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ESCUELA TÉCNICA SUPERIOR DE INGENIERÍA DE BILBAO
DEPARTAMENTO DE INGENIERÍA QUÍMICA Y DEL MEDIO AMBIENTE

Ph.D. THESIS

OPTIMIZATION OF THE PYROLYSIS PROCESS FOR THE PRODUCTION OF A BIOMASS DERIVED REDUCING AGENT AND HYDROGEN-RICH GASES

A dissertation submitted to the University of the Basque Country
in partial fulfillment of the requirements for the degree of
Ph.D. in Chemical Engineering by:

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¡Gracias! Eskerrik asko! Thanks! Vielen dank!

TABLE OF CONTENTS

TABLE OF CONTENTS

ABSTRACT

ABSTRACT

This thesis is devoted to the optimization of the biomass pyrolysis process for the simultaneous production of bioreducing agents and high value gases. The thesis is part of the existing collaborative research work between the Befesa Steel R&D S.L. Company and the Chemical and Environmental Engineering Department of the Faculty of Engineering of Bilbao. This company was interested in developing the pyrolysis process at large scale to produce biocoke to be used as reducing agent in some of their industrial plants.

In order to obtain pyrolysis solids useful as reducing agents in metallurgical processes, a slow pyrolysis process at high temperatures is required. In order to obtain high value gases, it is necessary to perform a second catalytic step for pyrolysis vapors upgrading by cracking and reforming so that tars are eliminated and H_2/CO is maximized.

Most of the pyrolysis experiments were carried out in an installation (swept with N_2) composed of two reactors connected in series: a first non-stirred batch 3.5 L pyrolysis reactor, where 100 g of biomass are pyrolyzed, and a second 0.5 L tubular reactor, where the pyrolysis vapors upgrading takes place.

The biomass samples used for this study were selected and provided by Befesa Steel R&D S.L. and consisted in two woody biomass samples: olives residues and eucalyptus. These biomass samples, as well as the pyrolysis solid, liquid and gases products, have been thoroughly characterized by means of the following techniques: proximate and ultimate analyses, constituents analysis, Py-GC/MS-FID characterization, higher heating value determination, GC/MS for the liquids and GC/TCD-FID for the gases.

Four main types of studies have been carried out in this thesis work:

(1) Study of the appropriate operating conditions for the simultaneous production of biocoke and high quality gases. With this aim, the effect of the heating rate (3-20 °C min^{-1}) and temperature (600-750 °C) of the first pyrolysis reactor, as well as the influence of the temperature and catalysts of the second reactor were studied.

(2) A comparative study of the effectiveness of different catalysts for the pyrolysis vapors upgrading (cracking and reforming). The following catalysts were tested: two homemade Ni/Al_2O_3 catalyst modified with CeO_2 and ZrO_2, two commercial zeolites (HY and HZSM5) doped with Ni and without doping, and a commercial catalyst (Katalco 57-4Q) also based on Ni and widely used in industry for steam reforming.

(3) Evaluation of the suitability of biocokes as reducing agents for metallurgical applications. For this to be possible, surface area and porosity measurements, as well as reactivity tests of the biocokes with CO_2, were carried out. The properties of the biocokes were compared with those of commercial reducing agents used in non-ferrous metallurgical processes (metallurgical coke, petroleum coke and anthracite) which were provided by Befesa Zinc Aser S.A. Company.

Finally, as a consequence of the differences on the pyrolysis results obtained with different shipments of the olives samples, a comparative study of the influence of the type of biomass on the pyrolysis yields and products was carried out.

RESUMEN

RESUMEN

El objetivo de esta tesis doctoral es la optimización del proceso de pirólisis de biomasa para la producción simultanea de agentes bioreductores y gases de alto valor añadido. Esta tesis se enmarca dentro de la colaboración existente entre la empresa Befesa Steel R&D S.L. y el Departamento de Ingeniería Química y del Medio Ambiente de la Escuela Técnica Superior de Ingeniería de Bilbao. Uno de los intereses de esta empresa es el desarrollo del proceso de pirólisis a gran escala para producir un biocoque útil como agente reductor en algunas de sus plantas industriales.

Para la producción de sólidos de pirólisis que puedan ser útiles como agentes reductores en procesos metalúrgicos, se requiere un proceso de pirólisis lento a altas temperaturas. Y para la producción de gases de alto valor añadido, se necesita una segunda etapa (catalítica) para la valorización de los vapores de pirólisis mediante craqueo y reformado para la eliminación de alquitrán y el aumento de H_2/CO.

La mayor parte de los experimentos de pirólisis se realizaron en una instalación purgada con nitrógeno y compuesta por dos reactores conectados en serie: un primer reactor de pirólisis no agitado de 3.5 L, donde 100 g de biomasa son pirolizados, y un segundo reactor tubular de 0.5 L, donde se lleva a cabo la valorización de los vapores de pirólisis.

Las muestras de biomasa utilizadas en esta tesis han sido seleccionadas y proporcionadas por Befesa Steel R&D S.L., y consisten en dos muestras de biomasa lignocelulósica: residuos de podas de olivos y eucaliptos. Estas muestras, así como los productos sólidos, líquidos y gaseosos de las pirólisis han sido caracterizados a fondo por medio de las siguientes técnicas: análisis inmediato y elemental, análisis de constituyentes, caracterización por Py-GC/MS-FID, determinación del poder calorífico superior, cromatografía GC/MS para los líquidos y GC/TCD-FID para los gases.

Los estudios que se han llevado a cabo pueden clasificarse en cuatro tipos:

(1) El primero se ha dedicado a establecer las condiciones de operación adecuadas para la producción simultánea de biocoque y gases de alta calidad. Con este propósito, se ha estudiado el efecto de la velocidad de calentamiento (3-20 °C min^{-1}) y de la temperatura (600-750 °C) del primer reactor de pirólisis y la influencia de la temperatura y catalizadores del segundo reactor.

(2) El segundo ha consistido en un estudio comparativo de la eficacia de diferentes catalizadores para la valorización de los vapores de pirólisis. Los catalizadores probados han sido los siguientes: dos catalizadores de Ni/Al_2O_3 modificados con CeO_2 y ZrO_2, dos zeolitas comerciales dopadas con Ni y sin dopar (HY y HZSM5), y un catalizador comercial (Katalco 57-4Q) también basado en Ni y frecuentemente utilizado en la industria para el reformado con vapor.

(4) El tercer estudio se ha centrado en la evaluación de la idoneidad de los biocoques como agentes reductores en aplicaciones metalúrgicas. Para ello, se han hecho medidas de área superficial y porosidad, así como pruebas de reactividad con CO_2 a los biocoques. Las propiedades de los biocoques han sido comparadas con las de agentes reductores comerciales utilizados en procesos metalúrgicos no férreos (coque metalúrgico, coque de petróleo y antracita), que fueron proporcionados por la empresa Befesa Zinc Aser S.A.

(5) Por último, como consecuencia de las diferencias halladas en los resultados de pirólisis obtenidos con los diferentes envíos de las muestras de olivo, se ha llevado a cabo un estudio comparativo de la influencia del tipo de biomasa en los rendimientos y productos de pirólisis.

LABURPENA

LABURPENA

Doktorego Tesi honen helburua biomasa pirolisi prozesuren optimizazioa da, agente bioerreduzitzaileak eta balio erantsi handiko gasak ekoizteko. Tesi hau Befesa Steel R&D S.L. enpresa eta Bilboko Ingeniaritza Goi Eskola Teknikoko Ingeniaritza Kimikoa eta Ingurumenaren Ingeniaritza Sailak ikerketa arloan duten hartu-emanean kokatzen da. Enpresa honen helburuetako bat bere metal ez-burdinazko enpresetan erabiltzeko agente bioerreduzitzaileak (biokokea, sintesi gasa) ekoizteko prozesu bat garatzea da.

Biokokeak (biomasa pirolisi-solidoak) metalurgia prozesuetan agente bioerreduzitzaile moduan erabilgarri izan daitezen, tenperatura altuko pirolisi motelak burutu behar dira. Balio erantsi handiko gasak (sintesi gasa) ekoizteko pirolisi-lurrunak balioztatu behar dira mundrunak ezabatuz eta H_2 eta CO produkzioa igoz. Hau lortu asmoz, urrats katalitiko bat erabili behar da.

Pirolisi esperimentu gehienak elkarren segidako bi erreaktoreez osatutako instalazio batean egin dira: lehenengoa 3.5 L-ko pirolisi-erreaktore bat da, bertan 100 g biomasa pirolizatzen direlarik; bigarrena pirolisi-lurrunak balioztatzen diren 0.5 L-ko hodi-erreaktore bat da.

Tesi honetan erabilitako biomasa laginak Befesa Steel R&D S.L. enpresak aukeratutako bi biomasa lignozelulosiko ezberdin izan dira: olibondoen inausketa hondakinak eta eukaliptoak. Biomasa laginak, pirolisi-solidoak, -likidoak eta -gasak honako teknika hauen bidez karakterizatu dira: bat-bateko analisia, analisi elementala, osagaien analisia, Py-GC/MS-FID karakterizazioa, goi bero ahalmenaren determinazioa, GC/MS kromatografia pirolisi-likidoentzat eta GC/TCD-FID kromatografia pirolisi-gasentzat.

Lau ildo ezberdin jarraitu dira doktorego tesi hau burutzerakoan:

(1) Lehenengoa, biokoke eta balio erantsi handiko gasen ekoizpenerako prozesu baldintza egokienak ezartzea izan da. Horretarako, pirolisi-erreaktoreko berotze-abiadura (3-20 °C min^{-1}) eta tenperaturaren (600-750 °C) efektua, eta hodi-erreaktoreko tenperatura eta katalizatzaileen eragina aztertu dira.

(2) Bigarren ildoa, pirolisi-lurrunak balioztatzeko erabili diren katalizatzaileak konparatzean datza: CeO_2 eta ZrO_2-az moldaturiko bi Ni/Al_2O_3 katalizatzaile, nikelaz dopaturiko eta dopatu gabeko bi zeolita komertzial (HY eta HZSM5), eta nikelean oinarrituriko katalizatzaile komertziala (Katalco 57-4Q). Azken hau industria mailan ur lurrunaren bidezko erreformatuetan oso erabilia da.

(3) Hirugarren ildoan aplikazio metalurgikoetan biokokeak agente erreduzitzaile bezala erabiltzeko duen gaitasuna aztertu da. Horretarako, biokokeen azalera eta porositate neurketak, eta erreaktibotasun-frogak egin dira. Biokokeen propietateak Befesa Zinc Aser S.A. enpresak ez-burdinazko prozesu metalurgikoetan erabiltzen dituen koke komertzialekin (koke metalurgikoa, petrolio-kokea eta antrazita) alderatu dira.

(4) Azkenik, jasotako olibondoen lagin desberdinekin lortutako pirolisi emaitzetan aurkitutako ezberdintasunak direla eta, biomasa-motaren eragina aztertu da pirolisi-errendimendu eta produktuetan.

CHAPTER 1

SCOPE AND OBJECTIVES

1. SCOPE AND OBJECTIVES

The general objective of this doctoral thesis is to optimize the biomass pyrolysis process in order to obtain pyrolysis solids which can be used as reducing agents in metallurgical applications, and at the same time, enhance the quality of the pyrolysis gases so that they can be used in applications as profitable as possible.

The metallurgical industry is a great consumer of energy as well as a great emitter of CO_2, since it uses both reducing agents (coke) and fuels of fossil origin. Therefore, the production of CO_2-neutral reducing agents (biomass derived biocokes) as well as a renewable high quality gas (pyrolysis gases) useful as fuel, reducing agent, hydrogen source or synthesis gas, has a great environmental, social and industrial benefit.

In order to achieve the abovementioned general objective, the following partial aims and steps have to be attained.

- Set up of a pyrolysis installation suitable for producing pyrolysis solids useful as reducing agents (biocoke) and for upgrading pyrolysis vapors. Additionally, the analytical techniques necessaries for a thorough characterization of the biomass samples and the solid, liquid and gaseous pyrolysis products should be tuned up.
- Acquisition, preparation and characterization of the lignocellulosic biomass samples to be used in this thesis.
- Selection, preparation or acquisition, and characterization of the catalysts to be tested in the pyrolysis vapors upgrading step.
- Evaluation of the influence of operating conditions on the pyrolysis yields and products, and selection of the most appropriate conditions for biocoke production and pyrolysis vapors upgrading.

- Study of the effectiveness of different catalysts, including both homemade and commercial catalysts, for pyrolysis vapors upgrading, so that tar formation is minimized and hydrogen production is maximized.

- Evaluation of the suitability of the biocokes produced as reducing agents, taking into account surface area, porosity and reactivity and comparison with the properties of typical commercial reducing agents used in non-ferrous processes.

CHAPTER 2

BACKGROUND AND CURRENT STATUS OF THE ISSUE

2. BACKGROUND AND CURRENT STATUS OF THE ISSUE

At times of global warming and climate change, effective methods for an integrative environmental protection from the industry are getting more and more important. This fact is also publicized by environmental legislation, where tighter regimentations occur. An example for that is the Kyoto Protocol, which stipulated a worldwide reduction of the emitted greenhouse gases (GHG) of 5 % in the years 2008 to 2012, referring to the greenhouse gas emissions from 1990. This protocol has been recently renovated till 2020 by Conference of Parties 18 (COP), celebrated in 2012. On the other hand, the 35th G8 summit of 2009 established that the GHG emissions should be reduced by 80 % by 2050. These ambitious targets, especially in the European Union, are only reachable if new ideas and concepts are developed by the industry. The production of biocoke by pyrolysis of biomass can be one of these ideas and a step further in the reduction of the environmental impact from industry.

2.1. From fossil fuels to biomass

Oil, coal and natural gas are the three most used materials for both energy production and products manufacturing all over the world. The industrial activity has been based on these three materials (known as “fossil fuels”) from the starting of the industrial revolution, and their demand will continue increasing in the near future, at least in the energy sector (IEA, 2007).

However, some major concerns surround the massive utilization of fossil fuels: (1) their reserves and future availability, (2) the price fluctuations, (3) the geopolitical instability in many producer countries and (4) the CO_2 emissions related to their use in applications where they are oxidized.

Data collected by the Environmental Protection Agency (EPA) of the United States, shown in Figure 2.1, indicate that more than 80 % of the U.S. CO_2 emissions come from three economic sectors: electricity production (33.1 %), transportation (27.5 %) and industrial manufacturing of products (20.1 %).

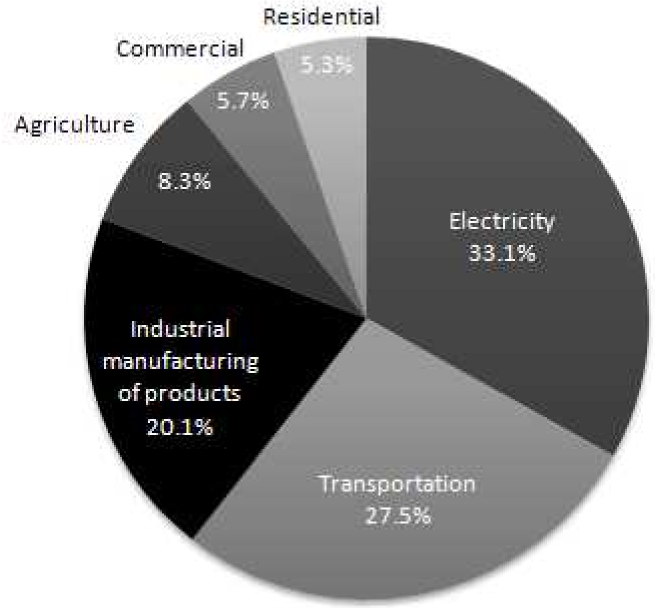


Figure 2.1. Distribution of CO_2 emissions by different economic sectors (adapted from EPA, 2011)

Concerning the CO_2 emissions related to the industrial manufacturing of products, Figure 2.2 shows the CO_2 emissions produced by different industrial sectors. The main sectors contributing to CO_2 emissions (in teragrams or million metric tons Equivalent) are, in order of importance:

- Production of metals such as iron and steel, aluminum, zinc and lead (44.1 %).
- Production and consumption of mineral products such as cement, lime and soda ash (30.6 %).
- Chemical production (e.g., ammonia, petrochemicals and titanium dioxide) (9.7 %).

These data highlight the important contribution of the metal production sector to the CO_2 atmospheric concentration.

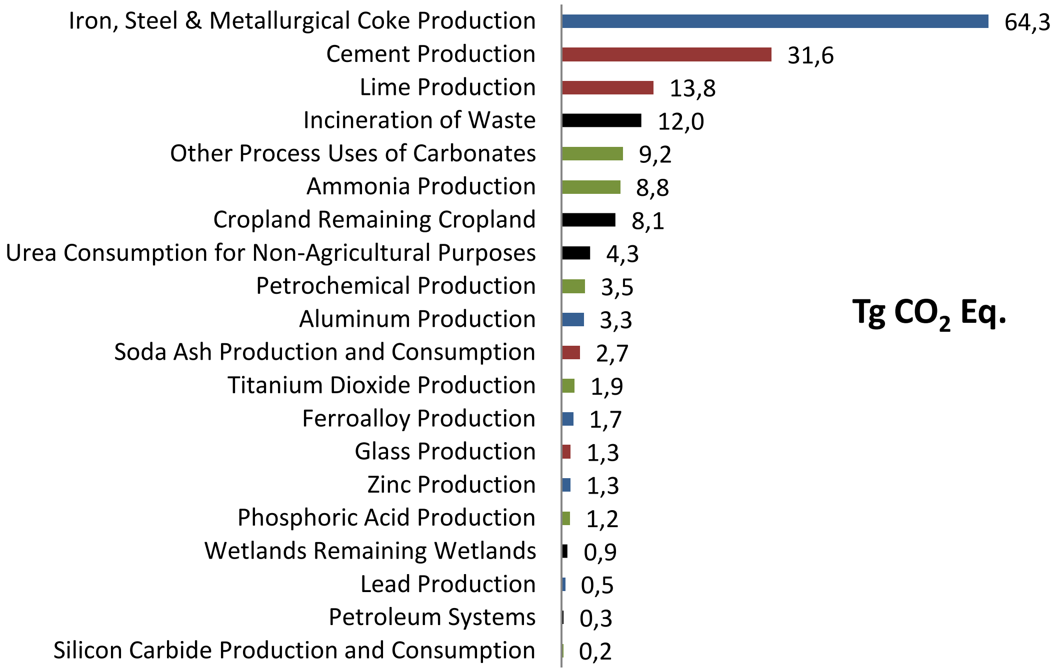


Figure 2.2. Sources of CO_2 emissions of different industrial manufacturing of products, 2011 (adapted from EPA, 2013)

The CO_2 emitted by the metals production sector comes mainly from the utilization of coal, petroleum coke and/or metallurgical coke in the process. The utilization of one or the other depends on the process itself. Blends of them are also usually used (Soncini et al., 2013; Wei et al., 2011; Weiland et al., 2012). When metals such as iron, lead, zinc or tin are obtained through primary production (from the mineral ore), the carbonaceous materials are used for the reduction of such minerals in order to obtain the metallic form of the species, which are the desired products. Additionally, these carbonaceous materials are also used to provide heat for the endothermic requirements of chemical reactions and for melting of the slag and metal.

A simplified explanation of the process is the following: carbonaceous materials are burned in the furnace with hot air forming carbon dioxide (Eq. 2.1). The generated carbon dioxide reacts in the furnace with carbon to produce carbon monoxide (Eq. 2.2 Boudouard reaction) which is the main reducing agent in the furnace. Consequently, this CO acts as reducer of metal oxides, oxidizing itself to CO_2. This is the second source of CO_2 of the process, the first one is the CO_2 generated by combustion.

Using as an example the production of iron from hematite and magnetite (Fe_2O_3 and Fe_3O_4), the main reduction reactions would be those of Eq. 2.3 and Eq. 2.4.

$$C + O_2 \rightarrow CO_2 \qquad \text{Eq. 2.1}$$

$$C + CO_2 \leftrightarrow 2CO \qquad \text{Eq. 2.2}$$

$$Fe_2O_3 + 3CO \rightarrow 2\ Fe + 3CO_2 \qquad \text{Eq. 2.3}$$

$$Fe_3O_4 + 4CO \rightarrow 3\ Fe + 4CO_2 \qquad \text{Eq. 2.4}$$

Apart from the production of metals, carbonaceous materials like coal and coke are also used in some metals recycling processes, such as those of zinc (Zn) and cooper (Cu), with the same purpose of both providing heat and reducing the metal oxides.

Particularly important in the Basque Country (Spain) is the recycling of zinc through the Waelz process since Befesa Zinc Aser S.A. (a company belonging to Befesa Group), located near Bilbao, is the only company in Spain that offers an integral collection and treatment service for recovering zinc from steel dust. Befesa Zinc Aser S.A. treats 160,000 tons per year of steel dust coming from Spain and also from other countries such as France, Italy and U.S. are recycled.

In the waelz kiln the dust is treated by adding coke as the reducer and lime for providing basic conditions. At temperatures between 1100 °C and 1300 °C zinc ferrite ($Zn_xFe_{3-x}O_4$) is decomposed and zinc oxide (ZnO), iron oxide and other oxides are reduced. The resulting zinc evaporates under these conditions and is carried to the upper part of the kiln together with carbon monoxide. In this area oxidizing conditions lead to the formation of fine particles of zinc oxide and carbon dioxide. The so called Waelz oxide is collected in the off gas filter system. The iron and some lead remain in the so called Waelz slag.

Befesa Steel R&D S.L. Company was created by Befesa Group in order to promote research & development in the steel and galvanization waste recycling area. This company was the promoter of this thesis work since this company was interested in producing a metallurgical charcoal by thermal treating of biomass in order to replace fossil coke in recycling plants and so minimize their carbon footprint. Together with the biocoke, Befesa wanted to produce a syngas of the maximum value and usefulness.

The key factor of the production of coke from biomass is the fact that biomass derived products and processes imply neutral CO_2 emissions. Biomass absorbs atmospheric carbon dioxide while it grows and returns it into the atmosphere when it is consumed, all in a relatively short amount of time. Because of this, biomass utilization creates a closed-loop carbon cycle.

Fossil fuels also contain carbon that was removed from the atmosphere, but under different environmental conditions and millions of years ago, in a previous geologic time. When burned, this carbon is released back into the atmosphere as carbon dioxide. Since the carbon dioxide being released is from ancient deposits, and new fossil fuels take millions of years to form, burning fossil fuels adds more carbon dioxide to the atmosphere than is being removed. In other words, the key difference between biomass and fossil fuels is age.

There are different thermal treatment processes that can be applied to woody biomass with the aim of obtaining different products. The main ones are summarized in Figure 2.3.

