	**8.23**	**9.98**	**2.57**	**4.64**	**5.69**	**37.97**	**43.84**
Furans								
2(3H)-Furanone, dihydro-	0.143							
2-Furancarboxaldehyde, 5-(hydroxymethyl)	0.720	0.142				0.178		0.122
2-Furancarboxaldehyde, 5-methyl-	1.103							
3(2H)-Furanone, dihydro-2-methyl-			0.126					
3-Furaldehyde		1.769						
3-Hydroxydihydro-2(3H)-furanone	1.754							
4-Methyl-5H-furan-2-one	0.027							0.103
Benzofuran					2.471			
Furan, 2,4-dimethyl-				2.010	0.176		1.028	
Furan, 2-ethyl-5-methyl-		0.246	0.571			1.726	0.050	
Furfural	9.523	14.453	16.963	1.130	3.474	5.880		

Total %	**13.27**	**16.61**	**17.66**	**3.14**	**6.12**	**7.78**	**1.08**	**0.23**
Nitrogen compounds (Total %)								
1H-Indazole, 3-methyl-			0.420			0.256		
1H-Pyrazole, 3-methyl-			1.005					
4(1H)-Pyridone	3.346					0.155	0.952	1.369
4-Aminopyrimidine					0.068			
5-Hydroxypyrimidine							0.073	
Acetamide							0.160	0.233
Acetamide, N-(aminoiminomethyl)-			0.049					
Benzene, 1,1'-(diazomethylene)bis-				0.074			0.040	
DL-Threonine, N-glycyl-		3.090						
Imidazole, 1,4,5-trimethyl-			0.416		0.218			
Pyridine	0.089					0.354		0.081
Pyrimidine-4,6-diol, 5-methyl-				0.984	0.181		0.075	1.088
Total %	**3.44**	**3.09**	**1.89**	**1.06**	**0.47**	**0.76**	**1.30**	**2.77**
Hydrocarbons								
1,3-Cyclopentadiene, 5-(1-methylethylidene)					4.230			
1H-Indene, 1-ethylidene-		2.334	1.254		4.994	5.671		
1H-Indene, 1-methylene-		3.585	0.985		7.099			
1H-Indene, 3-methyl-	0.94	0.222	2.559	4.356	0.482			
2,3-Heptadien-5-yne, 2,4-dimethyl-					0.343	4.670		
3-(2-Methyl-propenyl)-1H-indene						2.766		
9H-Fluorene, 1-methyl-				0.832			0.003	
Anthracene, 2-methyl-				8.632		2.372	0.002	
Benzene, 1,3,5-trimethyl-			0.830	4.276	6.148			
Benzene, 1-ethynyl-4-methyl-		1.294			4.604			
Benzene, 1-methyl-4-(1-propynyl)-					1.086	1.375		
Benzene, 4-ethenyl-1,2-dimethyl-			0.374		0.213			
Benzocycloheptatriene		0.137		1.658		3.610	0.018	
Bicyclo[2.1.1]hex-2-ene, 2-ethenyl-					2.083			
Naphthalene, 1,4-dimethyl-		0.895	1.934	6.581	2.622	2.460	0.008	
Naphthalene, 1,4,6-trimethyl-			1.543	0.530	0.274	2.743	0.018	
Naphthalene, 1,6,7-trimethyl-				4.697		3.500	0.001	
Octadecane, 6-methyl-		0.164	0.832					
Total %	**0.94**	**8.63**	**10.31**	**31.56**	**34.18**	**29.17**	**0.05**	**0.00**

Table 4.7: Main chemical compounds present in the bio-oils obtained at 500°C

As expected, degradation of lignocellulosic components (hemicellulose, cellulose and lignin) by pyrolysis produced many types of organic compounds with different molecular structures and molecular weights. In particular, hemicellulose decompose first (200-280 °C) forming the acidic compounds such as acetic acid. On the other hand, decomposition of cellulose (240-350 °C) produces levoglucosan as the primary breakdown product during thermal treatment, but other anhydroglucoses, furan and furan derivatives are also produced. Phenols and derivatives such as 2,6-dimethoxy phenol and 2-methoxyphenol are the primary products of degradation of lignin (280-500 °C) during pyrolysis [249]. For these reason, bio-oils are composed to complex mixtures of organic compounds which included hydrocarbons, alcohols, phenols, furans, aldehydes, ketones, carboxylic acid and nitrogen compounds. These functional groups can be divided into two groups which were desired compounds and undesired compounds. Desired compounds include hydrocarbons, alcohols, phenols and furans, which can be used as alternatives for fuel or high valued chemicals. On the other hands, bio-oils also contain undesired compounds such as aldehydes, ketones, carboxylic acid and nitrogen compound, which results in the low heating value and low stability of bio-oils. The distribution of desired and undesired compounds for families of non-catalytic and catalytic bio-oils are shown in **Figures 4.8 and 4.9**.