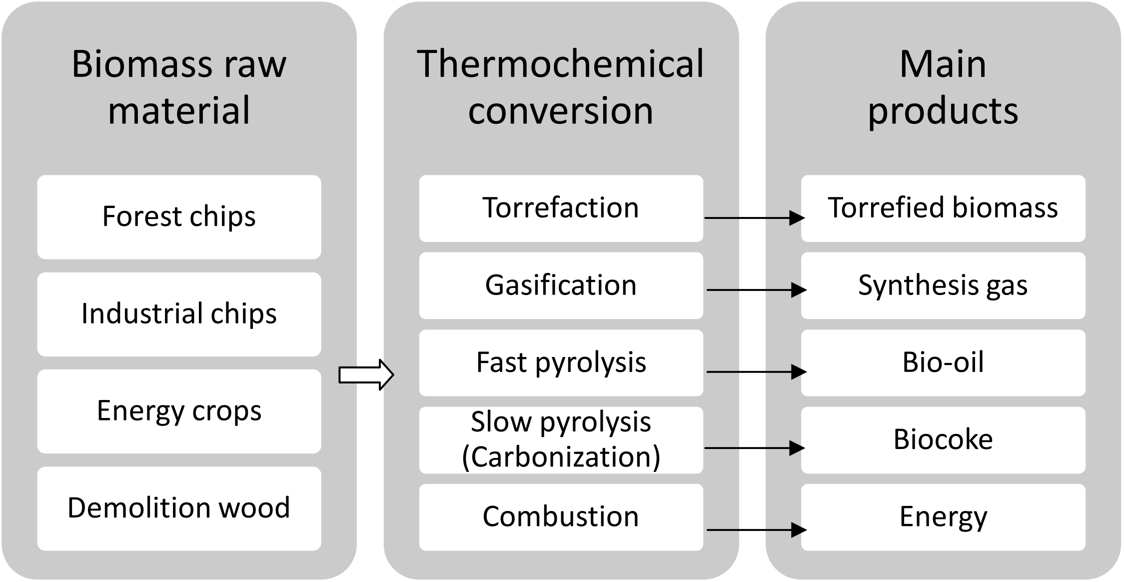


Figure 2.3. Bioproducts obtained from wood thermochemical conversion processes

The production of char from biomass is not new; in fact it is the update and modernization of the traditional process of obtaining charcoal from wood. In recent years the effects of biomass type and operating parameters on the properties of the obtained char have been investigated (Avila et al., 2011; Demirbaş, 2001; Elyounssi et al., 2012; Park et al., 2012; Xiao et al., 2012; Xu et al., 2011).

However the production of a coke-like product requires more demanding process conditions, since (traditional) coke is a macroporous carbon material produced by carbonization of coals or coal blends of specific rank and characteristics (Díez et al., 2002). In other words, to obtain a coke-like product from wood, the carbonization of wood followed by the carbonization of the resultant coal must occur in the same process. Griessacher and Antrekowitsch, (2011) and Griessacher et al., (2012) have reported that a coke-like product can be obtained by slow high temperature pyrolysis of wood.

One of the most important influencing parameter of the slow pyrolysis (carbonization) process is temperature. There is evidence in the literature that increasing temperature the amount of volatile components in the coal decreases and therefore the carbon content in the coal becomes higher (Demirbas, 2004) reaching the carbon content of cokes. Heating rate is also a very important parameter that influences the amount and characteristics of pyrolysis products; the fraction of produced solid increases with decreasing heating rate. Because of the slow emergent volatile components, this solid has a lower porosity and reactivity. It has been reported (Angın, 2013) a higher char yield with decreasing heating rate, since the wood slow emerging products have more time to react and carbonize. It may be expected that the lower the heating rate, the lower the char porosity and reactivity since more slowly emerge the volatile products from the pyrolyzed biomass.

Finally, the feedstock material is also a key factor for the production of biocoke. It is well known that woody biomass is the best biomass feedstock for coke production.

Therefore, in this thesis the production of biocoke by pyrolysis of woody biomass and working at high temperatures and slow heating rates is explored.

2.2. Woody biomass

In this section a quick glance to the structure and composition of woody biomass as well as some considerations regarding woody biomass origin devoted to justify the reason for the biomass samples selected for this thesis is included.

2.2.1. Woody biomass constituents

Woody biomass is a lignocellulosic material composed of rigid cellulose fibers embedded in a cross-linked matrix of lignin and hemicellulose that binds the fibers. Figure 2.4 shows the chemical structure of lignocellulosic biomass. Lignocellulose plant structures also contain a variety of plant-specific chemicals in the matrix, called extractives (resins, phenolics, and other chemicals), and minerals (calcium, magnesium, potassium, and others).

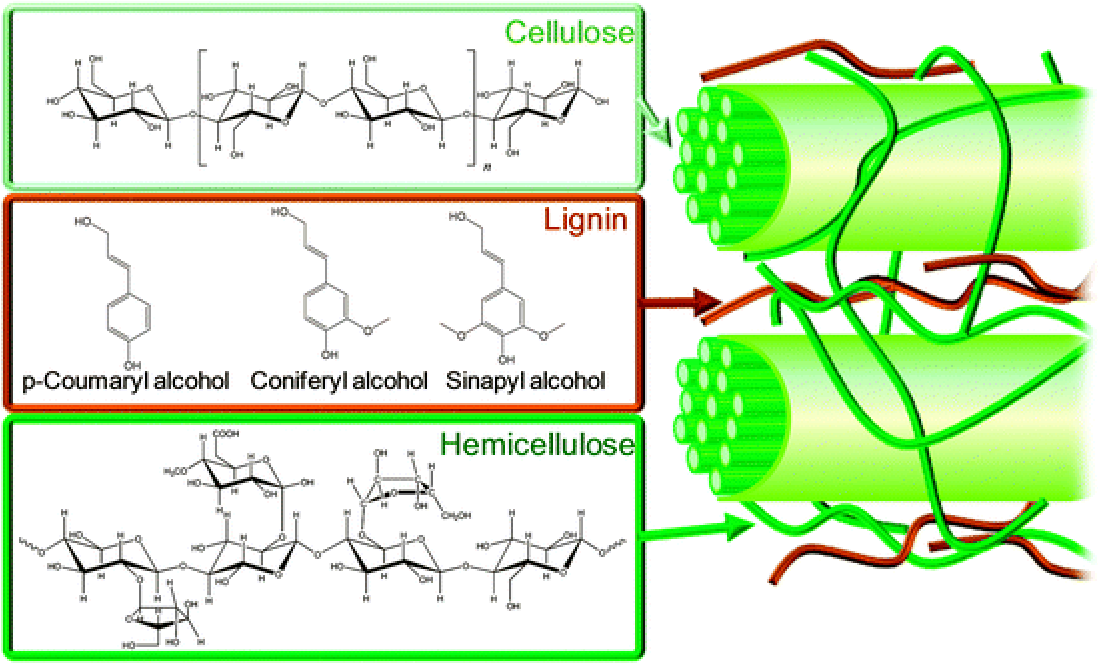


Figure 2.4. Structure of lignocellulosic biomass (Alonso et al., 2012)

Although lignocellulose materials vary in their proportions of cellulose, hemicellulose, and lignin, typical lignocellulosic biomass contains 40-60 wt.% cellulose, 20-40 wt.% hemicellulose, and 10-25 wt.% lignin. Extractives and minerals generally account for less than 10 wt.% of the dry biomass weight (Yang et al., 2007).

Cellulose is the major component of cell walls of wood fiber and is a linear homopolymer of D-glucose molecules bound together by β-glycosidic linkages. The molecular linkages in cellulose form linear chains that are rigid, highly stable, and resistant to chemical attack. The degree of polymerization (the number of glucose molecules in a cellulose chain) is normally in the range of 7,500-15,000 for plant cellulose.

The cellulose chains are bound together by hydrogen bonds to form a very rigid macromolecular structure, microfibrils, with diameters in the range of 10-25 nm (Figure 2.5). Microfibrils are built up to fibrils and finally to cellulose fibers. Most of the cellulose chains are highly ordered or crystalline, due to hydrogen bonding occurring between linear molecules, but small parts of the cellulose are amorphous. The degree of crystallinity varies within different plants.

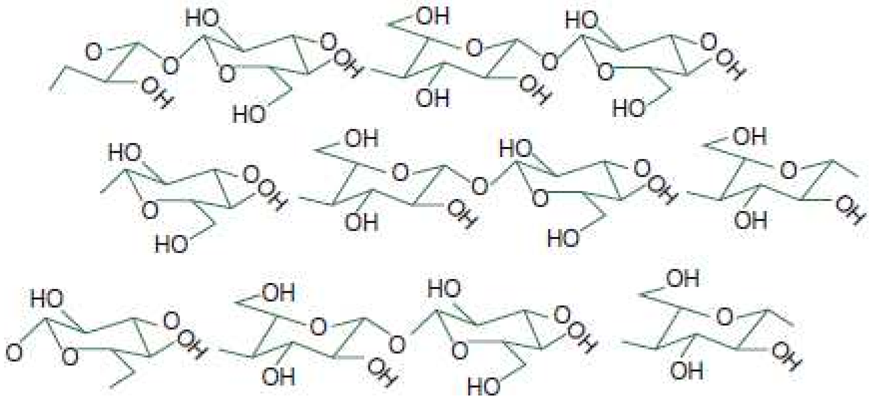


Figure 2.5. Chemical structure of cellulose (Sierra et al., 2009)

Hemicellulose is a low degree polymerizated (~200) and highly branched polymer (Figure 2.6). It surrounds the cellulose fibers. The role of this component is to provide a linkage between lignin and cellulose. The structure of the hemicellulose varies depending on the source of the lignocelluloses, and it may consist of 5-carbon sugars (usually D-xylose and L-arabinose), 6-carbon sugars (D-galactose, D-glucose and D-mannose) and uronic acid. Its structure is characterized by a long, linear backbone of one repeating sugar type, with short, branched side chains composed of acetate and sugars. Hemicellulose is amorphous and more easily to hydrolyze to its constituent sugars than cellulose.

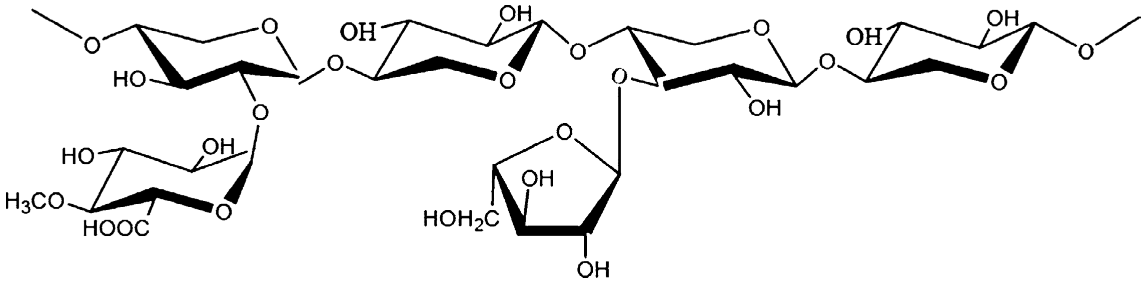


Figure 2.6. Hemicellulose structure (Sierra et al., 2009)

Lignin is an amorphous polymer constructed of non-carbohydrate, alcohol units that are not fermented. It is a highly complex, probably the most complex, and least well characterized molecular group among wood constituents. It varies in structure depending on the biomass source (Sjöström and Alén, 1999). The molecular structure of lignin polymers is very random and disorganized and consists primarily of carbon ring structures containing benzene rings with methoxyl, hydroxyl, and propyl groups. They are interconnected by polysaccharides (sugar polymers) (Figure 2.7). In wood, the lignin network is concentrated between the outer layers of fibers. Lignin gives structural rigidity to wood by stiffening and holding the fibers of polysaccharides (cellulose and hemicellulose) together.

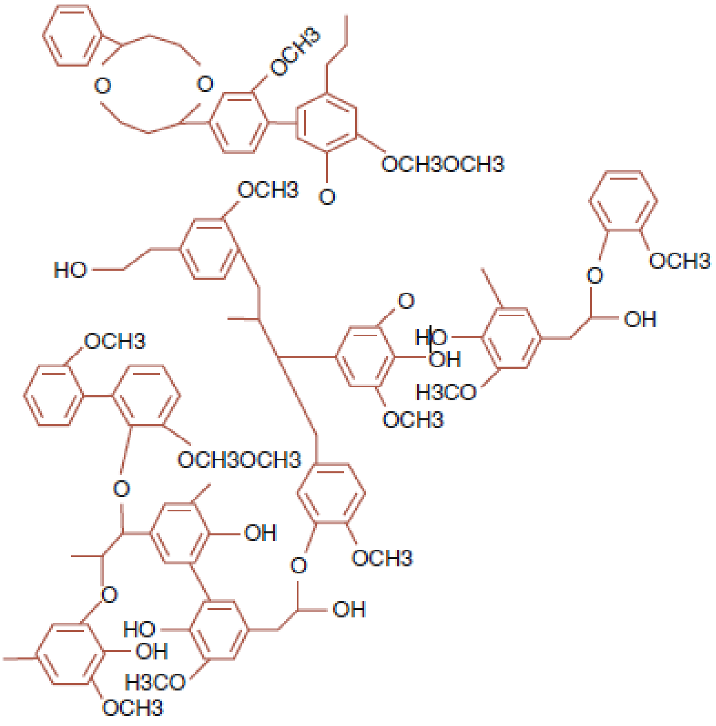


Figure 2.7. Lignin structure (Sierra et al., 2009)

There are other components present that refer to all non-cell wall materials. These components consist of a wide variety of chemicals. Based on their solubilities in water and neutral organic solvents, these chemicals can be classified as **extractives** or non-extractives. The extractives can be crudely divided into three groups, namely resins, phenols and terpenes. In addition, low molecular weight carbohydrates, alkaloids, and soluble lignin can also be extracted. The non-extractives mainly consist of inorganics mostly present in ash minerals. The dominating components are alkali and alkali earth carbonates, and oxalates. In spite of their small quantity, the role of these compounds is very significant because they protect cellulose from decay and insect attack.

2.2.2. Woody biomass origin

The main woody biomass feedstocks can be classified in three vast categories (Ghosh and Prelas, 2011): energy crops, forest and agricultural residues, and wood waste from construction industry (the so called urban waste).

Among these three main categories the biomass processing residues and energy crops are the sources which better biomass feedstocks provide for the production of biocoke, since urban waste is usually heterogeneous in composition and contains different chemical products like paint or varnish.

Wood coming from a well-selected crop would be the best option from the biocoke production’s point of view, since the plantation of the desired crop guarantees a well characterized and homogeneous feedstock material for the process. One of such crops is the eucalyptus family, normally used for the paper industry, wood or production of chemicals, due to its fast growth rate. Befesa Group, promoter of this PhD thesis, has a eucalyptus plantation in Uruguay, and therefore, eucalyptus has been one of the woods used in this thesis for biocoke production. Because of its fast growing behavior, it is considered a potential candidate for producing metallurgical charcoal by pyrolysis. It is worth mentioning that Eucalyptus occupies 70 % of the 950,000 ha of the forest plantation in Uruguay. Nevertheless, the massive utilization of energy crops could imply some problems such as the loss of biodiversity and the implications in terms of food prices.

At this point it becomes evident that the industrial production of biocoke from forest and agricultural residues could be a better option of a great interest, especially in Spain, where intensive agriculture is extended all over the south of the country and high quantities of agriculture residues are continuously produced.

The major Spanish woody crop corresponds to olive production. In Spain there are 2,584,067 ha of olive groves, which represents 52.6 % of total Spanish woody crops (ESYRCE, 2013). Three communities cover the 86.3 % of olive trees, specifically Andalusia (60 %), Castilla-La Mancha (15.8 %) and Extremadura (10.5 %). Figure 2.8 shows where these communities are placed in the map of Spain.

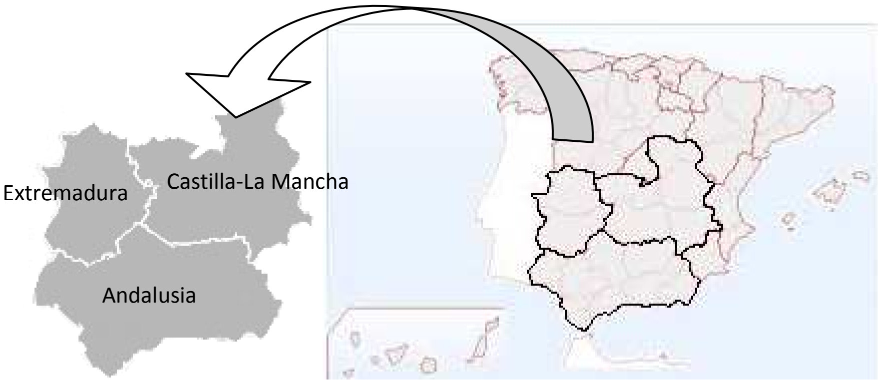


Figure 2.8. Map of communities of Spain

One hectare of olive grove generates three tons of pruning residues (Figure 2.9) which means 4,650,654 tons of branches and leaves per year from Andalusia, 1,222,002 tons per year from Castilla-La Mancha and 813,150 tons per year from Extremadura, most of which are illegally burnt or left on the ground partially for recirculation of nutrients.

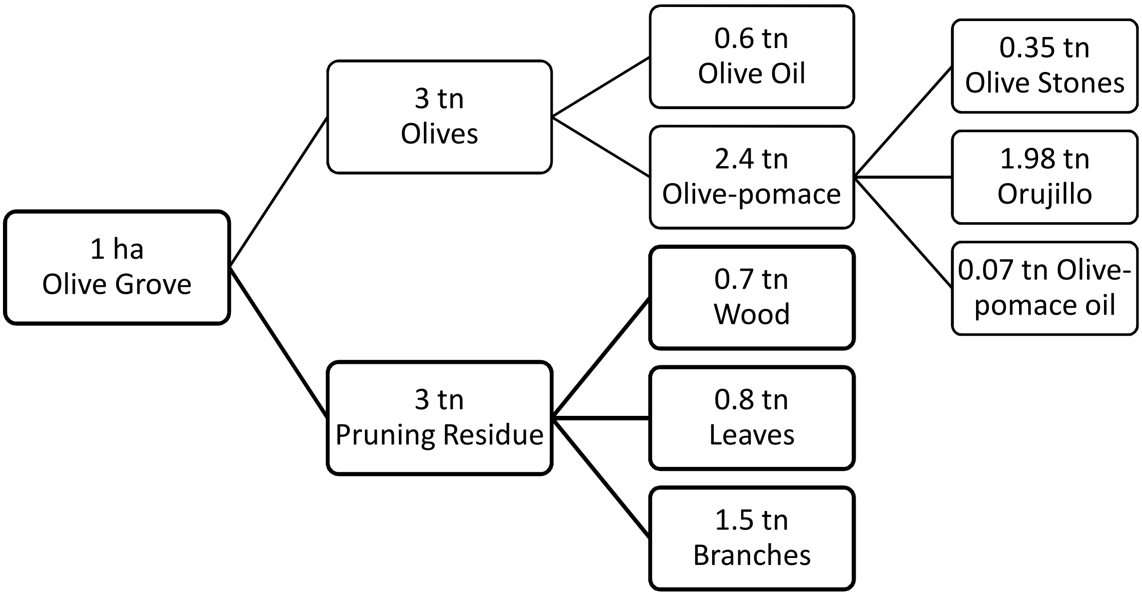


Figure 2.9. Biomass potential from olive grove (García-Maraver et al., 2012)

These numbers show the potential of these agricultural residues to be used as feedstock for the industrial production of biocoke. For this reason Befesa Steel R&D S.L. considered developing a biomass (olives) based metallurgical industry in the Spanish autonomous community of Extremadura, and therefore, olive wastes has been one of the biomass samples used in this thesis.

2.3. Optimization of the pyrolysis process

During the pyrolysis wood structures are cracked to lower molecular products (from now on called pyrolysis vapors) which evolve from the pyrolysis reactor system. These vapors are composed of many chemicals which can be divided into two fractions according to their condensability: liquids, which are the products that condensate once cooled to room temperature and are frequently named bio-oils, and pyrolysis gases, which are the non-condensable products (Figure 2.10).

The industrial application of the whole pyrolysis vapors is very difficult since strong thermal insulation would be necessary in order to avoid condensation and blockages in the pipelines. The only possibility to use the pyrolysis vapors as a whole would be burning them without getting coal (Agirre et al., 2013). However, achieving more valuable applications of these vapors (different from combustion) is essential for the economy of the biocoke production process. Therefore, other alternatives must be taken into account.

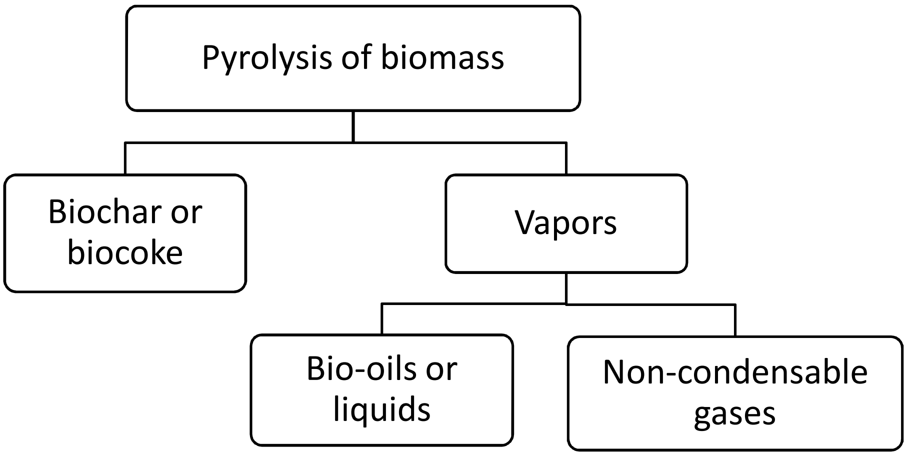


Figure 2.10. Pyrolysis products of biomass

Wood pyrolysis liquids are frequently composed of two different fractions, an organic phase usually named tars, and an aqueous phase mainly composed of water. The tars fraction includes aromatic and non-aromatic hydrocarbons, and oxygenated organic compounds. Generally speaking, bio-oils are highly oxygenated, viscous, corrosive, relatively unstable and chemically very complex products (Bridgwater and Bridge, 1991; Stoikos, 1991). As a consequence, the direct utilization of bio-oils is not possible and it normally requires upgrading through hydrotreating, hydrocracking, hydrothermal liquefaction or other processes (e.g. DOE/EERE, 2010; Jones et al., 2009; NABC, 2013; Wright et al., 2010; Yue et al., 2013). On the other hand, the non-condensable gases are mainly composed of H_2, CO, CO_2 and light hydrocarbons, with a relatively high proportion of H_2 and CO, which confers this gas the potential to be used in different worthwhile applications (reducing agent, source of H_2 or synthesis gas) interesting for industrial applications.

Since one of the objectives of this thesis is to obtain a metallurgical grade char, slow heating rates and high temperatures are required, and therefore, low liquid yields were to be expected. This fact together with the low quality and suitability for direct application of bio-oils led to focus this thesis, in agreement with Befesa Steel R&D S.L. indications, on liquids minimization and gases maximization.

The fact that liquids and gases evolve together from the reactor during pyrolysis is the basis of the hypothesis developed in this thesis work, i.e.: provided that a good quality biocoke is produced, would it be possible to upgrade the whole pyrolysis vapors as they leave the reactor in order to produce great gas yields, minimum or no tars, and a hydrogen rich gas?

The way to do that is by installing a second reactor after the pyrolysis reactor, in order to “in-situ” upgrade the vapors evolved from pyrolysis. Thermal cracking and catalytic cracking and reforming are the alternatives considered in this thesis, in order to obtain short carbon chain organic chemicals and hydrogen.

2.3.1. Thermal cracking

Thermal cracking is the process in which complex organic molecules are subjected to high heat and temperature to break the molecular bonds and reduce the molecular weight by breaking carbon-carbon bonds.

When thermal cracking of hydrocarbons is produced many reactions occur, giving as a result a wide range of different products, most of them based on free radicals created at the sites where molecular bonds are broken. The mechanism of thermal cracking takes place through the typical initiation, propagation and termination reactions. In the initiation step molecules break apart into free radicals. During propagation several reactions take place: (1) hydrogen abstraction, where free radicals remove hydrogen atoms from other molecules, turning the second ones into free radicals; (2) radical decomposition, where free radicals break again into molecules; and (3) radical addition, which is the reverse of radical decomposition reactions, because radicals react with alkenes to form larger free radicals. Finally, in the termination step, free radicals react with each other to produce products that are not free radicals.

The rate of cracking and the end products are strongly dependent on the temperature. Generally speaking, higher temperature leads to higher cracking yields. However, it is important to remark that cracking pyrolysis vapors is not only conditioned by the temperature used, but also by the reactor type, processing conditions (like residence time) and feed rate. The effect of thermal cracking can be increased using long residence times.

The objective of using thermal cracking for the treatment of pyrolysis vapors is to crack the tar molecules and obtain chemicals of shorter carbon chain, i.e. organic gaseous species, and hydrogen. Regardless, some biomass derived vapors molecules have been reported to be very hard to crack just by thermal treatment (Bridgwater, 1995). Therefore, the addition of catalysts that may help to upgrade (cracking + reforming) pyrolysis vapors is to be recommended.

2.3.2. Catalytic cracking and reforming

The use of catalysts has a great influence on pyrolysis processes, both in pyrolysis yields and in the composition of pyrolysis liquids and gases. On the one hand, catalysts may increase cracking giving rise to lower liquid yields and higher gas yields. On the other hand, catalysts may promote reactions such as water gas shift reactions ($CO + H_2O \leftrightarrow CO_2 + H_2$) or reforming reactions ($C_xH_y + H_2O \rightarrow CO/CO_2 + H_2$) which increase H_2 production.

Due to the extensive use of zeolite catalysts in cracking processes of the petroleum industry, these catalysts have been very much investigated for upgrading biomass derived pyrolytic vapors (e.g. Aho et al., 2008; Diebold and Scahill, 1988; Evans and Milne, 1988; Horne and Williams, 1996; Milne et al., 1988; Williams and Horne, 1995).

Zeolite catalysts most investigated has been ZSM5 zeolite, mostly in its calcined form (hydrogen form), HZSM5. This zeolite has strong acidity, high activities and shape selectivities, which confers it great cracking and deoxygenation ability. The cracking ability of the HZSM5 zeolite is well known, as it has been reported by many authors (e.g. Adjaye and Bakhshi, 1994; Atutxa et al., 2005; Olazar et al., 2000). This cracking ability is mainly attributed to its strong acidity and leads to the increase of gases and thereby to the decrease of the liquid product yields.

On the other hand, HZSM5 catalyst can convert oxygenated fractions into light hydrocarbon mixtures in the C_1-C_{10} range by dehydration and deoxygenation reactions, forming CO, CO_2 and H_2O (Costa et al., 1992; Diebold et al., 1987; Stoikos, 1991). A proof of this deoxygenating ability is the fact that ZSM5 zeolite is nowadays used in the commercial process for the conversion of methanol-to-gasoline (MTG) (Bhatia, 1990) and in several bio-oil upgrading processes (Chantal et al., 1984; Evans and Milne, 1988; Mathews et al., 1985; Scahill and Diebold, 1988; Sharma and Bakhshi, 1991).

For these reasons, HZSM5 is one of the catalysts that has been used in this thesis for pyrolysis vapors upgrading (diminishing liquids and increasing H_2 content of the gases).

Although the hydrogen content in gases is usually increased as a consequence of cracking reactions, a more effective way of obtaining hydrogen, in terms of selectivity, is by steam reforming process (Garcia et al., 2000; Kaewpanha et al., 2013; Kantarelis et al., 2014a; Luo et al., 2009; Mahmood et al., 2013; Remón et al., 2014; Seyedeyn-Azad et al., 2011). This is a water demanding process, but it is not necessary to feed steam for promoting reforming reactions since water is already present in such vapors in enough quantity; just the use of an appropriate reforming catalyst is needed.

Reforming catalysts are normally composed by an acidic support and an active phase (metal). The incorporation of a metal to zeolites (multifunctional catalysts), modifies the reaction environment promoting hydrogen production. Besides, the use of multifunctional catalysts which can shift the hydrogen limited environment to a carbon limited one by in situ hydrogen generation via water gas shift (WGS) reaction is desirable to limit coke formation.

Nickel is the metal most frequently used in catalysts for biomass processing (Corella et al., 1991; Narváez et al., 1997; Rei et al., 1986; Wang et al., 1997). Ni catalysts promote tar cracking to a very great extent if the appropriate operating conditions are used (Caballero et al., 2000; Lv et al., 2007; Pfeifer and Hofbauer, 2008; Pinto et al., 2009). Additionally, it has been reported that with Ni-based catalysts the hydrogen gas yield is improved (Efika et al., 2012; Zhang et al., 2004). Studies reported in the literature of catalytic biomass pyrolysis over Ni and in the presence of steam have shown that Ni, besides promoting H_2 production, has also deoxygenation activity (Kantarelis et al., 2014b).

Nickel can also be added to zeolites. The modification of ZSM-5 zeolites of medium acidity (SiO_2/Al_2O_3_30) with 1 wt.% Ni is a suitable strategy for obtaining stable catalysts (Valle et al., 2010). Because of the incorporation of metals to the zeolites, the relative activity of different catalytic functions (metal/acidic) is also of great interest (Kantarelis et al., 2014a). An additional advantage by the use of metal modified zeolites is the bifunctional activity (acid and metal functions) which also reduces the rate of coke formation (Guisnet and Magnoux, 1997). Additionally, modified zeolites show enhanced activity toward cracking (Lü et al., 2003; Stöcker, 2005).

For this reason, zeolites modified with Ni have been testate in this thesis for pyrolysis vapors upgrading.

Concerning supports, different materials have been tested for Ni-based catalysts (Al_2O_3, ZrO_2, TiO_2, dolomite, olivine, etc.). Among them, alumina is one of the most widespread supporting carrier of active metals (Ferella et al., 2013) and it has been found that Ni/Al_2O_3 has greater activities than Ni over other supports (Miyazawa et al., 2006; Simell and Bredenberg, 1990).

On the other hand, several studies in the literature repeat that reducible oxides, such as cerium oxide (ceria) and zirconium oxide (zirconia), improve the performance of some metal catalysts such as Ni (de Abreu et al., 2012; Kimura et al., 2006; Tomishige et al., 2007). Ceria (CeO_2) is often employed in combination with other oxides or in conjunction with active metals and thermally stable supports. Therefore, strictly speaking, ceria may function either as a structural/electronic promoter or as a co-catalyst, depending on the type of application, but not as a true catalyst (Trovarelli et al., 1999). The main reason why CeO_2 alone is of comparatively little interest as a support or catalyst is its low textural stability and its price.

For this reason, in this thesis two homemade Ni/Al_2O_3 catalysts modified with ceria and with zirconia have been tested for pyrolysis vapors upgrading.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3. EXPERIMENTAL PROCEDURE

Biomass from two different origins have been used for this thesis: on the one hand, a woody biomass waste obtained from olive tree cuttings of the South of Spain, and on the other hand, a woody biomass (eucalyptus) coming from an energy crop in Uruguay. All the samples were supplied by Befesa Steel R&D S.L. which, as a promoter of this thesis work, wanted to prove different sample types for the process.

3.1. Biomass Samples

The first kind of biomass (olive tree cuttings) was provided in three different times. The first shipment was only wood, basically thin branches (olives 1) 30-50 mm long and 2-10 mm in diameter (Figure 3.1).

Figure 3.1. Thin branches of olive tree cuttings (olives 1)

The second shipment of olive tree cuttings (olives 2), was also only wood but in this case the branches were thicker than in the previous sample: 200 mm long and 40 mm in diameter (Figure 3.2). These branches had to be chopped before being ground. In the chopping process the bark was removed from the wood.

Figure 3.2. Thick branches of olive tree cuttings (olives 2)

When the thick branches sample came to an end, a new olive tree cuttings sample was received (olives 3). This biomass sample came from raking activities and consequently, apart from small branches (twigs), it was also composed of leaves, stones and soil (Figure 3.3).

Figure 3.3. Twigs and leaves from olive tree cuttings (olives 3)

This sample was pyrolyzed as received, but since soil and stones distort the pyrolysis results and in order to understand the influence of each component in the process, three new samples were derived from the olives 3 sample: twigs and leaves (without soil/stones) (olives 3.1), twigs (olives 3.2) and leaves (olives 3.3). To obtain the twigs-leaves mixture, the original whole sample was sieved to remove the soil and small stones by size, and big stones were manually separated. To obtain the twigs sample (olives 3.2) and leaves (olives 3.3) sample, olives 3 was manually separated into twigs and leaves.

The biomass sample coming from the energy crop was Eucalyptus wood. This sample came from chopped pre-crushed trees, and so the received material was very homogenous and pure (no soil and stones) (Figure 3.4).

Figure 3.4. Eucalyptus wood

A list of all the biomass samples used for the pyrolysis experiments of this thesis is presented below:

- Olives 1: thin branches
- Olives 2: thick branches
- Olives 3: twigs + leaves + soil
- Olives 3.1: twigs + leaves
- Olives 3.2: twigs derived from Olives 3
- Olives 3.3: leaves
- Eucalyptus *(Eucalyptus camaldulensis)*

3.2. Catalysts

Several catalysts have been used in this thesis for the catalytic treatment of the pyrolysis gases and vapors: two alumina modified catalysts prepared in our laboratories, two commercial zeolites and a nickel based commercial catalyst from Katalco Johnson Matthey. Zeolites have been also tested adding nickel to improve their performance. A description of all the catalysts is presented below.

3.2.1. Alumina modified catalysts: Ni/CeO_2-Al_2O_3 and Ni/ZrO_2-Al_2O_3

Two different alumina supported catalysts were prepared: a nickel catalyst supported on alumina modified with ceria (Ni/CeO_2-Al_2O_3) and a nickel catalyst supported on alumina modified with zirconia (Ni/ZrO_2-Al_2O_3).

The catalysts preparation method consists in the preparation of the catalysts in powder and after that, the powder is introduced into a ceramic monolith structure by means of an ethanol (C_2H_6O) solution. Hence, the first step is the preparation of the powdered catalysts. An aqueous solution consisting of 10 mL of water per gram of support (γ-alumina: BET surface area 255 $m^2\ g^{-1}$, pore volume 1.14 $cm^3\ g^{-1}$; Alfa Aesar) is used to dissolve the promoter (CeO_2 and ZrO_2). The amounts of the ceria or zirconia salt precursor is calculated to achieve a nominal content of 6 wt.% Ce ($Ce(NO_3)_3 \cdot 9H_2O$, 99.5 %; Alfa Aesar) and 8 wt.% Zr ($ZrO(NO_3)_2 \cdot xH_2O$, 99.99 %; Sigma Aldrich) for the cerium- and zirconium-doped γ-Al_2O_3 supports. Then, the supports are dried at 110 °C overnight and calcined at 800 °C for 2 h. The addition of Ni catalyst is carried out with a similar method ad that used to modify the support. The nickel nitrate precursor ($Ni(NO_3)_2 \cdot 6H_2O$, 99.99 %; Sigma Aldrich) is added to achieve an intended load of 13 wt.% of Ni. After impregnation of the support in the rota-vapor, the powder catalyst is dried at 110 °C overnight and calcined at 800 °C for 2 h.

3.2.2. Nickel based commercial catalyst

This catalyst is commercially named $KATALCO_{JM}$ 57-4Q and it is a non-alkalised nickel oxide catalyst (NiO 16 wt.%) on a calcium aluminate support (CaO/Al_2O_3). It is usually used in industry for steam reforming of natural gas, other light hydrocarbons and hydrogen rich streams (Katalco. Johnson Matthey, 2014).

3.2.3. Commercial zeolites

The two commercial zeolites used for the catalytic experiments were provided by Zeolyst International: ZSM-5 (CBV 5524G) and HY (CBV 400). Both catalysts were pretreated by calcination at 550 °C for 3 h for the stabilization of their textural and acidic properties. ZSM-5 was received in NH_4^+ cation form and during calcination, NH_3 was removed and the zeolite was transformed in HZSM5 with H^+ cation. Table 3.1 shows the properties of both zeolites.

Table 3.1. Textural and acidic properties of commercial zeolites (data from Zeolyst International)

Zeolite	SiO_2/Al_2O_3 mole ratio	Na_2O wt.%	Surface area ($m^2\ g^{-1}$)	Total acidity mmol $NH_3\ g^{-1}$
ZSM-5	50	0.05	425	0.50
HY	5.1	2.8	730	0.65

HZSM5 zeolite was used directly after calcination and also after adding 13 wt.% of nickel. HY zeolite was only used with 13 wt.% of nickel added. The method used for nickel addition is the same as that explained for the homemade alumina modified catalysts.

3.2.4. Placement of the catalyst in the reactor

The catalysts used in the pyrolysis experiments were used in vapor phase contact, therefore they acted only into the pyrolysis gases and vapors and not in the pyrolysis (carbonization) process itself. Therefore, they were placed in a second reactor placed after the pyrolysis reactor, called from now on catalytic reactor (Figure 3.6, page 50).

In order to place the catalysts in the reactor they were impregnated into monolithic cordierite ceramic carrier (400 cpsi corning) through the incipient wetness impregnation (IWI) method (IUPAC, 1995). The composition of the monolith is the following: 13.8 wt.% MgO, 30.8 wt.% of Al_2O_3 and 51.4 wt.% of SiO_2. These monoliths can be easily placed inside the catalytic reactor in the form of cylindrical blocks of 1 inch diameter (the reactor diameter) and 2 cm length. These blocks were obtained by cutting larger commercial monolith pieces.

The amount of catalyst impregnated in the monoliths was calculated to be around 1 wt.% of the pyrolysis vapors. The first thermal pyrolysis experiments generated around 75 wt.% of vapors, therefore, around 0.7 g of catalyst was impregnated into the monoliths.

For the introduction of the powder into the monolith, the catalyst powder is mixed with ethanol in the weight ratio of catalyst/ethanol 0.2. Cordierite monoliths are then immersed into the catalyst/ethanol slurry and dried at 100 °C. This procedure is repeated until the required weight of catalyst (≈0.7 g) is incorporated. The coated monoliths are then calcined at 800 °C for 2 h.

Figure 3.5 outlines the main facts of the catalysts preparation and impregnation method.

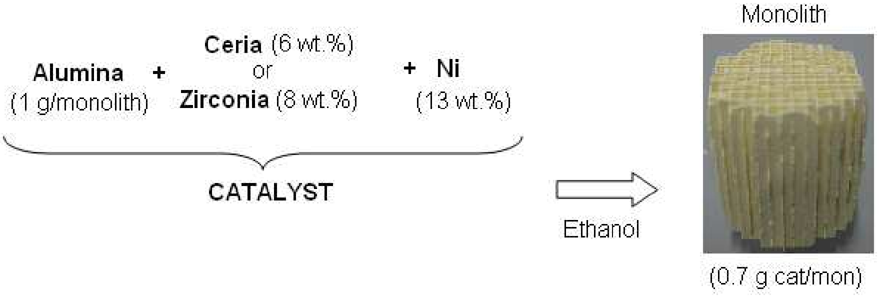


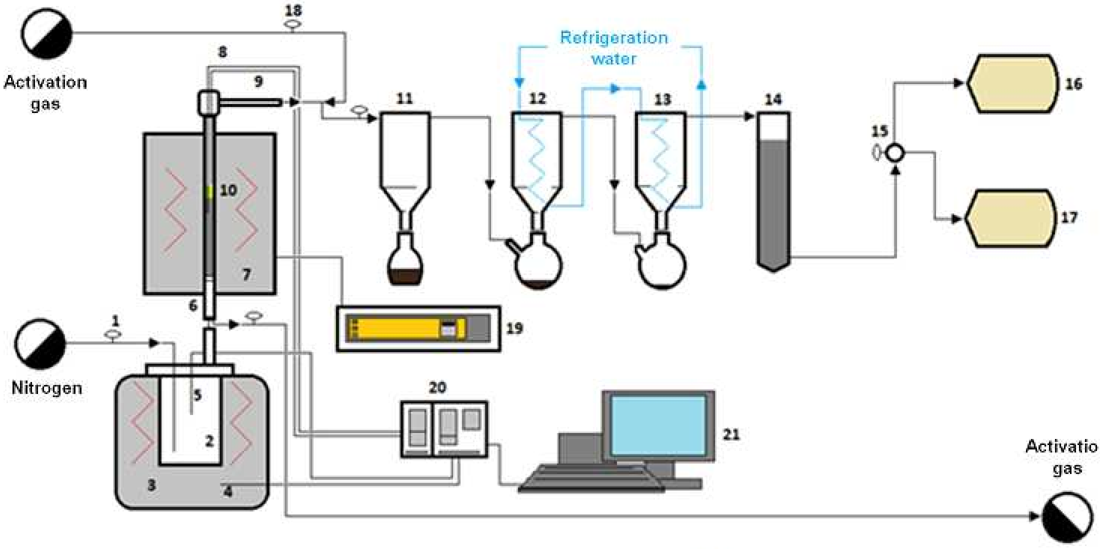
Figure 3.5. Catalysts preparation and impregnation scheme

3.3. Pyrolysis Experiments

Most of the pyrolysis experiments of this thesis were carried out in a slow pyrolysis plant of the faculty of Engineering of Bilbao. Additionally, some fast pyrolysis experiments were carried out for the sake of comparison and for a better understanding of the results. The fast pyrolysis experiments were performed in the Thünen Institute of Wood Research of Hamburg.

3.3.1. Slow pyrolysis experiments

The slow pyrolysis experiments were performed using a lab-scale plant consisting of two reactors connected in series and a vapors condensation and gas-liquid separation unit. The flow sheet of the experimental setup used for these experiments is presented in Figure 3.6. A photograph of the installation is shown in Figure 3.7.



1. Rotameter 1
2. Pyrolysis reactor
3. Lower electric furnace
4. Furnace thermocouple
5. Reactor thermocouple
6. Catalytic reactor
7. Up electric furnace
8. Thermocouple before monolith
9. Thermocouple after monolith
10. Monolith
11. Condenser 1
12. Condenser 2
13. Condenser 3
14. Activated carbon column
15. Valve
16. Gas bag 1
17. Gas bag 2
18. Rotameter 2
19. Up furnace temperature controller
20. Lower furnace temperature controller
21. PC

Figure 3.6. Flow sheet of the slow pyrolysis plant

In a typical run 100 g of sample with particle size < 10 mm are introduced in the first non stirred 3.5 L steel reactor where pyrolysis takes place. The reactor is heated at the desired heating rate to 750 °C and maintained there for 30 min. The temperature of this reactor is measured by a thermocouple which is placed in the middle of the reactor chamber. This implies that, although the reactor is an unstirred one and biomass has low thermal conductivity, the whole biomass sample reaches at least the preset temperature.

The second reactor is a vertical tubular reactor, where the pyrolysis vapors are treated at different temperatures either with or without catalyst. This reactor is a 309 stainless steel tube, 1 inch in diameter and 50 cm long. The tubular reactor is loaded with a charcoal bed, followed by the catalyst monolith. The charcoal bed is used in order to resemble a continuous process in which the pyrolysis vapors would be in contact with the pyrolysis solid (charcoal) which would be continuously produced. Besides, the charcoal bed makes pyrolysis vapors flow more slowly through the second reactor, and thus, makes them stay longer at the set temperature and in contact with the catalyst. Additionally, it has been reported that charcoal is catalytically active for reducing tars (Acharya et al., 2013; Agirre et al., 2013; El-Rub et al., 2008; Gilbert et al., 2009). The charcoal used in the experiments was charcoal produced in other previous similar pyrolysis experiments carried out in the Christian Doppler Laboratory for Optimization and Biomass Utilization in Heavy Metal Recycling from Leoben (Austria). The second tubular reactor is preheated to the desired temperature before the pyrolysis experiment starts.

The vapors leaving the second reactor flow to a series of water-cooled gas-liquid separators where part of the vapors are condensed and collected. Then, the remaining vapors go through an activated carbon column to ensure total elimination of condensable vapors before entering the Tedlar plastic bags used to collect the non-condensable gases which are afterwards analyzed by gas chromatography. All the apparatus are connected with silicone tubing. It has been proved by the authors that activated carbon does not modify significantly the C_1-C_6 hydrocarbon contents of the gases, while it does retain some condensable products which are not previously condensed and otherwise would condense inside the gas collecting plastic bags (de Marco et al., 2009). A continuous nitrogen flow of 775 mL min^{-1} is used during the whole experiment, in order to maintain the inert atmosphere and to carry the pyrolysis vapors through the installation. All the apparatus and tubing are weighed before and after the experiments.

The amount of solids and liquids generated after each experiment are weighed and the corresponding pyrolysis yields are calculated as weight percentage with respect to the initial biomass sample weight. The gas yield is determined by difference to 100. All the yield values presented in this study are the mean value of at least two experiments carried out with the same operating conditions. The experiments must not differ more than three points in the pyrolysis yields to take them into account.

Figure 3.7. Photograph of the slow pyrolysis plant

As it is usual in many industrial processes, metal-containing catalysts must be activated before the test. The activation process consists in a chemical reduction of the metal oxides added to the catalyst supports, in order to reduce them to metallic state, which is the catalytic active state. For this purpose an activating gas composed of 10 vol.% H_2, 10 vol.% N_2 and rest Ar is passed through the catalyst in the tubular reactor for 4 h at 800 °C before the experiment starts. This temperature was selected based on temperature programmed reduction (TPR) of the catalysts. Once the catalyst is activated, the two reactors are connected, nitrogen flows through both of them, the catalytic reactor is heated to the desired temperature, and then the pyrolysis experiment starts.

3.3.2. Fast pyrolysis experiments

A few fast pyrolysis experiments were performed for a better understanding of the results since the pyrolysis yields and above all the characteristics of the liquids obtained in the slow pyrolysis experiments were quite different to the data reported in the literature most of which correspond to fast pyrolysis experiments.