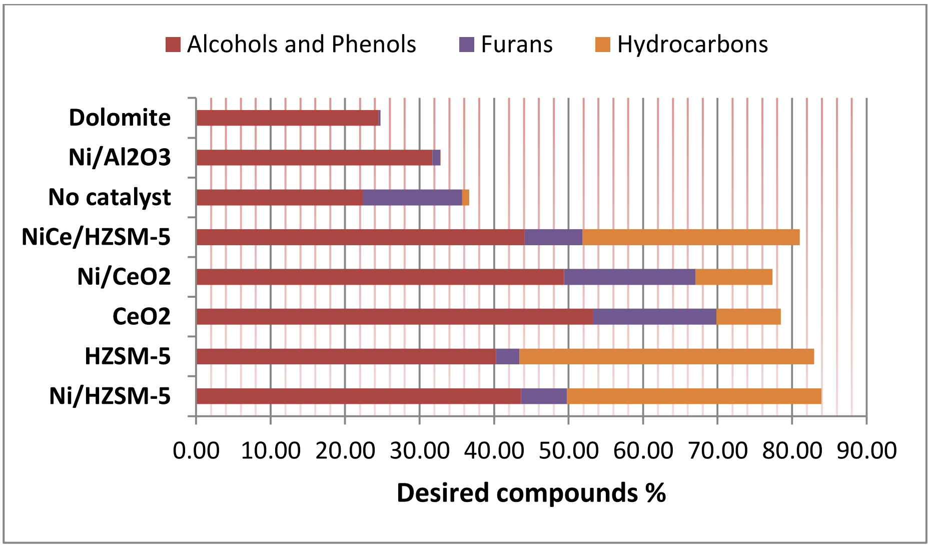


Figure 4.8: Composition of desired compounds in non-catalytic and catalytic bio-oils

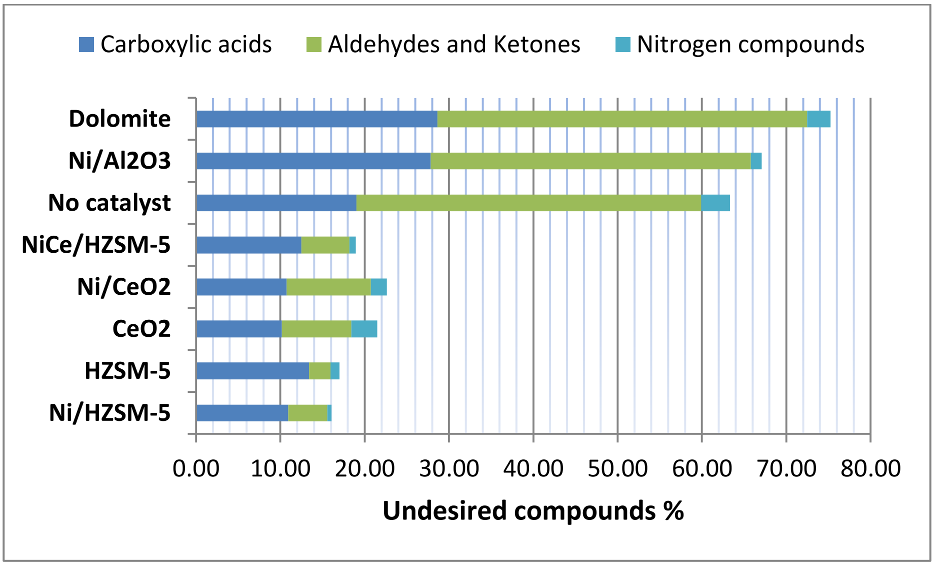


Figure 4.9: Composition of undesired compounds in non-catalytic and catalytic bio-oils

In terms of GC-MS compositions Zeolite and cerium based catalysts were the best. Compared to non-catalytic treatment, all these catalysts have induced a significant increase of hydrocarbons in bio-oil. In the zeolite based catalysts the increase of hydrocarbons is due to the rise of aromatic hydrocarbons which results from the aromatization reaction on zeolites[111-193]. Ni/HZSM-5 generated the second highest hydrocarbons at 34.91% which is a little lower than HZSM-5 (39.56 %). Instead, bio-oils obtained with CeO_2 and Ni/CeO_2 catalysts contained a lower amount of hydrocarbons if compared than zeolites catalysts but a highest contents of alcohols and phenols (53.26%, 49.4%), and furans (16.61%, 17.66%). This is due at a different conversion pathway in presence of metal oxides catalysts, which do not enhance the formation of aromatics compared to the runs carried out with other catalysts.

Despite this an improvement was observed also for phenols in Ni/HZSM-5 and HZSM-5 and the highest proportion of phenols was from Ni/HZSM-5 (43.65%). This could be related with the decrease of Bronsted sites which are masked by the nickel ions [250].