The fast pyrolysis experiments were performed using the experimental equipment shown in Figure 3.8 which belongs to the Thünen Institute of Wood Research of Hamburg. A photograph of the installation is shown in Figure 3.9. This equipment can be divided into a reaction section and a trapping section. The reaction section consists of a quartz tube reactor and a temperature programmable oven.

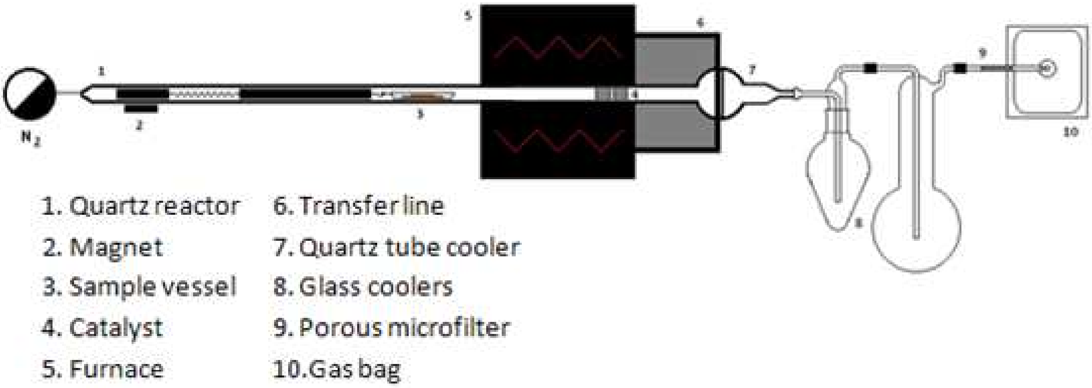


Figure 3.8. Flow sheet of the fast pyrolysis minireactor

The trapping section consists of a quartz tube cooler, which is directly coupled to the reactor, glass devices where the condensable products condense, and a porous micro-filter (pore size 0.2 µm) to enable to trap the aerosols.

The connection between both sections is heated to 400 °C to ensure that all volatile pyrolyzates can leave the reactor and condense afterwards on the glass devices at room temperature. All uncondensed product gases plus the carrier gas, are collected in a polyethylene gas bag.

At the beginning of each experiment the whole installation is purged thoroughly with the inert transport gas (N_2) at a flow rate of 60 mL min^{-1}, while the oven and the heating line are heated to the desired temperature. Next, the vessel with 200 mg of pulverized sample is manually introduced (by means of a magnet) into the oven to be pyrolyzed during 60 s.

After each experiment, the vessel (with the remaining biocoke) is pulled back outside the oven so that it can be cooled with pressurized air from the outside of the quartz tube.

In the catalytic experiments performed in the minireactor 4 mg of HZSM5 zeolite are placed between two quartz wool pieces inside the reactor, between the pyrolysis section and the trapping section. The catalyst amount used in these experiments is proportionally higher than that used in the slow pyrolysis plant because it was not possible to cover the whole cross section of the reactor with a lower amount of catalyst.

All the devices are weighed before and after the experiments in order to determine the corresponding solids and liquids yields, calculated as weight percentage with respect to the initial biomass sample weight. The gas yield is determined by difference to 100. All the yield values presented in the results and discussion section are the mean value of at least two equivalent experiments carried out with the same operating conditions and which did not differ more than three points in the pyrolysis yields.

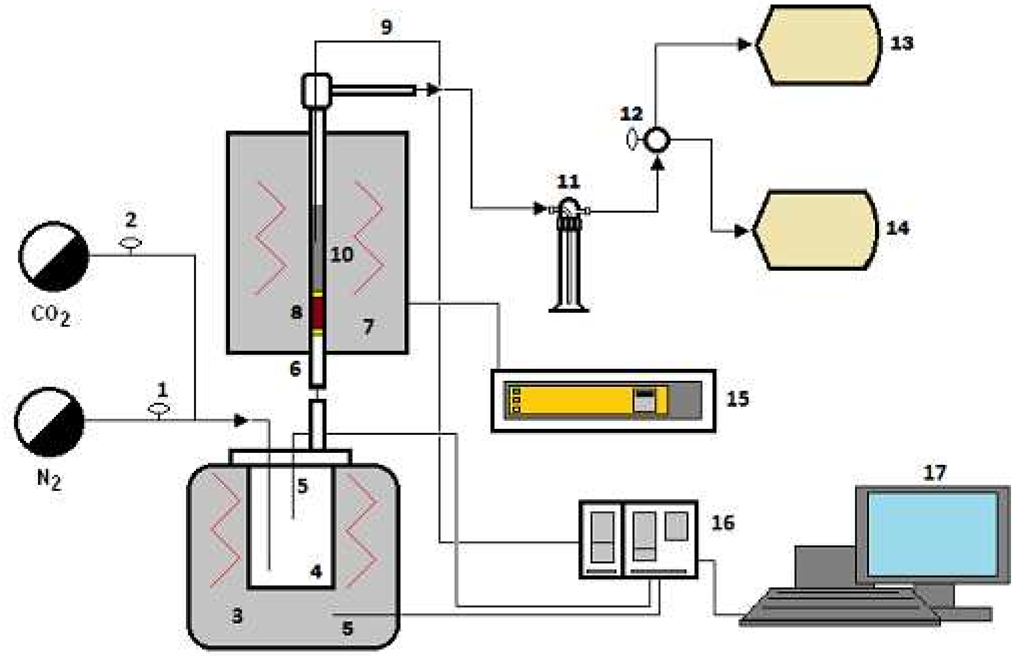
Figure 3.9. Photograph of the fast pyrolysis minireactor

3.4. Reactivity experiments

The biocoke reactivity experiments were carried out in the same installation used for the slow pyrolysis experiments but with some modifications. A flowsheer of the plant is shown in Figure 3.10 and a photograph in Figure 3.11.

This installation is composed of four units connected in series: (1) a first 3.5 L empty preheater, where the feed gases are pre-heated to 800 °C, (2) a second tubular reactor where the biocoke is placed in a column, (3) a dust trapper (empty bubbler) where the small solid particles swept by the CO_2 flow are retained, and (4) Tedlar plastic bags where all the gases are collected. All the apparatus are connected with silicone tubing.

One of the main differences between this installation and the one used for slow pyrolysis experiments is the second reactor. The tubular reactor used for the reactivity experiments is 1 inch in diameter and 60 cm long and made of INCONEL alloy 601, a material able to work at temperatures as high as 1200 °C, while in the pyrolysis experiments was a 309 stainless steel reactor.



1. Rotameter 1
2. Rotameter 2
3. Lower electric furnace
4. Preheater
5. Thermocouples
6. Tubular reactor
7. Up electric furnace
8. Silicon carbide bed
9. Tubular reactor thermocouple
10. Biochar
11. Dust trapper
12. Valve
13. Gas bag
14. Gas bag
15. Up furnace temperature controller
16. Lower furnace temperature controller
17. PC

Figure 3.10. Flow sheet of the reactivity plant

While both reactors are heated to the desired temperature (800 °C and 1100 °C respectively), nitrogen flows through the system. Once the operation temperature in the tubular reactor is reached (1100 °C) the gas is changed to carbon dioxide and the experiment starts. CO_2 goes first through the preheater, where is heated to 800 °C and flows to the tubular reactor connected in series. Here, it reacts with the biocoke placed in the column taking place Boudouard reaction. After two hours at 1100 °C, the system is cooled down with nitrogen. The generated gases are collected in plastic bags during the whole reaction time. All the devices (sample, reactor, dust trapper, valve, silicone tubing) are weighed before and after the experiments.

Figure 3.11. Photograph of the reactivity plant

The design and experimental methodology used are based on ASTM D 5341-99 standard. This test method is designed to evaluate the reactivity of coke for blast furnaces. When coke lumps descend in a blast furnace, they are subjected to reaction with countercurrent CO_2 and to abrasion as they rub together and against the walls of the furnace. On the one hand, lumps are physically weakened and, on the other hand, they chemically react with CO_2, producing an excess of fines that can decrease burden permeability and may result in a lost of hot metal production. Although the using of wood derived biocoke in blast furnaces is not the objective of this thesis, reactivity is an interesting parameter in order to know the behavior of biocoke in CO_2-rich environments (typical of metal production processes).

Two metallurgical parameters, coke reactivity index (CRI) and R factor, were calculated for each of the reactivity experiments. Both measures are based in the Boudouard reaction ($C + CO_2 \leftrightarrow 2CO$) where the carbon reacts with CO_2 yielding CO. The extent of this reaction depends on the reactivity of the sample.

CRI is the measurement of the mass loss after the reactivity test and it is the chemical degree of conversion usually used in metallurgy. The sample must be weighed before and after the reactivity test and the CRI is calculated with the following formula:

$$\mathrm{CRI}_{\mathrm{sample}}\,(\%) = \frac{\mathrm{initial\ weight} - \mathrm{final\ weight}}{\mathrm{initial\ weight}} * 100 \qquad \text{Eq. 3.1}$$

The R factor represents the amount of CO in the gas stream after reaction with respect to the originally existing CO_2. For its calculation, the areas below the GC curves of CO and CO_2 with respect to time must be integrated. The R factor is calculated with the following formula:

$$\mathrm{R\ factor}\,(\%) = \frac{\mathrm{CO}}{\mathrm{CO_2} + {}^{\mathrm{CO}}/_{2}} * 100 \qquad \text{Eq. 3.2}$$

High CRI values indicate a high reactivity of the sample, while high R factor values denote a high conversion of coke into CO, and therefore, a high stoichiometric consume of CO_2. Both values are higher as higher is the reactivity of the material.

The objective is to come to an agreement between the reactivity of the reducer and the decomposition of it. That is, the material must be reactive enough to generate CO, but it should not be so reactive that it completely disappears at the beginning of the process.

3.5. Characterization and Analytical Techniques

All the initial samples, as well as all the products obtained in the pyrolysis experiments (solids, gases and liquids) were thoroughly characterized. The catalysts and commercial reducing agents were also characterized.

3.5.1. Characterization of the Biomass Samples

For the biomass characterization, a small fraction of each sample was ground to a particle size under 2 mm in a RETSCH SM 2000 cutting mill.

3.5.1.1. Ultimate Analysis (C, H, N, S, Cl)

Ultimate analysis of the biomass samples were carried out including carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and chlorine (Cl). The percentages of C, H and N were determined with a LECO TruSpec CHN analyzer, which complies with the ASTM D5373 standard for ultimate analysis of fuels. The analysis consists in the complete and instantaneous oxidation of the sample by combustion with pure oxygen at 950 °C. The main products formed are CO_2, H_2O and NO_x, which are swept away via a carrier gas (oxygen for CO_2 and H_2O, and helium for the NO_x) and selectively separated in specific columns. CO_2 and H_2O are measured by specific infrared detectors that use pure oxygen as reference value. NO_x are reduced to elemental nitrogen, which is measured by a thermal conductivity detector that uses helium as reference value. In a normal analysis, 0.1 g of sample is placed in a tin cup that is then placed in the sampler which introduces it directly into the combustion furnace.

For sulfur measurement, a LECO TruSpec S analyzer was used; this analyzer complies with the ASTM D1552 and D4239 standards for ultimate analysis of fuels. In this case, the samples are placed in ceramic crucibles and burned in pure oxygen at 1350 °C; the sulfur content is determined by measuring by the amount of SO_2 in an infrared detector. The initial quantity of sample used is 0.1 g.

The percentage of chlorine was determined by using method 5050 of the United State Environmental Protection Agency (EPA) for the determination of total chlorine in solid waste, virgin and used oils, fuels and related material. The method consists in oxidizing the sample in a calorimeter (which is described in section 3.5.1.3) and collecting the generated gases, which include hydrogen chloride, in a basic solution that is placed with the sample inside the calorimetric bomb. The chlorine from the sample, which has been transformed into HCl during combustion, remains in the form of dissolved chloride in the basic solution. This solution is later analyzed to determine the amount of chlorides in the solution. Once the concentration of chlorides in the basic solution is determined, it is necessary to extrapolate this value to the weight of the sample that was placed inside the calorimetric bomb to determine the percentage of chlorine.

The weight of the initial biomass samples for the determination of chlorine was 0.5 g. The basic solution used was 0.25 M NaOH, prepared from a 50 wt.% liquid NaOH solution from the J.T. Baker Company. To determine the amount of chlorides in this solution, a DIONEX ICS-3000 ionic chromatograph was used. The details of the method used can be seen in Table 3.2.

Table 3.2. Method used in the DIONEX ICS-3000 ionic chromatograph

Column:	Dionex IonPac AS19
Guard column:	Dionex IonPac AG19
Eluent:	NaOH (17.5 mM)
Flow rate:	1.0 mL min^{-1}
Oven temperature:	30 °C
Cell temperature:	35 °C
Injection volume:	25 µL
Suppressor:	Dionex ASRS-ULTRA II 4-mm
Suppressor intensity:	44 mA
Data collection rate:	5 Hz s^{-1}

The eluent for the ionic chromatograph was also prepared from the J.T. Baker NaOH solution. In order to quantify chloride in the basic solutions obtained, the ionic chromatograph was calibrated using a commercial salt of sodium chloride from Fluka of ≥99.5 % purity. Furthermore, the efficiency of the method itself (percentage of chlorine recovered after all of the described analytical steps) was highly scrutinized and quantified by applying the method to a standard oil sample of known chlorine content, IKA AOD 1.11 control standard oil of 0.98 ± 0.05 wt.% chlorine content.

3.5.1.2. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis and proximate analysis of the biomass samples were carried out. Two thermobalances were used: METTLER TOLEDO TGA/SDTA851^e and LECO TGA-500. In both equipments, the sample is placed in a crucible that rests on a balance inside the furnace, where different atmospheres can be used. The weight loss of the material as a function of temperature and atmosphere (inert or reactive) is continuously measured. In the case of the METTLER TOLEDO TGA/SDTA851^e thermobalance, these measurements are continuously recorded and can be plotted. The main difference between these equipments lies in the sample size. The LECO TGA-500 allows macro sample analysis (up to 2 g samples) and is used when the sample representativeness is critical, while the METTLER TOLEDO TGA/SDTA851^e is more precise but requires samples < 50 mg. Both thermobalances employed and the parameters studied are described at length in the following sections.

3.5.1.2.1. Thermal Characterization

Thermal characterization of the biomass samples was carried out with the METTLER TOLEDO TGA/SDTA851^e thermobalance. For each thermal characterization run, a 10 mg sample was used. It was heated at 3 and 20 °C min^{-1} from room temperature to 750 °C. To ensure an inert atmosphere during decomposition, 50 mL min^{-1} of N_2 was pumped into the furnace. The temperatures at which the sample underwent the maximum rate of decomposition were determined from the derivative thermogravimetric curve (DTG).

3.5.1.2.2. Proximate Analysis

Proximate analysis includes the determination of moisture, volatile matter, ash and fixed carbon, and was carried out with the LECO TGA-500 thermobalance, which follows ASTM D3173-87, ASTM D3175-89 and ASTM D3174-97 standards respectively. Moisture, volatile matter and ash are sequentially and automatically determined as a function of weight loss in the conditions indicated in Table 3.3 while the fixed carbon content is determined by difference to 100.

Table 3.3. Method for the determination of moisture, volatile matter and ash

ASTM Standard	Property	T (°C)	Time (min)	Atmosphere
D3173-87	Moisture	106	Until constant weight	N_2
D3175-89	Volatile matter	950	7	N_2
D3174-97	Ash	750	Until constant weight	O_2

For this analysis, around 1 g of sample was used for each run.

3.5.1.3. Higher Heating Value (HHV)

The HHV of the biomass samples was determined using the LECO AC-500 automatic calorimeter, which combusts the samples in a calorimetric bomb complying with the ASTM D3286 standard. This technique is based on the combustion of the sample with pure oxygen in a high-pressure container (calorimetric bomb) situated inside a water bath. The heat released from the combustion is measured as the change in temperature of the water that surrounds the bomb and this change is proportional to the heating value. The samples are placed inside a crucible in the bomb, where the ash will remain after combustion. The sample size for these tests was 0.5 g.

3.5.1.4. Determination of the Extractives, Cellulose, Hemicellulose and Lignin contents

The determination of extractives, cellulose, hemicellulose and lignin content in biomass samples was carried out by the *Centro de Energías Renovables* (CENER) located in Pamplona (Navarre – Spain), which is specialized in applied research and development and promotion of renewable energy technology. With the aim of properly understanding the experimental results, the main principles of this determination are described below.

The determination of extractives material of biomass (non-chemical bound components of biomass) was carried out following the NREL/TP-510-42619 standard. A two-step extraction process is used to remove water soluble and ethanol soluble material. Water soluble materials may include inorganic material, non-structural sugars, and nitrogenous material, among others. Inorganic material in the water soluble material may come from both the biomass and any soluble material that is associated with the biomass, such as soil or fertilizer. Ethanol soluble material includes chlorophyll, waxes, and other minor components.

The determination of cellulose, hemicellulose and lignin content was carried out following the NREL/TP-510-42618 standard.

Cellulose, hemicellulose and lignin make up a major portion of biomass samples. These constituents must be measured as part of a comprehensive biomass analysis. Cellulose and hemicellulose can be structural or non-structural carbohydrates. The structural ones are bound in the matrix of the biomass, while non-structural ones can be removed using extraction or washing steps.

The procedure used is only suitable for samples from which extractives have already been removed. This procedure uses a two-step acid hydrolysis to fractionate the biomass into forms that are more easily quantified. The lignin is fractionated into acid insoluble material and acid soluble material. The acid insoluble material may also include ash and protein. The acid soluble lignin is measured by UV-Vis spectroscopy. During the mentioned two-step hydrolysis, the polymeric carbohydrates (cellulose and hemicellulose) are hydrolyzed into the monomeric forms, which are soluble in the hydrolysis liquid. They are then measured by HPLC.

3.5.1.5. Py-GC/MS-FID characterization

The biomass samples were also characterized by micropyrolysis coupled to a gas chromatogram. The Py-GC/MS-FID analyses were carried out in the Thünen Institute of Wood Research of Hamburg.

The equipment used consisted of a Frontier Lab Micro furnace Doubleshot Pyrolyzer Py-2020iD with an Autosampler AS-1020 E and an Agilent GC 6890 N chromatograph equipped with a flame ionization detector (FID) and a mass spectrometry (MS) detector. The FID signal was used for quantification and the MS signal was used for identification. The chromatograph was fitted with a Varian VF-1701ms (Agilent) fused-silica capillary column (60 m × 0.25 mm i.d., 0.25 µm film thickness) and an Agilent 5973c mass selective detector.

Approximately 90 µg of powered biomass sample (Retsch MM 2 Ball Mill) were weighed into steel cups (Eco-cup, Frontier Laboratories) and analyzed on the system. Two replicates per feedstock were carried out and the average values of both analyses are presented as result. Pyrolysis was carried out at 750 °C with an interface at the temperature of 360 °C. The GC oven conditions are presented in Table 3.4. The compounds were identified by comparing their mass spectra profiles to those in the National Institute Standards Technology (NIST) and in-house developed libraries, using MassFinder software.

Table 3.4. Conditions of the Py-GC/MS-FID chromatograph

Column:	Varian VF 1701ms
Carrier gas:	He
Carrier gas flow per column:	2.0 mL min^{-1}
Injector temperature:	250 °C
Injection volume:	split 15:1 for GC split 1:1 for MS-FID
Detector temperature (Source/Quad):	230 °C / 150 °C
Acquisition Mode:	Scan
Initial temperature/time:	45 °C / 4 min
Oven program:	3 °C/min to 280 °C and maintained 10 min
Run time:	102.33 min
Scan parameters	
Low mass/High mass:	15/550 a.m.u.

3.5.2. Characterization of the Pyrolysis Solids (Biocokes)

After each run, the pyrolysis solids were collected and characterized according to the following techniques and methods.

3.5.2.1. Ultimate Analysis (C, H, N)

The ultimate analysis of the pyrolysis solids was done using the equipment and methods described in section 3.5.1.1. The procedure to conduct the ultimate analysis of the pyrolysis solids is exactly the same as the procedure described in the previously mentioned section. The amount of sample used for the CHN analysis was 0.1 g.

3.5.2.2. Thermogravimetric Analysis (TGA)

The proximate analysis of the pyrolysis solids was conducted using the LECO TGA-500 thermobalance described in section 3.5.1.2.2. In this same section an explanation of the method for the analysis can be found. The sample amount used was 1 g.

3.5.2.3. Higher Heating Value (HHV)

The higher heating value of the pyrolysis solids was determined using the LECO AC-500 automatic calorimeter described in section 3.5.1.3. The operational procedure is identical to that described in the mentioned section. Samples of 0.5 g were analyzed.

3.5.2.4. Textural Characterization

The textural characterization of the biocoke samples was carried out by the *Instituto Nacional del Carbón* (INCAR) located in Oviedo (Asturias – Spain), which belongs to the *Consejo Superior de Investigaciones Científicas* (CSIC).

Three determinations were performed: real density, N_2 adsorption and CO_2 adsorption. All the biocokes were degassed at 120 °C for 18 h.

The determination of the **real density** of the samples was performed in an AccuPyc 1330T Micromeritics equipment, using helium (He) 99.9995 % quality as analysis gas. The system consists of two chambers filled with He at a controlled temperature of 35 °C. The sample chamber was previously calibrated with two steel balls. Once calibrated, a weighed amount of substance was introduced. To eliminate the possible contamination by condensable vapors it was washed with pressurized He several times and then a known amount of He was introduced in the reserve chamber, which expanded to the sample chamber until the pressures were balanced. Since the initial and equilibrium pressure and the volume of the reserve chamber were known, the volume occupied by the sample could be calculated.

Nitrogen adsorption at -196 °C was performed in a Micromeritis ASAP 2420 (Accelerated Surface Area and Porosimetry System). The determination of specific surface areas of solids is usually performed with the analysis of adsorption-desorption isotherms of N_2 at -196 °C, using the Brunauer-Emmett-Teller (BET) method in the appropriate range of relative pressures. However, it is difficult to obtain reliable results with N_2 adsorption methods with carbonaceous materials, since this measurement is carried out at -196 °C and at such low temperature N_2 has diffusion problems in narrow micropores. Therefore, it may take a long time to reach the thermodynamic adsorption equilibrium, it may last (if reached) even weeks.

CO_2 adsorption was performed at 0 °C in a Quantachrome Nova 4200 apparatus. The degasification and CO_2 adsorption conditions are presented in Table 3.5.

Table 3.5. Conditions of degasification and CO_2 adsorption

Samples degasification time and temperature:	120 °C / 18 h
Analysis temperature:	0 °C
P_0:	24142 mmHg
Pressure tolerance:	0.1
Equilibrium time during adsorption:	300 s
Time-out during adsorption:	2400 s

CO_2 adsorption is a widely used method to analyze materials with narrow micropores, as is the case of carbonized materials. The particularity of CO_2 is that the analysis is done at 0 °C, a much higher temperature than in the case of N_2, therefore, it has a higher kinetic energy, which does not present problems in narrow pore size distribution and balance is quickly reached. The isotherms were analyzed using the Dubinin-Radushkevich equation (DR) for calculating the micropores volume ($cm^3\ g^{-1}$) and the equivalent micropore surface area ($m^2\ g^{-1}$). Adsorption in the micropores takes place by a filling mechanism and not by multilayer adsorption. This implies that the area obtained by the DR method is not the surface area of the sample, as in the case of the area obtained by the BET equation. The area correspond to the area that the adsorbed molecules in the micropores would cover (the micropores volume calculated by DR is transformed to number of gas molecules and is multiplied by the area occupied by a molecule of CO_2). The pore size distribution is calculated using the Non-Local Density Functional Theory (NL-DFT) available in the software of the equipment.

3.5.3. Characterization of the Pyrolysis Gases

The characterization of pyrolysis gases consisted on the determination of their composition and higher heating value (HHV). The composition was determined by means of chromatography, while the HHV was calculated theoretically. Two different chromatographs have been used, one for the gases produced in the slow pyrolysis experiments and the other one for the gases produced in the fast pyrolysis runs, since these two types of experiments were carried out in different research centers.

3.5.3.1. Chromatography (GC/TCD-FID) for slow pyrolysis gases

Chromatography of the pyrolysis gases was carried out with an AGILENT 7890A gas chromatograph (GC) equipped with two independent detectors: a FID and a thermal conductivity detector (TCD). The compounds analyzed were H_2, CO, CO_2, alkanes up to C_6 and alkenes up to C_6. For the simultaneous separation and determination of this complex mixture of gas compounds, the chromatograph has two columns interconnected with each other and with the detectors through a system of valves. This creates a multidimensional chromatography system in a single furnace. In Table

3.6 the columns used and the conditions maintained in the analysis method of the pyrolysis gases are detailed.

In the first column (molecular sieve column: HP-MOLISIEVE), H_2, CO, N_2 and O_2 are separated out, while the rest of the compounds are separated in the second column (HP-PLOT Q). H_2, CO, CO_2, N_2 and O_2 are detected in the TCD, while the hydrocarbons are detected in the FID. The gases were analyzed with He as a carrier gas.

Table 3.6. Method utilized in the GC/TCD-FID analysis

Columns:	HP-MOLISIEVE HP-PLOT Q
Carrier gas:	He
Carrier gas flow per column:	5 mL min^{-1}
Initial temperature/time:	40 °C / 9.5 min
Oven program:	20 °C min^{-1} to 100 °C and maintained 2.5 min 10 °C min^{-1} to 180 °C and maintained 0 min 20 °C min^{-1} to 200 °C and maintained 4 min
Run time:	28 min
Injector temperature:	150 °C
TCD detector temperature:	250 °C
FID detector temperature:	300 °C

To quantify these compounds, four standard samples were prepared by the Air Liquide Company according to the specifications indicated in Table 3.7, Table 3.8, Table 3.9, Table 3.10 and Table 3.11.

Table 3.7. Concentrations of the H_2 and N_2 standard sample

Component	Concentration (vol.%)
H_2	10
N_2	10
Ar	rest

Table 3.8. Concentrations of the CO and CO_2 standard sample

Component	Concentration (vol.%)
CO	15
CO_2	7
N_2	rest

Table 3.9. Concentrations of the alkane standard sample

Component	Concentration (vol.%)
CH_4	3
C_2H_6	2
C_3H_8	1
C_4H_{10}	1000 ppm
C_5H_{12}	1000 ppm
C_6H_{14}	1000 ppm
N_2	rest

Table 3.10. Concentrations of the alkene standard sample

Component	Concentration (vol.%)
C_2H_6	1
C_3H_6	1
C_4H_8	1
C_5H_{10}	1
C_6H_{12}	1
N_2	rest

Table 3.11. Concentrations of the CO_2 and H_2 standard sample

Component	Concentration (vol.%)
H_2	20
CO_2	80

3.5.3.2. Chromatography (GC/MS-FID) for fast pyrolysis gases

The pyrolysis gases produced in fast pyrolysis were analyzed in an Agilent GC 6890 N chromatograph equipped with a FID detector. Gases were separated in an Agilent CP PoraPlot Q 7554 (25 m x 0.53 mm x 20 μm) column. After the chromatographic separation the gas was hydrogenated in a methanizer. CO and CO_2 were hydrogenated to methane, and hence it was detectable with FID. This chromatogram detected CO, CO_2 and hydrocarbons in the range of C_1-C_6. Hydrogen was not detectable. The chromatogram oven conditions are presented in Table 3.12.

Table 3.12. Method utilized in the GC/MS-FID analysis

Columns:	CP PoraPlot Q 7554
Carrier gas:	He
Carrier gas flow per column:	4.3 mL min^{-1}
Initial temperature/time:	30 °C / 7.5 min
Oven program:	20 °C min^{-1} to 175 °C and maintained 22 min
Run time:	36.75 min
Injector temperature:	60 °C
FID detector temperature:	300 °C

3.5.3.3. Calculation of Higher Heating Value (HHV)

The HHV of pyrolysis gases is a theoretical calculation based on the composition determined by chromatography and the higher heating values of the individual gas components at 20 °C and 1 bar (standard laboratory conditions). The heats of combustion used for this calculation are listed on Table 3.13.

Table 3.13. HHV of the individual components of the pyrolysis gas (Perry et al., 1992)

Component	HHV (MJ Nm $^{-3}$)
Hydrogen	11.69
Carbon monoxide	11.58
Methane	36.44
Ethane	63.84
Propane	90.85
n-Butane	117.80
n-Pentane	144.71
n-Hexane	171.67
Ethene	57.74
Propene	84.24
1-Butene	111.26
1-Pentene	138.15
1-Hexene	161.01

3.5.4. Characterization of the Pyrolysis Liquids

The pyrolysis liquids are frequently composed of two phases (organic phase and aqueous phase). In this thesis, the amount of the organic phase was normally rather small, and for this reason was only just quantified and occasionally analyzed by gas chromatography-mass spectrometry (GC/MS). The aqueous phase was always analyzed by the GC/MS, and the CHN analysis was also performed. The techniques and methods employed in the characterization of the pyrolysis liquids are described in the following sections.

3.5.4.1. Phase Separation

The separation of the organic and the aqueous phase was carried out by just pouring the aqueous phase out of the collecting devices because the scarce organic phase obtained was sticked to the glass devices and could not be directly collected.

3.5.4.2. Chromatography (GC/MS) for slow pyrolysis liquids

The composition of the organic and aqueous phases of pyrolysis liquids were determined using a gas chromatograph coupled to a mass detector (GC/MS), AGILENT 6890 and AGILENT 5973 respectively. Analysis quality (99.9% purity) tetrahydrofuran (THF) was used as solvent and was supplied by Panreac. The samples to solvent ratios were 1/100 ratio for the organic phase samples and 1/10 for the aqueous phase samples. The selected solvent guaranteed the complete dissolution of the sample and at the same time did not “hide” significant compounds that appear during the period of time when the detector is intentionally disconnected because it is when the solvent is eluted. THF (C_4H_8O), besides being a good solvent of biomass derived compounds, is a relatively small molecule that, with the method used is quickly eluted and therefore practically does not disturb the chromatographic analysis.

Two methods were used to analyze the pyrolysis liquids named aqueo-thf for aqueous liquids and org-thf for organic liquids. The aqueo-thf method determines the amount of water in the aqueous liquids together with some other compounds. The org-thf method is the method used for the organic liquids and it identifies all the compounds of this fraction. The conditions of the chromatograph are presented in Table 3.14, and the conditions of the aqueo-thf and org-thf methods are presented in Table 3.15 and Table 3.16 respectively.

Table 3.14. Conditions utilized in the GC-MS analysis

Column:	Agilent 123-3262
Carrier gas:	He
Carrier gas flow per column:	2.3 mL min^{-1}
Injector temperature:	250 °C
Injection volume:	0.5 µL (split 75:1)
Detector temperature (Source/Quad):	230 °C / 150 °C
Acquisition Mode:	Scan

Table 3.15. Conditions of aqueo-thf method of GC/MS

Initial temperature/time:	40 °C / 5 min
Oven program:	8 °C min^{-1} to 150 °C and maintained 5 min
	8 °C min^{-1} to 240 °C and maintained 4 min
Final temperature/time:	240 °C / 5 min
Run time:	39 min
Scan parameters	
Start time/Low mass - High mass:	0 min / 10 - 80 a.m.u
	10 min / 30 - 200 a.m.u.

Table 3.16. Conditions of org-thf method of GC/MS

Initial temperature/time:	40 °C / 5 min
Oven program:	8 °C min^{-1} to 150 °C and maintained 5 min
	8 °C min^{-1} to 240 °C and maintained 10 min
Final temperature/time:	240 °C / 10 min
Run time:	45 min
Scan parameters	
Start time/Low mass - High mass:	0 min / 10 - 120 a.m.u
	10 min / 50 - 350 a.m.u.

3.5.4.3. Ultimate Analysis (C, H, N)

The ultimate analysis of the pyrolysis aqueous liquids was carried out using the equipment and method described in section 3.5.1.1. The amount of sample used was again 0.1 g. The operation procedure is similar to that previously explained, but in this case, since the sample is a liquid, it is introduced in the tin cup absorbed in a solid named Com-Aid, provided by LECO, which does not disturb the CHN results.

3.5.5. Characterization of the Catalysts

The BET surface area, total pore and micropore volume and average pore diameter of the catalysts were determined by N_2 adsorption/desorption using an Autosorb-1C (Quantachrome) automatic instrument. Prior to the analysis the samples were degassed for 12 h at 150 °C. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. Total pore volume and average pore diameter were estimated using the Barrett-Joyner-Halenda (BJH) method (desorption data), while micropore volume was estimated using the Dubinin-Radushkevich (DR) method.

The catalysts were chemically analyzed by Inductively Coupled Plasma Atomic Emission System (ICP-AES) using a Perkin-Elmer Optima 2000-DV instrument. 50 mg of catalyst were first properly dissolved using a digester (Milestone ETHOS 1) with a mixture of

HNO_3:HCl:HF = 3:2:3 for the determination of nickel and zirconium. With this method it was not possible to detect any cerium, due to CeF_2 precipitate formation. For the quantification of this metal, a solution that consisted of HNO_3:H_2O_2 = 1:4 was used. Both disintegrations were carried out at 190 °C, and thereafter analyzed by ICP-AES instrument. The purity and commercial brand of the acids used for the digestions are the following: HNO_3 65 %, Panreac; HCl 37 %, Panreac; HF 48 % EMSURE®; H_2O_2 30 %, Sigma Aldrich.

Temperature-programmed reduction (TPR) was performed. With TPR the reducible species formed during calcination step of the catalysts, and the reduction temperature were determined. The measurements were carried out using an Autosorb 1C-TCD (Quantachrome) automatic apparatus, equipped with a thermal conductivity detector. A continuous flow of 5 vol.% H_2/Ar (40 mL min^{-1}) was passed over 500 mg of calcined catalyst powder. The temperature was increased from room temperature to 1000 °C at a rate of 10 °C min^{-1}. The sample was previously outgassed at 300 °C during 30 minutes.

3.5.6. Characterization of the Commercial Reducing Agents

The three commercial reducers provided by Befesa Zinc Aser S.A. Company, located in Erandio (Biscay – Spain), (metallurgical coke, petroleum coke and anthracite) were characterized following the same procedure used for pyrolysis solids (section 3.5.2, page 65), consisting in ultimate analysis (C, H, N), proximate analysis by TGA, HHV and textural properties measurement.

CHAPTER 4

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

In this chapter all the results obtained in this thesis are presented including the pyrolysis yields as well as the characterization results of both, the biomass samples and the pyrolysis products.

This chapter has been organized in six sections: the first one deals with the characterization of the biomass samples including proximate, ultimate and constituents analyses, thermal characterization and Py-GC/MS-FID. The second one concerns the characterization of the catalysts used for upgrading the pyrolysis vapors.

The next three sections are devoted to the pyrolysis experiments. In the first one the influence of different operating conditions and reactor configurations is analyzed in order to select the appropriate operating conditions for biocoke production and pyrolysis vapors upgrading. The second one is devoted to the study of the effects of catalysts, and the third one to compare the results obtained with different types of biomass in order to analyze the influence of the characteristics of the raw biomass in the pyrolysis products.

Finally, the sixth and last section is devoted to study the suitability of pyrolysis solids as reducing agents comparing them with commercial reducing agents used in metallurgical industrial processes.

4.1. Characterization of the Biomass Samples

The seven lignocellulosic biomass samples used in the pyrolysis experiments were thoroughly characterized using the analytical techniques explained in section 3.5.1 (page 59).

4.1.1. Proximate, Ultimate and Constituents Analyses

The proximate analysis (as received basis) and ultimate analysis (dry and ash free basis), as well as the HHV (as received basis) and constituents composition (dry basis) of the seven biomass samples studied in this thesis were performed following the procedures explained in sections 3.5.1.1 (page 59), 3.5.1.2.2 (page 61), 3.5.1.3 (page 62) and 3.5.1.4 (page 62). All the results are presented in Table 4.1. The ultimate analysis includes C, H, N and others (by difference). It has to be mentioned that S and Cl analyses were also carried out but the contents were very low ($S < 0.01$ wt.% and $Cl < 0.1$ wt.%) and under the detection limits of the analytical equipment. Therefore, they have not been included in Table 4.1.

It can be observed that the eucalyptus and olive tree cuttings derived samples are quite different. The eucalyptus sample has more moisture, less volatiles and more fixed carbon. Concerning the ultimate analysis the eucalyptus sample has more C %, less H % and less N % than any of the olive samples, and as a consequence has lower H/C and higher C/N ratios than the olive samples. The lower the C/N ratio, the higher the degradability of the organic matter, so the results indicate that eucalyptus is more resistant to biodegradation than the olive samples.

Concerning the constituents' composition, Table 4.1 shows that the eucalyptus sample has greater lignin content and lower hemicellulose content than the olive samples. This can be attributed to the fact that eucalyptus is a softwood while olive is a hardwood. It has been reported that, as a general rule, softwoods have 23-33 wt.% lignin while hardwoods have 16-25 wt.%, and that hardwood contain more hemicellulose than softwood (Mohan et al., 2006), which is in agreement with the results obtained in this thesis. With respect to extractives, it has been reported that they are more abundant in bark than in inner wood parts (Räisänen and Athanassiadis, 2013). This justifies that the eucalyptus sample as well as the olive thick branches, which have fewer bark/wood ratio, have less extractives than olives thin branches, twigs + leaves and twigs which are thinner parts of the olive plant and therefore have higher bark/wood ratio.

Table 4.1. Proximate, ultimate and constituents analyses of the biomass samples pyrolyzed

(weight %)		**Olives 1** Thin Branches	**Olives 2** Thick Branches	**Olives 3** Twigs + Leaves + Soil	**Olives 3.1** Twigs + Leaves	**Olives 3.2** Twigs	**Olives 3.3** Leaves	**Eucalyptus**
Proximate analysis (ar)	Moisture	8.8	8.9	8.4	9.1	8.9	6.8	11.4
	Volatile matter	74.3	75.4	68.7	73.6	73.8	75.3	69.7
	Ash	2.1	0.8	10.3	2.4	2.0	4.9	2.1
	Fixed carbon[1]	14.8	14.9	12.7	14.9	15.3	13.0	16.8
Ultimate analysis (daf)	C	49.4	48.2	51.0	49.4	48.8	51.6	52.7
	H	6.2	6.0	6.6	6.3	6.2	6.6	3.7
	N	0.3	0.2	1.0	0.7	0.6	1.6	0.1
	Others[1]	44.1	45.6	41.4	43.6	44.4	40.2	43.5
HHV (ar) (MJ kg^{-1})		16.1	17.3	16.0	17.4	17.2	18.4	16.6
H/C atomic ratio		1.5	1.5	1.6	1.5	1.5	1.5	0.8
C/N weight ratio		146.7	217.5	51.9	72.8	87.0	32.6	455.0
Constituents (dry)	Extractives	12.1	8.4	n.d.	19.8	16.3	41.0	8.1
	Cellulose	32.1	37.3	n.d.	27.7	30.8	12.8	37.6
	Hemicellulose	19.3	20.9	n.d.	16.6	18.6	7.1	13.3
	Lignin	18.9	19.1	n.d.	17.3	17.1	14.1	28.6
	Ash	2.3	0.9	11.2	2.6	2.2	5.3	2.4
	Others[1]	15.3	13.4	n.d.	16.0	15.0	19.7	10.0

[1] *By difference; n.d.: not determined; ar: as received; daf: dry and ash free*

Constituents analysis of eucalyptus samples reported in the literature (Carrier et al., 2013; Elyounssi et al., 2012) show discrepancies among them and also with the results obtained in this thesis. While Elyounssi et al., 2012 reports a lignin content (35.8 wt.%) comparable to that obtained in this thesis (28.6 wt.%) Carrier et al., 2013 reports a very low lignin content (15.2 wt.%). Concerning extractives, both of them report lower contents (2.2-2.6 wt.%) than that of this thesis (8.1 wt.%). These discrepancies put forward the uncertainty of these determinations although they may be also attributed to differences in the analytical methodology used.

Concerning the olive derived samples, Table 4.1 shows that even though all of them come from the very same vegetal species, there are worth mentioning differences among them. First of all, it has to be mentioned that olives 3 has significantly higher ash content than olives 1 and 2. On view of these results, the sample was macroscopically analyzed and it was observed that it contained soil dust and small stones. Therefore, a cleaner olive sample (olives 3.1) was obtained by sieving and manual screening of olives 3 sample, and then olives 3.2 (twigs) and olives 3.3 (leaves) were derived from the soil free sample.

As might have been expected, the leaves sample is the one that most differs from the other olive samples. It has the higher ash content which is attributed to its different nature compared to wood, but also to dust that may have adhered to leaves. Other authors have also reported greater ash contents in olive leaves than in olive wood (García-Maraver et al., 2013, 2011). Another difference is that the leaves sample has the highest N content and, as a consequence, it has the lowest C/N ratio, which as has been mentioned before, is a biological parameter related to biodegradability of organic matter; this was to be expected since it is an evident fact that leaves degrade more easily than wood. The C/N ratio progressively increases from leaves to twigs + leaves, then twigs, thin branches and finally thick branches, which is the logical expected tendency according to its degradation ease.

Olives 1, 2 and 3.2 are quite similar, both in proximate analysis and ultimate analysis, since the three of them are woody olive biomass which only differ in the thickness of the branch; the only worth mentioning fact is that olives 2 (thick branches) has the lowest ash content. This is attributed to the fact that during the slicing process of this sample, bark was removed from the wood, and as has been reported in the literature, the bark is richer in ash than the inner wood (Agirre et al., 2013; Lambert, 1981; Lee et al., 2013; Melin, 2008).

Concerning the constituent's composition, it can be seen that once more, the olive leaves sample is significantly different. It has an extractives content (41 wt.%) much higher than those of the other olive samples (8-19 wt.%) and, as a consequence, has less cellulose, hemicellulose and lignin. Comparable extractives contents in olive leaves (≈36.5 wt.%) have been obtained by García-Maraver et al., 2013, however she reports also very high contents of extractives in olive wood and in olive pruning samples (27-37 wt.%), while in this thesis all of the other olive samples have lower extractives contents (8-19 wt.%). Again the discrepancy may be attributed to the uncertainty of these determinations and to differences in the analytical procedure.

Concerning olives 3.1 (twigs + leaves) it can be seen that, as a general rule, all the characterization data (proximate, ultimate and constituents analyses) lay between those of olives 3.2 (twigs) and olives 3.3 (leaves). However, they are much closer to the twigs than to the leaves analysis, since in olives 3.1 the predominant component was twigs.

Regarding the higher heating value of the biomass samples, there are not significant differences among them. All the values are in the range of 16.0–18.4 MJ kg^{-1}, which are heating values comparables to those of low quality fuels like lignites (≈16 MJ kg^{-1}).

4.1.2. Thermal characterization

Thermogravimetric analyses (TGA) were carried out in order to study the thermal decomposition behavior of the biomass samples. The experimental procedure has been presented in section 3.5.1.2.1 (page 61). Figure 4.1 and Figure 4.2 show the results obtained for all the biomass samples, in the TG analyses carried out from room temperature to 750 °C in nitrogen atmosphere, and with a heating rate of 3 °C min^{-1}; in the case of olives 1 (thin branches) and eucalyptus samples, a heating rate of 20 °C min^{-1} was also used.

Figure 4.1 shows the weight loss curves of olives 1 (thin branches) and eucalyptus samples, heated at 3 and 20 °C min^{-1}, and Figure 4.2 shows the TGA weight loss curves obtained with the biomass samples at the lower heating rate (3 °C min^{-1}). For better understanding the results, the main data derived from the TGA have been summarized in Table 4.2. It includes solid residue %, decomposition temperature range and temperature at which the weight loss rate is maximum (peak of the derivative weight loss curve).

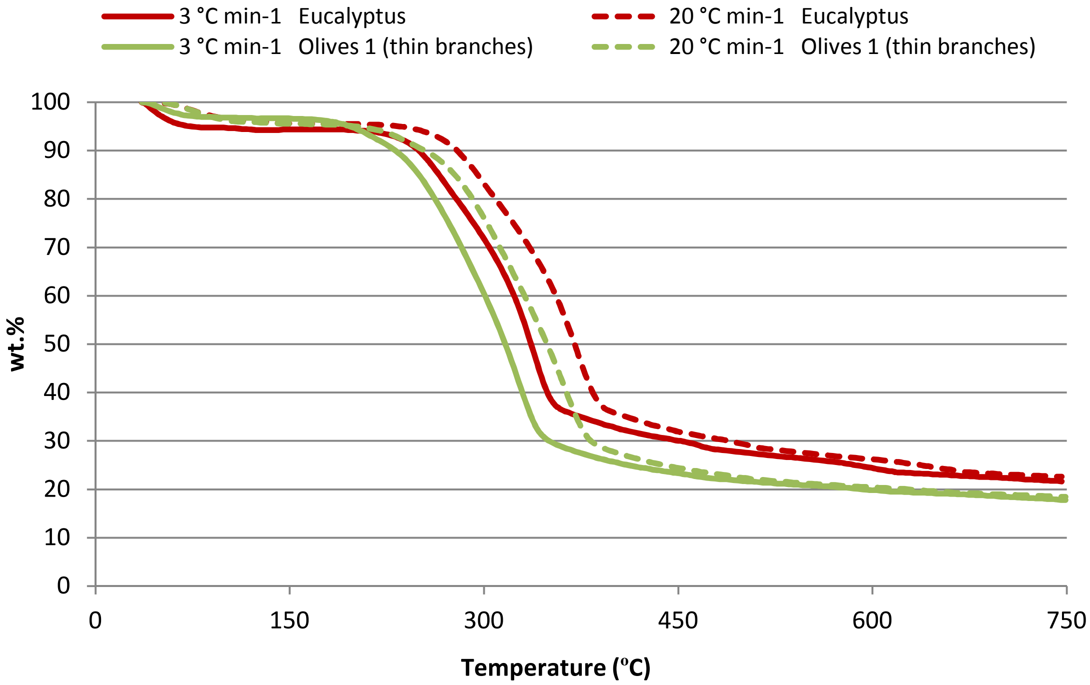


Figure 4.1. TGA weight loss of olives 1 (thin branches) and eucalyptus (heating rate 3 and 20 °C min^{-1})

Figure 4.1 shows that the eucalyptus sample decomposes at somewhat higher temperatures than the olives 1 sample, and that with lower heating rate decomposition is produced at lower temperatures.