NiCe/HZSM-5 showed an intermediate behavior between cerium and zeolite catalysts and this has been due to simultaneous presence of Ni,Ce and HZSM-5. Dolomite and Ni/Al_2O_3 were the worst catalysts, indeed have not led to no improvement of bio-oils quality. Furthermore, the high content of these bio-oils into carboxylic acids, aldehydes and ketones compared to non-catalytic treatment makes them bio-oils unstable and no suitable for energy purposes as biofuels. All catalysts induced a decrease of nitrogen compounds derived from protein degradation of algal biomass.

5. Chapter 5: Conclusions

The world currently consumes large quantities of non-renewable hydrocarbons at an ever-increasing rate. The reserves of fossil fuels are limited, and there are many other problems associated with their consumption. Biomass has the potential to be a renewable source of hydrocarbons, which could replace a significant percentage of the world's fossil fuels in a variety of applications. Currently, several biological and chemical routes utilize biomass as a source of chemicals and fuels. However, thermochemical routes can use a wider variety of feedstock, allowing them to utilize non-food based, lignocellulosic material. Specifically, catalytic fast pyrolysis is touted to be a promising method to convert solid biomass to a liquid product in high yields and then to produce potential fuels.

- In this work pyrolysis of Posidonia Oceanica was performed in a stainless steel fixed-bed reactor with and without catalyst for production of bio-char and bio-oil.
- Posidonia Oceanica was evaluated as feedstock for the catalytic production of pyrolysis oils. Its high carbon content (40.30 wt%) and low decomposition temperatures compared to lignocellulosic biomass makes it a suitable feedstock for biofuel production.
- The highest liquid yields were obtained at 500°C. Particularly, CeO_2 (51.15wt.%), NiCe/HZSM-5 (50.66 wt.%) and Ni/CeO_2 (49.74 wt.%) were the most effective catalysts and have increased the bio-oil yields of Posidonia Oceanica compared to non-catalytic ones (47.74 wt.%). This can be related to the craking activity of Ni and synergic effect of Ni-Ce, where CeO_2 increases the catalysts stability, dispersion of Ni and carbon suppression, due to its oxidative properties, which promote

dedeoxygenation reactions (decarbonylation, decarboxylation and dehydration).

- The lowest bio-char yield (19.19%) was obtained with Ni/HZSM-5, this is due to greater activity of the catalyst on gasification of char by secondary reactions.
- All catalysts have increased the conversions of Posidonia Oceanica compared to non-catalytic tests. The highest conversions were obtained with Ni/HZSM-5 (80.81%) and CeO_2 (79.07%) which were the most efficient catalysts.
- Alumina based catalyst and dolomite have resulted to the worse conversions, 66.38 and 66.00% respectively and this is due to the catalyst acidity and propension for dehydration reaction with formation of charred species.
- NiCe/HZSM-5 had the lowest amount of coke (0.14 wt. %) while dolomite had the highest (5.57). This is in agreement with the pyrolysis mass balance which shows their catalytic activities in terms of total volatiles.
- All obtained bio-chars have higher carbon content (62-66 wt.%) than the original raw material (40 wt.%) and accordingly have also high HHVs (22-24 MJ/kg) when compared with that of the raw material (16.20 MJ/kg). Furthermore, the high ash and nitrogen contents them suitable for utilization as soil amendment.
- The bio-oils have higher carbon content (60-83 wt.%) than the original raw material (40 wt.%) and accordingly have also a high HHVs (26-40 MJ/kg) when compared with that of the raw material (16.20 MJ/kg).
- Overall, oxygen level was decreased in all bio-oils from 25.66 wt.% in the starting biomass to 6-8 wt.% with CeO_2, Ni/CeO_2 and NiCe/HZSM-5 catalysts. In terms of energy content, the most effective catalysts in improving the bio-oil quality were CeO_2, Ni/CeO_2 and NiCe/HZSM-5 which increased the HHVs of bio-oils, up to 40.60, 37.48 and 38.46 MJ/kg respectively, compared to non-catalytic test (26.08 MJ/kg). These results

indicates the higher deoxygenation power of ceria and Ni-Ce/Zeolite catalysts.

- In terms of GC-MS compositions Zeolite and cerium based catalysts were the best. Compared to non-catalytic treatment (0.94%), all these catalysts have induced a significant increase of hydrocarbons in bio-oil. In absolute term the highest content of hydrocarbons was obtained with HZSM-5 and Ni/HZSM-5, 39.56 and 34.91% respectively. Instead bio-oils obtained with CeO_2 and Ni/CeO_2 catalysts contained a lower amount of hydrocarbons if compared than zeolites catalysts but a highest contents of alcohols and phenols (53.26%, 49.4%), and furans (16.61%, 17.66%).

The results indicate that the fast catalytic pyrolysis of Posidonia Oceanica is a promising process for both renewable fuel production and chemical feedstocks.

Future aim will be to improve the previously tested catalysts but also synthesize new ones with the purpose to enhance the bio-oil "quality" more and more.

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