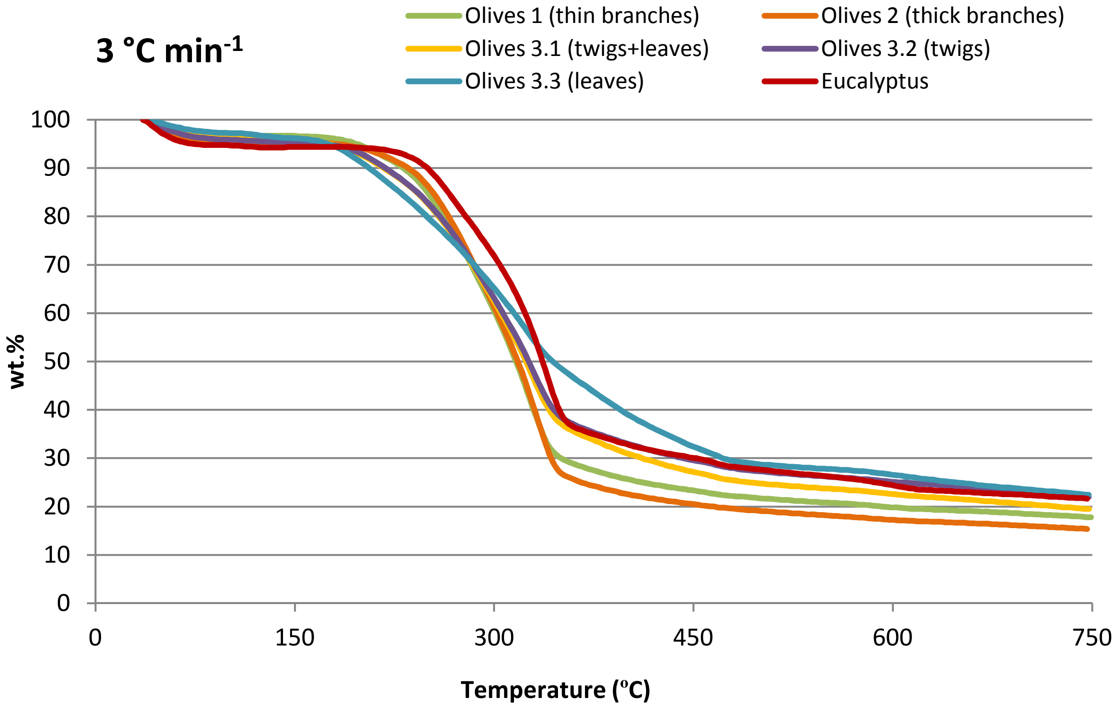


Figure 4.2. TGA weight loss of all the biomass samples (heating rate 3 °C min^{-1})

Figure 4.2 shows that the weight loss curves of the different samples follow similar tendencies. However, there are some differences that can be better analyzed if the curves are analyzed together with the data collected in Table 4.2.

Table 4.2. TGA derived data of the biomass samples

Sample	Heating rate (°C min^{-1})	Solid residue (wt.%)	Solid residue (ash free) (wt.%)	Decomposition T range (°C)	Decomposition T max[1] (°C)
Olives 1 (thin branches)	20	18.5	16.7	264 - 385	359.9
Eucalyptus	20	22.6	20.9	270 - 393	371.7
Olives 1 (thin branches)	3	17.8	16.0	228 - 348	326.8
Olives 2 (thick branches)	3	15.4	14.7	242 - 355	333.1
Olives 3.1 (twigs + leaves)	3	19.5	17.5	188 - 355	329.6
Olives 3.2 (twigs)	3	22.0	20.4	200 - 355	329.7
Olives 3.3 (leaves)	3	22.4	18.4	177 - 482	322.6
Eucalyptus	3	21.7	20.0	250 - 355	340.3

[1] *Temperature of maximum weight loss rate*

It can be seen that once more olives 3.3 (leaves) is the sample that most differs from the others. It starts to decompose at the lowest temperature (177 °C) and ends decomposition at the highest one (482 °C). Table 4.2 also shows that the greater the thickness of the sample (olives 2 > olives 1 > olives 3.2) the later the decomposition begins and that the eucalyptus sample is the one that starts decomposing at the highest temperature (250 °C). There seems to be a relationship between the thickness of the sample, the C/N ratio (Table 4.1) and the initial decomposition temperature: the smaller the thickness the lower the C/N ratio, and the lower the C/N ratio the lower the initial decomposition temperature. These tendencies are rather coherent since, as has been mentioned before, C/N ratio is related to biodegradability, so it is plausible that the lower the C/N ratio (more easily degradable), the earlier the thermal decomposition starts.

Concerning the solid residues, it can be seen that are in the range (15-23 wt.%) and these values are the theoretical yields that should be obtained in the pyrolysis tests. The solid residues include the carbonized material (char) derived from the organic matter of the biomass samples and the inorganic components (ash) of the original biomass. In order to analyze the tendency of the different type of biomasses to carbonize the solid residue ash free wt.% has been included in Table 4.2. It can be seen that the eucalyptus sample gives the highest solid (ash free) residue, so it has a greater tendency to carbonize and it is to be expected that this biomass will give higher biocoke yields in the pyrolysis experiments than the olive samples. Regarding the olive samples, Table 4.2 shows that the greater the thinness of the sample, the higher the solid residue. This may be attributed to the fact that the relative proportion of bark is higher as thinner is the sample and it has been reported that bark is more prone to carbonize (Mourant et al., 2013).

The main conclusions that can be drawn from this section with a view to the pyrolysis experiments are the following:

- Decomposition will take place almost completely in the range 170-490 °C, therefore 500 °C seems to be a temperature high enough for the process in terms of pyrolysis yields; however, since it has been reported (Agirre et al., 2013;

Griessacher et al., 2012) that for metallurgical grade biochars higher temperatures are required, the pyrolysis experiments were mostly carried out at 750 °C which is the maximum allowable temperature in the pyrolysis reactor.

- It is expected to obtain biocoke yields of at least 15-22 wt.% in the pyrolysis experiments.
- Higher biocoke yields are expected to be obtained with the eucalyptus than with the olives samples.

4.1.3. Py-GC/MS-FID characterization

All the biomass samples were characterized by micropyrolysis coupled to gas chromatography following the procedure presented in section 3.5.1.5, page 63. The olive samples were pyrolyzed only at 750 °C, while the eucalyptus sample was pyrolyzed at 500 °C and 750 °C. An example of the chromatograms obtained is presented in Figure 4.3; it corresponds to olives 1 (thin branches) sample pyrolyzed at 750 °C. A list of the chemical products obtained with all the biomass samples is presented in Table 4.3; these results are the mean value of two replicated runs. The criteria to include the name of the products in the table are the following: (1) to have an area greater than 1 %, or (2) to be present at least in six of the biomass samples. Therefore, such products present only in one of the biomass samples but with area greater than 1 area% have been included.

The length of the table is quite great and it would have been much greater if all the identified products had been included. This gives an idea of the complexity of biomass thermal decomposition reactions and of the type of products that will be obtained in the pyrolysis runs. At first sight, Table 4.3 shows that the results obtained with all the olives samples look similar, while there are some differences with the products obtained from eucalyptus at 750 °C and there are great differences with the products obtained at 500 °C. Many products are only obtained at this temperature and many others obtained at 750 °C are not obtained at 500 °C.

Table 4.3. Chemical products obtained by Py-GC/MS-FID (area%)

			750 °C			750 °C	500 °C
Name	Olives 1 Thin branches	Olives 2 Thick branches	Olives 3.1 Twigs + Leaves	Olives 3.2 Twigs	Olives 3.3 Leaves	Eucalyp.	Eucalyp.
1,2-Pentadiene	-	-	-	-	-	1.8	-
2-Methyl-1,3-butadiene	-	-	-	-	3.6	-	-
Acetaldehyde	-	-	-	-	-	5.4	-
Acetone	2.5	3.0	2.2	2.7	1.8	3.6	-
1,3-Cyclopentadiene	2.0	2.3	2.4	2.4	2.6	3.5	-
Furan	1.2	1.8	1.1	1.3	0.7	2.2	0.4
2-Propenal,(Acrolein)	4.3	4.9	3.9	4.2	2.2	3.3	0.3
Methylglyoxal (Propanal-2-one)	2.6	2.3	2.4	2.9	1.9	2.6	3.4
1,3-Cyclohexadiene	2.0	2.7	2.3	2.2	2.1	2.7	-
5-methyl-1,3-Cyclopentadiene	1.7	2.5	2.2	2.0	1.9	2.6	-
2-Butenone	1.5	2.2	1.6	1.6	1.1	1.9	-
2-Butanone	1.2	1.4	1.2	1.0	0.6	-	0.3
Isomer of C6H8 like Cyclohexadiene	0.8	1.3	1.2	1.2	1.4	1.1	-
Benzene	4.6	6.2	6.2	6.1	6.7	6.5	-
Hydroxy-acetaldehyde	4.0	1.2	3.5	1.9	0.9	-	-
Acetic acid	8.0	6.1	4.4	5.1	2.2	4.7	3.0
Acetol (Hydroxypropanone)	3.8	1.8	3.1	2.7	1.9	1.2	1.1
Toluene	4.6	5.2	5.7	5.6	7.1	6.4	-
3-Hydroxy-propionaldehyde	1.7	1.7	1.1	1.3	0.5	-	1.4
m-Xylene	0.6	0.8	0.8	0.8	1.3	-	-
Ethyl-benzene	1.5	1.7	2.0	1.9	2.4	1.7	-
o-Xylene	0.7	0.9	0.8	0.9	1.1	0.8	-
Styrene	3.9	4.2	4.5	4.5	3.6	3.5	-
Propanal	-	-	-	-	-	-	1.2
2-Furaldehyde	1.3	1.4	1.1	1.2	0.5	0.4	2.1

Indene	1.5	1.5	1.6	1.6	1.7	1.8	-
3-Hydroxy-5,6-dihydro-(4H)-pyran-4-one	-	-	-	-	-	-	1.8
Guaiacol	-	-	-	-	-	-	1.6
Phenol	2.4	2.6	2.4	2.5	1.9	3.3	0.2
o-Cresol	1.3	1.2	1.1	1.1	0.7	2.5	0.1
m-Cresol	1.5	1.5	1.3	1.9	0.8	3.4	0.1
p-Cresol	0.7	0.5	0.7	0.8	0.9	0.9	0.1
Naphthalene	0.8	0.6	1.2	1.1	1.4	1.0	-
4-Methyl-guaiacol	-	-	-	-	-	-	1.4
4-Vinyl-guaiacol	-	-	-	-	-	-	3.5
Syringol	-	-	-	-	-	-	5.0
4-Propenyl-(trans)-guaiacol (Isoeugenol)	-	-	-	-	-	-	1.9
4-Methyl-syringol	-	-	-	-	-	-	4.9
4-Ethyl-syringol	-	-	-	-	-	-	1.2
4-Vinyl-syringol	-	-	-	-	-	-	10.4
4-Allyl-syringol	-	-	-	-	-	-	1.5
6-Hydroxy-5,7-dimethoxy-1H-indene	-	-	-	-	-	-	2.1
6-Hydroxy-5,7-dimethoxy-2H-indene	-	-	-	-	-	-	1.6
Cis-4-(1-Propenyl)-syringol	-	-	-	-	-	-	1.1
1,6-Anhydro-ß-D-glucopyranose (Levoglucosan)	1.2	0.4	0.7	0.3	-	6.2	11.8
Trans-4-(1-Propenyl)-syringol	-	-	-	-	-	-	7.4
Homosyringaldehyde	-	-	-	-	-	-	1.4
Syringaldehyde	-	-	-	-	-	-	2.2
Syringyl acetone	-	-	-	-	-	-	1.2
Acetosyringone	-	-	-	-	-	-	1.8
Sinapaldehyde (trans)	-	-	-	-	-	-	2.6
Total	63.9	63.9	62.7	62.8	55.2	75.0	80.2
Minor compounds	29.1	30.3	29.9	29.9	40.0	25.0	15.4
Not identified	7.0	5.8	7.4	7.3	4.8	-	4.4

- not detected

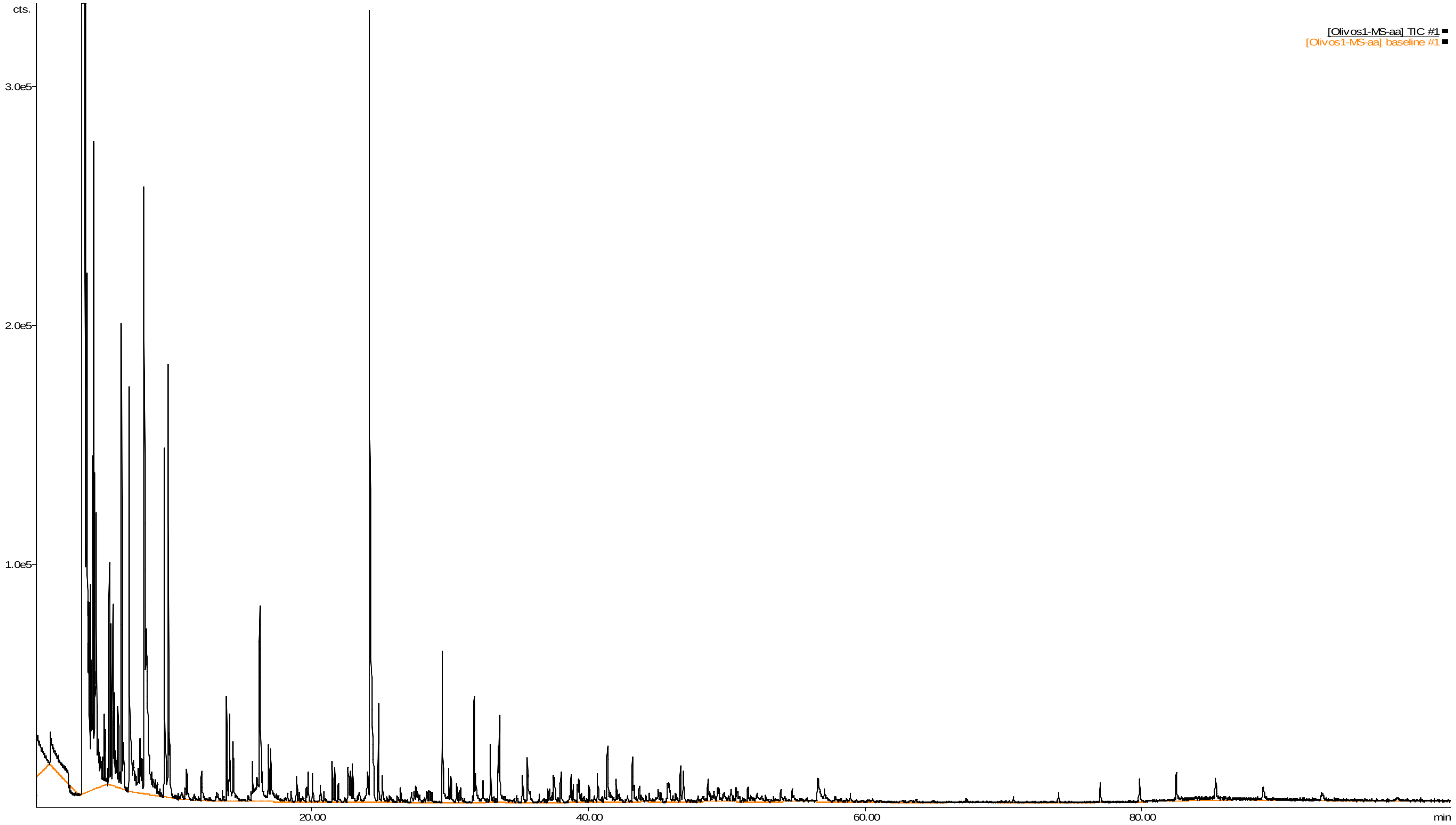


Figure 4.3. Example of chromatogram obtained by Py-GC/MS-FID (Olives 1: thin branches sample – 750 °C)

Table 4.4. Chemical families reported of the pyrolysis products obtained by Py-GC/MS-FID (area%)

Pyrolysis temperature	750 °C					750 °C	500 °C
Substance group	**Olives 1** Thin Branches	**Olives 2** Thick Branches	**Olives 3.1** Twigs + Leaves	**Olives 3.2** Twigs	**Olives 3.3** Leaves	**Eucalyptus**	**Eucalyptus**
Nonaromatic Compounds	38.2	33.9	31.5	30.6	27.7	37.0	14.0
Acids	7.9	5.6	3.9	4.4	0.9	4.8	3.0
Nonaromatic Aldehydes	12.7	10.0	10.4	9.8	5.3	12.0	6.2
Nonaromatic Ketones	11.5	10.1	8.8	8.8	7.6	8.4	4.8
Hydrocarbons	6.1	8.2	8.5	7.5	14.0	11.8	-
Heterocyclic Compounds (Furans)	3.5	4.3	3.4	3.5	3.0	3.9	7.1
Aromatic Compounds	38.9	44.0	48.5	44.2	50.0	51.8	60.6
Benzenes	29.5	35.3	39.9	36.3	44.0	33.4	5.5
Lignin derived Phenols	9.4	8.7	8.6	7.9	6.0	18.4	0.6
Guaiacols (Methoxy phenols)	-	-	-	-	-	-	12.4
Syringols (Dimethoxy phenols)	-	-	-	-	-	-	42.1
Carbohydrates (Sugars)	1.1	0.4	0.3	0.2	0.1	5.6	12.6
Other Organic Compounds	18.3	17.4	16.3	21.5	19.2	1.7	5.7
N-compounds	1.0	0.6	1.2	1.1	4.0	-	-
Not identified	7.0	5.8	7.4	7.3	4.8	-	4.4
Miscellaneous	6.2	6.2	6.3	8.1	4.7	1.6	0.2
Minor compounds	4.1	4.8	1.4	5.0	5.7	0.1	1.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

- not detected

In order to make the comparison of the results easier, a summary of the results obtained in the Py-GC/MS-FID characterization is presented in Table 4.4, in which the identified chemical compounds have been classified into chemical groups.

Concerning the effect of temperature, which can be analyzed with the eucalyptus sample, Table 4.4 shows that more aromatics (mainly guaiacols and syringols), carbohydrates and heterocyclic compounds are obtained at the lower temperature. At 750 °C there are no guaiacols and syringols; these are molecules which contain a phenol group, so raising the temperature from 500 °C to 750 °C brings about stronger thermal cracking turning guaiacols and syringols into benzenes and phenols. On the other hand, Table 3.3 shows that levoglucosan (LG) is one of the major compounds obtained at both temperatures. This compound is typical in bio-oils from woody biomass as has many times been reported (e.g. Lourenço et al., 2013; Oudia et al., 2007). Table 3.3 shows that the amount of LG decreases significantly from 750 °C to 500 °C. Demirbas, 2007 has reported that LG decreases at higher temperatures due to secondary decomposition reactions to acetic acid, acetone and phenols, which is in agreement with the results obtained in this thesis.

On the other hand, no clear tendencies concerning the different biomasses analyzed at 750 °C can be observed. The most worth mentioning facts are the following:

- Eucalyptus yields no nitrogenated compounds, which is coherent with the very low N content that this sample contains (Table 4.1).
- Eucalyptus gives rise to a significantly higher amount of phenols than the olives samples. This may be attributed to the fact that eucalyptus has higher lignin content than the olive samples, and as has been reported in the literature (Kleinert and Barth, 2008; Stefanidis et al., 2014), the products derived from lignin are almost exclusively phenols.
- Eucalyptus gives rise to a significantly higher amount of levoglucosan (LG) than the olives samples. On the contrary, eucalyptus does not yield hydroxyacetaldehyde (HAA) while all the olives samples give rise to some amount of HAA. Isahak et al., 2012 has reported that LG is the main decomposition product of cellulose, and secondary decomposition reactions derive LG into HAA by different pathways. The

higher amount of LG obtained in the pyrolysis of eucalyptus compared to those of the olives samples together with the fact that no HAA is obtained with the eucalyptus sample indicate that the decomposition of LG to HAA takes place to a greater extent in the olives samples than in the eucalyptus sample. This may be attributed to the lower tendency of eucalyptus sample to degrade compare to olives. As has been mentioned before (section 4.1.1), olives have lower C/N ratio than eucalyptus and therefore, the former are more prone to degrade than the latter.

- Concerning leaves, once more this is the sample that most differs from the others. Leaves derived products contain less oxygenated compounds (acids, aldehydes, ketones) and more nitrogenated compounds which is coherent with the lower oxygen content and greater N content of the original leaves sample. On the other hand, leaves yield significantly higher amounts of hydrocarbons than the other samples; this may be attributed to the higher extractives contents of leaves (Table 4.1), since extractives include aliphatic products, waxes and fatty acids from which hydrocarbon products may be derived. Another significant difference of leaves is that this sample yields the lowest amount of acids. It has been reported that the hemicellulosic fraction of lignocellulosic biomass contains high proportion of groups able to produce acetic acid (Penner et al., 1996). This may justify the few acids derived from leaves, since leaves is the sample with the lowest hemicellulose content.

The unknown compounds group corresponds to the peaks which it has not been possible to identify with any of the mass spectra profiles of the NIST or the in-house developed libraries.

4.2. Characterization of the Catalysts

The BET surface area and porosity as well as the metal contents of all the catalysts used in this thesis for upgrading the pyrolysis vapors were determined following the analytical techniques described in section 3.5.5 (page 73). The results are presented in Table 4.5.

Table 4.5. Surface area and porosity of the catalysts

Catalyst	BET ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Average pore diameter (Å)	Metal contents (wt.%)		
				Nominal	ICP measured	Metal
Ni/CeO_2-Al_2O_3	163.3	0.5949	143.7	13.0 6.0	10.8 3.3	Ni Ce
Ni/ZrO_2-Al_2O_3	166.6	0.6218	146.3	13.0 8.0	11.4 5.5	Ni Zr
Katalco 57-4Q	29.0	0.1312	179.3	16.0	15.9	NiO
HZSM5	328.6	0.4071	62.0	-		-
HZSM5 + Ni	273.9	0.3887	70.7	13.0	11.0	Ni
HY + Ni	441.4	0.2851	42.7	13.0	11.8	Ni

The Ni/CeO_2-Al_2O_3 and Ni/ZrO_2-Al_2O_3 catalysts have quite similar characteristics since both are homemade Ni alumina supported catalysts prepared following the same procedure, which only differ in the promoter (Ce or Zr). Concerning zeolites, it can be seen that the addition of nickel reduces the BET surface area and the total pore volume. Comparing the experimental results with those given by the zeolites provider (Table 3.1) it can be seen that the surface area of the as received ZSM5 zeolite (425 $m^2 g^{-1}$) is higher than that of the HZSM5 zeolite (328.6 $m^2 g^{-1}$). Therefore, the calcination of the process which converts ZSM5 zeolite reduces the surface area of the catalyst. Similar results concerning zeolites calcination have been reported by Fathi et al., (2014).

As a general rule, the greater the surface area the higher the catalyst activity to be expected. However, since large molecules, as are typical in pyrolysis products, are implicated in the reactions, pore blockage can take place. Consequently, high surface areas, which entail very small pore sizes, may not be the best option.

Table 4.5 shows that zeolites are the catalyst with greater surface areas followed by the homemade Ni/CeO_2-Al_2O_3 or Ni/ZrO_2-Al_2O_3 catalysts, while the commercial Katalco has a significantly lower surface area. Accordingly, the pore size follows the opposite tendency. The Katalco catalyst has the greater pore diameter while the zeolites have the smallest size.

The experimental metal contents measured for all the catalysts are lower than the nominal ones. In the case of the commercial Katalco 57-4Q catalyst, the NiO content is practically coincident with the nominal value reported by the company.

4.3. Selection of Operating conditions for Biocoke production and Pyrolysis Vapors upgrading

This section is devoted to analyze the results obtained with different layouts of pyrolysis installations and with different operating conditions to establish the most appropriate procedure for achieving the objectives of this thesis: the production of biocoke simultaneously with the upgrading of the pyrolysis vapors generated. On the one hand, a comparison of slow and fast pyrolysis is carried out. Secondly, the benefit of using a second reactor, as well as the effect of the temperature and catalyst of the second reactor is studied. And finally, the effect of the heating rate of the first pyrolysis reactor is analyzed.

4.3.1. Fast pyrolysis versus Slow pyrolysis

The objective of this thesis was to obtain metallurgical grade biocoke and, at the same time, optimize the vapors obtained in the pyrolysis process. It is well known that if the aim of the process is the production of biocoke, a slow type pyrolysis process is required.

In the initial slow pyrolysis experiments carried out in this thesis, the liquid products obtained were mainly composed of an aqueous fraction (50-70 wt.%). This seemed somewhat surprising since it was not found in the scientific literature references reporting such high water yields, but just the contrary, lots of references placed great emphasis on bio-oils (e.g. Bertero et al., 2012; Mohan et al., 2006; Pattiya, 2011; Wang et al., 2005) and, in some of them, the formation of water was not even mentioned.

For this reason, it was decided to carry out fast pyrolysis experiments with some of the very same samples and with the same temperatures used in this thesis in order to self evaluate if performing slow or fast pyrolysis did have such a great influence on pyrolysis products.

The fast pyrolysis experiments were carried out in the Thünen Institute of Wood Research of Hamburg with the installation and experimental procedure described in sections 3.3.2, page 53 and 3.5.3.2, page 69, respectively.

It is worth mentioning the main and probably the most influential differences between both pyrolysis plants:

- The amount of pyrolyzed biomass: 100 g for slow pyrolysis, 200 mg for fast pyrolysis.
- The heating rate: in slow pyrolysis the heating rate in the first pyrolysis reactor was 20 °C min^{-1} and the reaction time, once reached the preset temperature, was 30 min. The vapors continuously evolved from the first pyrolysis reactor and went through the second tubular reactor which was already heated at the preset temperature. In the fast pyrolysis runs the pyrolysis oven was already heated at the desired temperature when the biomass was fed, and it was pyrolyzed just for 60 s.

The biomass samples that were pyrolyzed in fast and slow pyrolysis were olives 1 (thin branches) and eucalyptus. The first sample was pyrolyzed at 750 °C and the second one at 600 and 750 °C, both without catalyst and with the HZSM5 zeolite.

The pyrolysis yields and gas compositions obtained in the **fast pyrolysis** runs of olives 1 (thin branches) and eucalyptus are presented in Table 4.6. It has to be mentioned that the pyrolysis gases most probably contain hydrogen; however, it could not be determined due to limitations of the available chromatographs at that moment in the Thünen Institute of Wood Research of Hamburg. The minor compounds group included in the table corresponds to products that were identified but were present in a very low proportion (< 1 area%). The not identified compounds correspond to the peaks of the compounds that were not calibrated in the GC/MS-FID.

Table 4.6. Fast pyrolysis yields and gas compositions

	Olives 1		Eucalyptus			
	Without catalyst	HZSM5	Without catalyst		HZSM5	
	750 °C	750 °C	600 °C	750 °C	600 °C	750 °C
Pyrolysis yields (wt.%)						
Solids	14.9	14.6	22.5	18.2	22.5	19.0
Liquids	31.6	26.5	35.8	28.2	36.7	11.0
Gases[1]	53.5	58.9	41.7	53.6	40.8	70.0
Pyrolysis gases (area%)						
CO	35.8	38.6	32.5	41.5	33.7	43.1
CO_2	25.1	19.9	34.8	22.1	29.2	15.9
CH_4	9.9	10.4	7.7	11.2	7.8	10.9
C_2H_4	1.9	1.2	0.0	0.0	0.0	0.0
C_2H_6	4.2	5.7	1.6	0.3	2.4	0.5
C_3H_6	2.7	1.8	0.3	0.4	0.3	0.4
Minor compounds	2.6	2.3	0.3	1.4	0.7	1.9
Total identified	82.2	79.9	77.2	76.9	74.1	72.7
Not identified	17.8	20.1	22.8	23.1	25.9	27.3

[1] *By difference*

Concerning the **effect of temperature** it can be seen that the increase of temperature from 600 °C to 750 °C gave rise, as was expected, to a reduction of liquid yield and solid yield and consequently an increase of gas yield. Regarding the effect of temperature in gas compositions, in all the cases there is an increase of CO and CH_4 and a decrease of CO_2 when the temperature is raised. Therefore, the gas composition is enhanced at higher temperatures.

On the other hand, solid yields decrease as the temperature is increased, probably due to the greater devolatilization and carbonization that takes place at the higher temperature; although these reactions diminish the amount of solids, they may have positive effects on its quality since they probably decrease its volatile matter and increase its fixed carbon content. This could not be demonstrated in the fast pyrolysis experiments because the small amount of solids available was not enough to carry out the corresponding analyses.

Therefore it can be expected that, even though the solid yield decreases with temperature, the higher temperature is more convenient to achieve the objectives of this thesis, not only because of the better quality of the gases, but also due to the better quality of biocoke.

A published critical review regarding pyrolysis of wood biomass for bio-oils (Mohan et al., 2006) reports that in fast pyrolysis bio-oil yields are in the range 60-75 wt.%, solid yields 15-25 wt.% and gas yield 10-20 wt.%. The solid yields obtained in this thesis are in agreement with the values reported in the mentioned review, but the liquid and gas yields, 11-37 wt.% and 40-70 wt.% respectively, are widely different. This is due to the fact that the review refers to fast pyrolysis processes focused on obtaining bio-oil, and therefore, operating at moderate temperatures (425-500 °C), while in this thesis, which is focused in biocoke production, higher temperatures (600-750 °C) have been used.

Comparing the results obtained with both biomass samples at the same temperature, eucalyptus gave rise to a greater solid yield than olives 1, as was expected based on the results that had been obtained in the thermal characterization of the samples (section 4.1.2, page 83). The fact that the solid yield of eucalyptus is higher than that of olives may be attributed to the fact that the former has a significantly higher lignin content, 28.6 wt.% compared to 18.9 wt.% (Table 4.1, page 81), and it has frequently been reported that lignin is the most prone to carbonize constituent of wood (e.g. Cagnon et al., 2009; Demirbas, 2004; Lee et al., 2013).

Concerning the **effect of the catalyst**, first of all it can be seen that it does not affect the solid yield, regardless the biomass or the temperature used, which was to be expected since the catalyst is placed after the biomass and only interacts with the pyrolysis vapors. On the contrary, there is a significant effect of the zeolite in the liquid and gas yields at the highest temperature (750 °C) but not at the lowest one (600 °C); at 750 °C the catalyst promotes cracking, decreasing liquids yields and increasing gas yields, especially with the eucalyptus sample where the liquid yield is reduced as much as 17 points by the effect of the catalyst. The composition of the gases is also influenced by the catalyst. As a general rule, the catalyst brings about an increase in CO and CH_4 and a decrease in CO_2 (Olazar et al., 2000).

The reason why the catalyst is effective at 750 °C but not at 600 °C may be that at lower temperatures, weaker thermal cracking is produced and therefore, longer size molecules are generated which cannot enter the narrower micropores of the catalyst, while the smaller molecules generated at 750 °C have a greater access to the micropores of the catalyst.

Slow pyrolysis (20 °C min^{-1}) experiments were carried out using the installation and experimental procedure described in section 3.3.1 (page 50). The pyrolysis yields and gases obtained in the slow pyrolysis runs are presented in Table 4.7.

Table 4.7. Slow pyrolysis yields and gas compositions

	Olives 1		Eucalyptus			
	Without catalyst		Without catalyst		HZSM5	
	600 °C	750 °C	600 °C	750 °C	600 °C	750 °C
Pyrolysis yields (wt.%)						
Solids	22.9	21.9	24.4	22.9	24.5	23.0
Total liquids	46.7	42.0	44.4	42.7	44.2	41.0
Liquids *Aqueous*	*33.7*	*30.3*	*40.7*	*39.4*	*40.4*	*37.7*
Organic-tars	*13.0*	*11.7*	*3.7*	*3.3*	*3.8*	*3.3*
Gases[1]	30.4	36.1	31.2	34.4	31.3	36.0
Pyrolysis gases (vol.%) and HHV (MJ m^{-3})						
H_2	12.1	10.0	16.0	23.8	15.3	24.6
CO	34.8	50.8	36.3	33.9	35.9	33.7
CO_2	27.9	12.3	28.9	23.7	29.7	22.8
CH_4	19.4	19.7	15.1	15.8	15.3	15.0
C_2H_4	1.8	1.7	0.0	0.1	0.0	0.0
C_2H_6	2.4	2.9	1.1	1.1	1.1	1.6
C3	1.2	1.4	0.6	0.6	0.7	0.6
C4	0.2	0.6	0.7	0.5	0.7	0.6
C5	0.2	0.3	0.5	0.3	0.5	0.4
C6	0.1	0.3	0.8	0.2	0.8	0.7
HHV	16.7	19.8	15.5	14.9	15.5	16.0

[1] *By difference*

The comparison of the results of Table 4.6 and Table 4.7 shows that the **solid yields** are higher in slow pyrolysis than in fast pyrolysis (Table 4.6), regardless the type of biomass and the temperature used. This was to be expected since it has several times been reported in the literature that slow heating rates and long reaction times increase solid yields (e.g. Mohanty et al., 2013; Shaaban et al., 2014; Zanzi et al., 1996). The difference between fast and slow solid yield is greater at 750 °C than at 600 °C.

This may be because the time required for reaching 750 °C is longer than that for 600 °C, therefore the biomass sample is pyrolyzed for longer time at the higher temperature and so, a greater difference between fast and slow solid yields is shown.

Total **liquid yields** are significantly higher in slow pyrolysis than in fast pyrolysis. This was somewhat surprising since it has many times been reported that fast pyrolysis yields more liquids than slow pyrolysis.

It is important to mention that slow pyrolysis liquids were mainly composed of water; more than 90 wt.% of the eucalyptus derived liquids and more than 70 wt.% of the olives derived liquids is an aqueous fraction, while tar (organic liquids) yields are just ≈3 wt.% for eucalyptus and 11 wt.% for olives. This is a very important difference between fast and slow pyrolysis. Most probably an aqueous phase is also produced in fast pyrolysis, at least the water coming from moisture. However, either the aqueous phase has no chance to condense and escapes with gases, or it cannot be distinguished from bio-oils because the fast pyrolysis liquid products are just an extremely thin layer which coats the glass devices of the installation used and therefore, the aqueous phase was neither detected nor quantified.

There are references in the literature dealing with fast pyrolysis of woody biomass at 500 °C which report water formation in the range of 6-9 wt.% with respect to the initial biomass weight (Kim et al., 2013). It has also been reported that less aqueous phase is formed as higher is the pyrolysis temperature (Pattiya, 2011; Yang et al., 2007). In the fast pyrolysis experiments of this thesis just 200 mg of sample were pyrolyzed at 750 °C, which could give rise to 12-18 mg of water if the above mentioned 6-9 wt.% water yield is considered. Such small amount of water, either in the gas or in the liquid phase, was not detected, and consequently, was not quantified.

Concerning the **effect of temperature** on slow pyrolysis yields, the same tendencies as those observed in fast pyrolysis are observed. The **solid yields** decrease with temperature, which seems contrary to one of the objectives of this thesis, the production of biocoke. In order to select the temperature for future experimentation not only solid yields have to be considered, but obviously the characteristics of the solids. Table 4.8 shows the proximate and ultimate analyses (as produced basis) of the solids obtained with olives 1 and eucalyptus at 600 °C and 750 °C. In order to simplify the discussion of the solids analyses results, the values included in Table 4.8 are the mean value of the results of the biocokes obtained with and without catalyst at each temperature since, as the catalyst is placed in the second reactor it does not influence the solid characteristics.

It is well known that the higher the fixed carbon and the lower the volatile matter content, the better is the quality of metallurgical reducing agents. Table 4.8 shows that for both biomass samples the fixed and elemental carbon contents of the biocokes are higher while the volatile matter is lower at 750 °C. Similar tendencies regarding the effect of temperature in fixed carbon and volatile matter contents have been found in literature (Imam and Capareda, 2012). Therefore, it is demonstrated that for a better quality biocoke higher temperatures are more convenient, even though they give rise to lower solid yields.

Table 4.8. Proximate and ultimate analyses of the pyrolysis solids of slow pyrolysis

As produced basis (wt.%)		Olives 1		Eucalyptus	
		600 °C	750 °C	600 °C	750 °C
Proximate analysis	Moisture	2.0	1.8	2.2	1.4
	Volatile matter	13.8	10.8	12.0	8.6
	Ash	4.6	5.1	5.9	6.2
	Fixed Carbon[1]	79.6	82.3	79.9	83.8
Ultimate analysis	C	85.8	87.7	87.9	90.0
	H	2.3	1.5	1.6	0.9
	N	0.8	1.0	0.5	0.6
	Others[1]	11.1	9.8	10.0	8.5
HHV (MJ kg^{-1})		30.2	29.5	30.9	30.6

[1] *By difference*

The total **liquid yield**, as well as both the aqueous and tar yields, decrease with temperature, the same as it occurred in fast pyrolysis. However, the decrease is less pronounced than in fast pyrolysis. This may be because in slow pyrolysis the vapors remain more time in the reactor and are therefore cracked by the combined effect of time and temperature, so that the effect of temperature alone is less evidenced.

Concerning **gases**, first of all it is worth mentioning that they have a significant proportion of H_2, specially the 750 °C gases, and H_2 enhances the value of the gas products for applications such as reducing agent, synthesis gas or even source of hydrogen. Table 4.7 shows also that both the gas yield and the H_2 content increase with temperature, so this is another reason that justifies the interest of using high temperatures for the objectives of this thesis.

It is not worthwhile to draw conclusions with respect to differences between slow and fast pyrolysis gases, for the following reasons: (1) different analytical procedures were used, (2) in fast pyrolysis, as has been mentioned before, H_2 could not be determined and, (3) the fast pyrolysis gases unit is area % since the equipment used in the Thünen Institute of Wood Research of Hamburg could not be calibrated with standards at that moment, while in slow pyrolysis is vol.%.

Regarding the effect of the **catalyst**, the solid yields are obviously not affected as it happened in fast pyrolysis, since the catalyst interacts with the pyrolysis vapors but not with the solid itself. Pyrolysis liquid and gas yields are not affected by the catalyst at 600 °C, while at 750 °C some effect can be noticed, although in this case it is less pronounced than in fast pyrolysis. The reason why the effect of the zeolite is stronger in fast than in slow pyrolysis may be that the catalyst/sample weight ratio was greater in fast pyrolysis, being greater the cracking effect of the catalyst in the pyrolysis vapors leading to greater gas yields and fewer liquid yields. Another reason may be that in slow pyrolysis the generated vapors remain more time in the reactor, cracking and reacting, so there is less margin for the catalyst to show its effect, while in fast pyrolysis the vapors leave the pyrolysis zone less cracked and when they go through the catalyst are further cracked and therefore, greater catalytic effect is put forward.

The conclusions that can be drawn from this study comparing fast and slow pyrolysis can be organized in two groups:

- Conclusions related to the comparison of flash pyrolysis studies presented in the literature and the fast pyrolysis runs of this thesis:

  - Fast pyrolysis carried out in the literature usually refers to processes devoted to maximize liquids and it is usually performed at moderate temperatures (425-500 °C). For this reason few water and much more liquids than at the conditions used in this thesis (750 °C) are obtained.
  - The high heating rate and good temperature control that is required for fast pyrolysis, determines that usually small samples are used in fast pyrolysis, so in most of the cases there is no evidence of the formation of an aqueous phase and it is not quantified.

- Conclusions related to the objectives of this thesis:
  - The pyrolysis experiments would be carried out at slow heating rates and at the highest possible temperature, which due to the operating limitations of the available installation was 750 °C.
  - A study of the influence of different catalysts for pyrolysis vapors upgrading would be carried out.

4.3.2. Effect of Temperature and Catalysts of the vapors upgrading reactor

The objective of this thesis was to optimize by means of catalysts the pyrolysis gases generated in the biocoke production process. That is why the pyrolysis installation used for the experiments, which has been described in section 3.3.1 (page 50), was composed of two reactors: a first reactor where the biomass was pyrolyzed and a second reactor where the vapors generated in the first reactor were catalytically treated.

In order to evaluate the benefit of the second catalytic reactor, a first experiment was carried out without the second reactor, so as to determine the effect of just the second reactor when no catalyst is used. The experiments were carried out with olives 1 (thin branches) sample using a heating rate of 20 °C min^{-1} and 750 °C in the first reactor. The pyrolysis yields and gas compositions are presented in Table 4.9.

Besides, three temperatures (600, 750 and 900 °C) were tested both without catalyst and with the two nickel/alumina supported monolithic catalysts modified with ceria and zirconia prepared in our laboratories (Ni/CeO_2-Al_2O_3 and Ni/ZrO_2-Al_2O_3). These sets of experiments were also carried out with the olives 1 (thin branches) sample and the first reactor heated at 20 °C min^{-1} to 750 °C. The pyrolysis yields and gas compositions obtained are presented in Table 4.9.

First of all it can be seen that the solid yields were about 21-22 wt.% in all the cases and obviously not temperature, catalyst or number of reactors dependant, since the solid remains in the first reactor and therefore is not affected by the conditions of the second reactor.

Pyrolysis liquids were composed of two different phases, an aqueous and an organic one (tars). The aqueous phase is more abundant than the organic phase, and the amount of it is much greater than the moisture content of the original sample (8.8 wt.%), therefore water is formed during the pyrolysis process.

It must be pointed out that the vapors left the pyrolysis reactor as they were generated (with the help of the N_2 that was swept during the whole experiment), so the biomass derived products formed in the initial stages of the process did not become to be exposed to 750 °C, but to lower temperatures.

Table 4.9 shows that the effect (just thermal effect) of the second reactor depends on its temperature. It almost has no effect when the temperature of the second reactor is low (600 °C) while it does have effect when the second reactor is at higher temperatures. Fewer liquids, both tars and aqueous phase, and more gases are obtained than with only one reactor, when 750 °C is used in the second reactor, even though this is the very same temperature as that of the first reactor. This is because the vapors leave the first reactor as they are generated (swept by N_2) and therefore, those generated in the first stages of the process are not exposed to 750 °C in the first reactor so they are further cracked in the second reactor which is at the preset temperature either 750 °C or 900 °C from the beginning.

Table 4.9. Effect of the temperature and catalysts of the second reactor in the pyrolysis yields and gas compositions (olives 1: thin branches, 20 °C min^{-1}, 750 °C)

		2nd reactor not used	Without catalyst			Ni/CeO_2-Al_2O_3			Ni/ZrO_2-Al_2O_3
			600 °C	750 °C	900 °C	600 °C	750 °C	900 °C	900 °C
Pyrolysis yields (wt.%)									
Solids		21.4	21.8	21.9	21.3	21.6	22.2	21.4	21.2
Liquids	Total liquids	45.4	45.6	42.0	33.8	40.8	36.8	28.4	31.5
	Aqueous	*28.6*	*32.6*	*30.3*	*22.2*	*27.1*	*25.0*	*19.3*	*19.5*
	Organic-tars	*16.8*	*13.0*	*11.7*	*11.6*	*13.7*	*11.8*	*9.1*	*12.0*
Gases[1]		33.2	32.6	36.1	44.9	37.6	41.0	50.2	47.3
Pyrolysis gases (vol.%) and HHV (MJ m^{-3})									
H_2		11.5	12.5	10.0	14.7	15.6	16.9	17.6	20.1
CO		48.2	45.4	50.8	41.5	46.6	48.3	47.4	33.5
CO_2		16.6	17.2	12.3	11.7	16.1	15.3	11.7	18.8
CH_4		18.4	18.4	19.7	24.1	17.8	17.1	17.5	19.9
C_2H_4		1.5	1.9	1.7	0.9	0.0	0.2	0.7	0.4
C_2H_6		2.4	2.0	2.9	5.6	3.0	1.8	3.6	6.1
C3		0.9	1.3	1.4	0.5	0.8	0.4	0.5	0.6
C4		0.3	0.5	0.6	0.2	0.1	0.0	0.2	0.3
C5		0.1	0.3	0.3	0.1	0.0	0.0	0.1	0.1
C6		0.1	0.5	0.3	0.7	0.0	0.0	0.7	0.2
HHV		17.4	18.7	19.8	18.5	16.2	15.3	18.5	18.5

[1] *By difference*

Concerning the effect of the temperature of the second reactor, it can be observed that the temperature had a significant effect on pyrolysis yields: fewer liquids and more gases were obtained as the temperature was increased, both with and without catalysts. It can be seen that the reduction of the aqueous phase is greater than that of the organic phase (without catalyst aqueous phase decreased 10.4 points from 600 to 900 °C, and the organic phase decreased only 2.6 points) so temperature not only promotes cracking but also reactions in which water participates, such as reforming reactions, water gas shift reaction, etc.

Comparing the pyrolysis yields obtained in the catalytic and non-catalytic experiments, it can be seen that as a general rule, when the catalyst is used liquid yield were about 5 points lower than in the thermal runs, while gases were about 5 points higher. Therefore the catalyst showed a clear cracking activity for the biomass pyrolysis vapors. The catalyst increases dehydration reactions of the oxygenated species in the product and product vapors, thus although the aqueous phase with respect to biomass decreases, the water yield in bio-oil is increased at the expense of organic liquid yield (Yildiz et al., 2013).

Comparing both catalysts, the Ni/CeO_2-Al_2O_3 catalyst was more effective than the Ni/ZrO_2-Al_2O_3 catalyst, since it increases gases and decreases liquids more than the Ni/ZrO_2-Al_2O_3 catalyst and additionally it reduces the organic liquid phase, which the Ni/ZrO_2-Al_2O_3 catalyst does not.

Table 4.9 shows the composition and HHV of the pyrolysis gases obtained in all this set of experiments. In all the cases CO is the main component of the gases (33-51 vol.%), followed by CH_4 (17-24 vol.%), H_2 (10-20 vol.%) and CO_2 (11-19 vol.%). The HHV of the gases is in the range of 15-20 MJ m^{-3}.

Concerning the effect of the second reactor in gas composition, no significant influence can be observed at 600 and 750 °C. There are a few slight differences in the content of each compound but not worth mentioning. The temperature of the second reactor has to be raised to 900 °C to detect an increase in H_2 and CH_4, and a decrease of CO and CO_2.

Concerning the effect of temperature in gas composition, it can be seen that both with and without catalyst, H_2 increased while CO_2 decreased as the temperature was raised. This may be attributed to reforming reactions ($C_xH_y + H_2O \rightarrow CO/CO_2 + H_2$), which are endothermic and therefore, are favored by high temperatures; these reactions transform hydrocarbons both into CO + H_2 and into CO_2 + H_2 increasing H_2 yield more than CO or CO_2 yields. Additionally, since the water gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) is an exothermic reaction, it is produced to a lesser extent at high temperatures so it would give rise to lower CO_2 and H_2 yields. Taking into account both reactions, the global effect of temperature is that H_2 yield increases while CO_2 yield decreases with temperature.

Concerning the effect of catalysts on gas composition, the most worth-mentioning effect of both catalysts is to increase H_2 and decrease hydrocarbons, which is attributed to the promotion of reforming reactions, since nickel catalyst supported on alumina are typical reforming catalysts. Comparing both catalysts it can be seen that the effect of the $Ni/CeO_2\text{-}Al_2O_3$ catalyst was more pronounced than that of the $Ni/ZrO_2\text{-}Al_2O_3$ catalyst: with the $Ni/CeO_2\text{-}Al_2O_3$ catalyst, more reduction of liquids, aqueous phase and carbon dioxide content in gases was achieved, and although fewer hydrogen was produced than with the $Ni/ZrO_2\text{-}Al_2O_3$ catalyst, the sum of CO + H_2, which is a useful and valuable mixture useful as synthesis gas or reducing agent, was higher with the $Ni/CeO_2\text{-}Al_2O_3$ than with the $Ni/ZrO_2\text{-}Al_2O_3$ catalyst.

If the results obtained in one step pyrolysis are compared to those obtained with the $Ni/CeO_2\text{-}Al_2O_3$ at 900 °C, which are the conditions that gave the best results, it can be seen that a very significant liquid yield reduction and a consequently gas yield increase (from 33.2 to 50.2 wt.%) is produced and additionally, the gas quality is enhanced increasing H_2 6 points and decreasing CO_2 5 points.

The main conclusions that were drawn from this set of experiments were the following:

- The use of a second catalytic step is very useful for optimizing the pyrolysis vapors (liquid and tar yields reduction and H_2 yield increase).
- The Ni/CeO_2-Al_2O_3 catalyst is more effective than Ni/ZrO_2-Al_2O_3 catalyst.
- The optimum temperature to be used in the second reactor is 900 °C.

Therefore, the subsequent experiments of this thesis were carried out using both reactors and with the second reactor at 900 °C, and in the further studies for screening of catalysts and of operating conditions the Ni/CeO_2-Al_2O_3 catalyst was preferred to the Ni/ZrO_2-Al_2O_3.

A detailed description of the characteristics of the liquid and solid products obtained in this section is presented in section 4.3.4 and 4.3.5 respectively.

4.3.3. Effect of Heating Rate of the pyrolysis reactor

The influence of the heating rate of the first pyrolysis step was investigated. Heating rates were varied from 20 °C min^{-1} (maximum heating rate achievable with the pyrolysis installation used) to 3 °C min^{-1}; lower heating rates were not investigated since it implied excessively long-lasting experiments. In all this set of experiments the temperature of the first reactor was 750 °C and the temperature of the second reactor was 900 °C.

The effect of heating rate was explored both without catalyst and with two catalysts, HZSM5 zeolite and the homemade Ni/CeO_2-Al_2O_3 alumina supported catalyst (Ni/CeO_2-Al_2O_3), which were placed on the second reactor over a monolith, as has been explained in section 3.2.4 (page 49). The amount of catalyst used in each run was ≈0.7 g.

The liquid, gas and solid pyrolysis yields obtained in the runs carried out with the three heating rates tested with and without catalysts are presented in Table 4.10. The composition of the gases and its HHV is also included in the table.

Table 4.10. Effect of the heating rate in the pyrolysis yields and gas compositions

		20 °C min^{-1}			15 °C min^{-1}		3 °C min^{-1}	
		Without Catalyst	HZSM5	Ni/CeO$_2$-Al$_2$O$_3$	Without Catalyst	HZSM5	Without Catalyst	HZSM5	Ni/CeO$_2$-Al$_2$O$_3$
Pyrolysis yields (wt.%)									
Solids		21.3	22.9	21.4	24.6	24.8	26.1	26.4	24.6
Liquids	Total liq.	33.8	35.9	28.4	30.0	31.1	19.7	19.0	17.8
	Aqueous	*22.2*	*23.4*	*19.3*	*20.5*	*21.3*	*19.7*	*19.0*	*17.8*
	Organic-tars	*11.6*	*12.5*	*9.1*	*9.5*	*9.8*	*0.0*	*0.0*	*0.0*
Gases[1]		44.9	41.2	50.2	45.4	44.1	54.2	54.6	57.6
Pyrolysis gases (vol.%) and HHV (MJ m^{-3})									
H_2		14.7	20.1	17.6	30.0	34.2	40.8	44.0	46.6
CO		41.5	33.5	47.4	28.3	22.0	27.3	26.7	29.3
CO_2		11.7	18.8	11.7	17.6	20.4	17.0	14.3	13.4
CH_4		24.1	19.9	17.5	17.8	18.0	12.1	12.5	9.6
C_2H_4		0.9	0.4	0.7	0.3	0.2	0.0	0.0	0.0
C_2H_6		5.6	6.1	3.6	5.2	4.7	2.7	2.4	1.1
C3		0.5	0.6	0.5	0.2	0.2	0.0	0.0	0.0
C4		0.2	0.3	0.2	0.1	0.1	0.0	0.0	0.0
C5		0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0
C6		0.7	0.2	0.7	0.4	0.2	0.1	0.1	0.0
HHV		18.5	18.5	18.5	17.5	16.6	14.0	14.4	13.0

[1] *By difference*

Concerning the effect of heating rate, Table 4.10 shows that gas yields increase while liquid yields decrease, both aqueous and tars, as the heating rate is decreased. Moreover, it can be seen that the reduction of the organic phase (tars) when decreasing heating rate is greater than that of the aqueous phase. As a matter of fact the whole organic phase is transformed to gases or char when the lowest heating rate (3 °C min^{-1}) is used.

This fact may be explained as follows. The decrease of the heating rate slows the decomposition of the biomass, the vapors flow more slowly and the residence time in the second tubular reactor increases having more time to be upgraded by the simultaneous effect of temperature and catalyst. Consequently, the vapors are more extensively cracked and reformed giving as a result fewer liquids and more gases. The same effect was observed by Duman et al., 2011 and Pütün et al., 2007, who pyrolyzed different biomasses using different heating rates and both of them obtained more char and gases and less liquids when the heating rate was lowered.

The heating rate has a significant influence not only in the gas and liquid yields, but also in the solid yields. Table 4.10 shows that the solid yields increase as the heating rate is decreased, which is in agreement with the results obtained by other authors (Ibarrola et al., 2012; Lehmann and Joseph, 2009). The pyrolysis solid yields are in the range of 21-23 wt.% at 20 °C min^{-1}, 24-25 wt.% at 15 °C min^{-1} and 25-26 wt.% when the lowest heating rate is used. Therefore the reduction of heating rate has two beneficial effects, on the one hand it reduces tars and on the other hand it increases pyrolysis solids yields.

Concerning the effect of the catalysts, the use of HZSM5 zeolite seems to have no influence on the pyrolysis yields obtained at any heating rate, while the Ni/CeO_2-Al_2O_3 do have influence, increasing gas yields and decreasing liquid yields.

There are several reasons that may justify the lower performance of the zeolite compared to the Ni/CeO_2-Al_2O_3 catalyst. On the one hand, the textural properties of the catalysts, which have been presented in Table 4.5 (page 94), showed that the average pore diameter of HZSM5 zeolite is smaller (62.0 Å) than that of the Ni/CeO_2-Al_2O_3 catalyst (143.7 Å). As a consequence there will be big molecules (liquids) which can access the Ni-catalyst pores but not the zeolite pores and therefore liquids will be cracked to gases with the former catalyst but not with the later one. Another reason for the lower activity of the zeolite may be the lack of Ni which its good performance in cracking and reforming reactions is well known (Caballero et al., 2000; Lv et al., 2007; Pfeifer and Hofbauer, 2008; Pinto et al., 2009; Simell and Bredenberg, 1990). Therefore, it was decided to dope the HZSM5 zeolite with Ni with the aim of improving its activity.

On the other hand, the lower activity of HZSM5 may be due to the fact that it is more easily deactivated than the Ni/CeO_2-Al_2O_3 catalyst. During solid catalyzed organic reactions, the catalyst always tends to be deactivated because of the formation and retention of heavy by-products which cause either active sites poisoning and/or pore blockage (Guisnet and Magnoux, 2001). These non-desorbed by-products derive in what is called coke. Avoiding or minimizing coke formation is of great importance since the lower the amount of deposited coke the longer the catalyst life. The rate of coke formation increases with increasing acid site density on the catalyst (Bhatia, 1990). Therefore, since HZSM5 is more acidic than Ni/CeO_2-Al_2O_3, it is probably earlier deactivated. Additionally it has been reported (de Abreu et al., 2012; Kimura et al., 2006; Tomishige et al., 2007) that ceria enhances the performance of the metal catalysts since it prevents or slows down coke formation.

In the case of the Ni/CeO_2-Al_2O_3 catalyst, when a heating rate of 20 °C min^{-1} is used, the effect of the catalyst in the liquid yield is clearly noticeable (5.4 points reduction) while it is rather slight (1.9 points reduction) when 3 °C min^{-1} is used. This is probably due to the fact that with such a slow heating rate, the vapors evolve from biomass more slowly and therefore are more intensively cracked, just thermally, both in the first and in the second reactor, and as a consequence no catalyst effect can be shown since no tar vapors are left to be catalytically cracked; the effect of the Ni/CeO_2-Al_2O_3 catalyst at 3 °C min^{-1} is just limited to a slight decrease of the aqueous phase.

Table 4.10 shows that pyrolysis gases are in all cases composed of H_2, CO, CO_2 and hydrocarbons ranging from C_1 to C_6. The main components by far are H_2, CO, CO_2 and methane.

Concerning the **effect of heating rate on gas composition**, more H_2 and less CO and hydrocarbons are obtained when the heating rate is lowered. Because of this, the HHV of the gases decreases as the heating rate is lowered, since the HHV per volume of H_2 is much lower than that of any hydrocarbon. Anyhow, the HHV of the pyrolysis gases obtained with any of the heating rates and catalysts is in the range 13-18 MJ m^{-3} which is comparable to that of town gas (18 MJ m^{-3}). It is worth mentioning that the H_2 amount is further than doubled when the heating rate is decreased from 20 to 3 °C min^{-1}. The highest amount of H_2 (46.6 vol.%) is obtained when the Ni/CeO_2-Al_2O_3 catalyst and 3 °C min^{-1} are used; additionally in these conditions no hydrocarbons greater than C_3 are obtained. This composition of gases is even better than that obtained by other authors (Griessacher et al., 2012) in the pyrolysis of olive tree cutting at 1000 °C, who obtained 19.0 vol.% of H_2 and 28.9 vol.% of CO. Therefore lower heating rates seem to favor the water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$), which converts CO in H_2 and CO_2 as well as reforming reactions which transform hydrocarbons ($C_xH_y + H_2O \rightarrow CO/CO_2 + H_2$) into CO and H_2.

Concerning the **influence of the catalysts on gas composition**, as a general rule more H_2 is obtained when any of the catalysts is used. On the contrary, the tendency of methane, CO_2 and CO is more variable, and do not follow a clear trend.

It is worth mentioning that although the zeolite has no influence on pyrolysis yields it does have influence on pyrolysis gases composition (increase in H_2 yield). Such influence is less pronounced as lower is the heating rate. Comparing the effect of both catalysts it can be seen that as far as hydrogen proportion is concerned, Ni/CeO_2-Al_2O_3 catalyst is more effective than zeolite with 3 °C min^{-1} but less with 20 °C min^{-1}.

The main conclusions drawn from the study of the influence of the pyrolysis reactor heating rates are the following:

- Concerning gas compositions, pyrolysis gases obtained with the operating conditions used in this section are valuable products which can be used either as fuel or in more worthwhile applications such as synthesis gas or reducing agent, due to its high proportion of H_2 and CO (H_2 + CO = 54-76 vol.%).
- Concerning the effect of heating rate, the use of low heating rates is very convenient for the objectives pursued in this thesis. Low heating rates increase solid and gas yields and decrease liquid yields. Moreover, the fact that with the lowest heating rate (3 °C min^{-1}) no tars are produced is a great success of this thesis. Therefore, in the subsequent experiments that were carried out throughout the thesis 3 °C min^{-1} heating rate was used.
- Concerning the effect of catalysts, it was decided to further investigate the effect of catalysts studying some more catalysts and in the case of zeolites, doping them with Ni in order to enhance their cracking and reforming performance.

A detailed description of the characteristics of the liquid and solid products obtained in this section is presented in section 4.3.4 and 4.3.5 respectively.

4.3.4. Characterization of the Pyrolysis Liquids

The characterization of the liquids obtained in all the experiments carried out in this section devoted to establish the appropriate operating conditions for biocoke production and vapors upgrading is presented next.

All the pyrolysis liquids obtained were composed of a majority aqueous phase and an organic phase (tars). The aqueous phase was a colorless transparent liquid which could be easily collected from the silicone tubing and glass devices of the condensing system. The organic phase was a tar like product that sticks to the pipes and glass devices and could not be recovered and analyzed; it was just quantified by weighing the pipes and devices before and after the experiment. As has been presented in the previous sections, the amount of tars obtained varied significantly with the operating conditions used. When very slow heating rate (3 °C min^{-1}) and high temperature (900 °C) in the upgrading reactor were used, no tars were obtained and pyrolysis liquids were composed only of the aqueous phase.

The aqueous phase was characterized including gas chromatography/mass spectroscopy (GC/MS) and ultimate analysis, following the analytical procedures explained in section 3.5.4 (page 71). The results are presented in Table 4.11. All the identified compounds included in Table 4.11 have a match quality identification provided by the MS search engine higher than 85 %. The compounds with a lower identification than rate were classified as not identified. The minor compounds group includes these products with an area% lower than 1 and detected in less than four of the liquids included in Table 4.11.

The aqueous liquids presented in Table 4.11 correspond to the experiments carried out in sections 4.3.2 and 4.3.3, which have been carried out with olives 1 (thin branches) sample and with the pyrolysis reactor at 750 °C. The heating rate used in the first reactor and the temperature and catalysts used in the second reactor for the vapors upgrading are specified in Table 4.11 for each liquid.

It can be seen that the main component of the aqueous phase is water with percentages ranging from 48 to 99 area%. There is also a very significant proportion of oxygenated compounds (all except pyridine) which are derived from the oxygenated nature of the biomass.

Concerning the **effect of the temperature** of the second reactor on the composition of the pyrolysis aqueous liquid phase, it can be seen that the carbon content decreases when temperature is increased due to the reduction of the organic content of the aqueous phase. Accordingly, the hydrogen and others (mainly oxygen) contents increase with temperature because there is more water and less organics in the aqueous phase.

Table 4.11. Ultimate analysis and GC/MS analysis of the aqueous liquid products (olives 1: thin branches sample)

		20 °C min^{-1}	20 °C min^{-1}								15 °C min^{-1}		3 °C min^{-1}		
		2nd reactor not used	600	750	900	600	750	900	900	900	900		900		
			Without catalyst			Ni/CeO$_2$-Al$_2$O$_3$			Ni/ZrO$_2$-Al$_2$O$_3$	HZSM5	Without catalyst	HZSM5	Without catalyst	HZSM5	Ni/CeO$_2$-Al$_2$O$_3$
Ultimate analysis (wt.%)	C	10.8	11.0	7.7	1.6	8.4	5.2	1.0	1.1	1.4	1.2	1.1	0.7	0.7	0.5
	H	9.7	9.7	10.1	11.1	10.4	11.2	12.4	10.9	10.6	10.9	10.7	11.0	10.8	11.6
	N	0.2	0.1	0.1	0.2	0.1	0.3	0.1	0.2	0.3	0.3	0.4	0.3	0.3	0.1
	Others[1]	79.3	79.2	82.1	87.1	81.1	83.3	86.5	87.8	87.7	87.6	87.8	88.0	88.2	87.8
Water (area%)															
with respect to liquids		48.7	48.4	52.5	92.9	55.9	61.9	93.9	94.6	94.3	95.9	95.3	99.2	99.2	99.6
with respect to biomass[2]		*13.9*	*15.8*	*15.9*	*20.6*	*15.1*	*15.5*	*18.1*	*18.4*	*22.1*	*19.7*	*20.3*	*19.5*	*18.8*	*17.7*
Identified organics (area%)															
Methyl acetate		2.3	2.1	1.7	-	0.8	0.3	-	-	-	-	-	-		-
Pyridine		-	-	0.5	-	-	0.5	0.2	-	0.4	0.5	0.5	0.3	0.2	-
2-Cyclopenten-1-one		0.7	0.8	0.6	-	0.6	0.6	-	-	-	-	-	-	-	-
Acetic acid		29.5	30.5	31.6	1.2	27.7	24.9	0.4	0.7	0.6	0.2	0.3	-	-	-
Furfural		0.9	1.2	0.7	-	0.7	0.3	-	-	-	-	-	-	-	-
Propanoic acid		1.3	1.5	1.6	-	1.6	1.5	-	-	-	-	-	-	-	-
Acetamide		-	-	-	0.4	-	-	0.4	0.2	0.6	0.4	0.6	-	-	-
Phenol		1.3	1.2	2.2	3.8	1.4	3.1	3.8	3.5	3.3	2.8	2.9	0.5	0.6	0.4
Methyl-phenol		-	-	2.0	1.1	-	2.5	0.7	0.7	0.8	0.2	0.4	-	-	-
Dianhydromannitol		1.1	1.4	1.0	0.6	1.1	0.6	-	-	-	-	-	-	-	-
Minor compounds		2.9	3.5	0.3	-	3.6	1.3	-	-	-	-	-	-	-	-
Total organics (area%)		40.0	42.2	42.2	7.1	37.5	35.6	5.5	5.1	5.7	4.1	4.7	0.8	0.8	0.4
Total identified (area%)		88.7	90.6	94.7	100.0	93.4	97.5	99.4	99.7	100.0	100.0	100.0	100.0	100.0	100.0
Not identified (area%)		11.3	9.4	5.3	-	6.6	2.5	0.6	0.3	-	-	-	-	-	-

[1] By difference; [2] Values calculated from the aqueous liquid yield and the water content of the correspondent liquid; - not detected

Regarding the water content, both the relative value with respect to liquids and the absolute value with respect to biomass increase with temperature (48-94 % and 14-18 % respectively). The increase of the water content yield with respect to biomass denotes that high temperatures generate, in absolute value, more water; this can be attributed to the fact that at higher temperature thermal cracking reactions are stronger and most of the organic liquid products are decomposed into lower molecular weight products, among them, water. It is also noteworthy the fact that there was a very significant decrease of organic compounds with temperature, consequently increasing the water content of the aqueous liquids. This may be due on the one hand to reactions among the pyrolysis gases and vapors, but on the other hand to the simple fact that if the amount of water content increases, the yield of any of the other compound had to proportionally decrease.

The main organic compound obtained at the lowest temperature is acetic acid, while at 900 °C the acetic acid proportion is minimum and phenol is the mayor compound. In fact, phenol amount in aqueous liquids increases with temperature (Yildiz et al., 2013).

Concerning the **effect of the heating rate** of the first reactor, it can be seen that the carbon content, even though is very low in the 900 °C runs, decreases when the heating rate is lowered, both when catalyst is used and when not.

The water content in the pyrolysis liquids is increased when the heating rate is lowered diminishing from ≈94 area% at 20 °C min^{-1} to more than 99 area% at 3 °C min^{-1}. Although the water content of the aqueous phase increases when heating rate decreases, since the aqueous phase yield (Table 4.10, page 109) also decreases, the absolute water yield produced with respect to the original biomass decreases when the heating rate is lowered (Table 4.11). This decrease may be attributed on the one hand to the increase of reforming reactions, which consume water, and on the other hand, as has been reported by other authors (Pütün et al., 2007), to secondary reactions such as hydration, decarboxylation and condensation that take place when long residence times are used.

The organic compounds contained in the aqueous phase decrease as the heating rate is lowered becoming almost non-existent at 3 °C min^{-1}. The decrease of the organics of the aqueous phase when lowering heating rate follows the same tendency as that observed in pyrolysis yields and in gas compositions: decrease of the organic phase (tars) and of C_3-C_6 hydrocarbons respectively. Both, tars and C_3-C_6 hydrocarbons in gases, were not obtained with the lowest heating rate. Hence, it was concluded that low heating rates not only favor cracking reactions but also reforming reactions which transform organic compounds in CO, CO_2 and H_2.

Concerning the **effect of the catalysts**, it can be seen that when 20 °C min^{-1} is used the catalysts increase the water content at 600 and 750 °C, while at 900 °C the increase is quite low. This is because at such high temperature the organic molecules are thermally cracked and there is no margin for the catalysts to show their effect. The catalyst that yielded the greatest water yield is the homemade Ni/CeO_2-Al_2O_3 catalyst, which already showed to be more effective than Ni/ZrO_2-Al_2O_3 catalyst with respect to pyrolysis yields and gas compositions.

If the liquids obtained with a single reactor at 20 °C min^{-1} are compared to those obtained with Ni/CeO_2-Al_2O_3 at 900 °C and 3 °C min^{-1}, which are the catalyst and temperature which gave the best results, it can be seen that the water content of the aqueous phase increases from 48.7 to 99.6 area%, and the organic content was very much reduced from 40.0 to 0.4 area%.

It is worth mentioning that although there are plenty of papers in the literature claiming the goodness of bio-oils obtained by pyrolysis of biomass, the quality and utility of pyrolysis liquids is almost non-existing when low heating rates (20-3 °C min^{-1}) and high pyrolysis temperatures (750 °C) are used. As a matter of fact, it has been demonstrated in this study that if very slow heating rate is used (3 °C min^{-1}) and a high temperature catalytic step is used (900 °C), the pyrolysis liquids are just water with a very low content of some organic products as phenol or pyridine.

The main conclusions that can be drawn from the characterization of the aqueous phase of the pyrolysis liquids obtained at different heating rates and with different temperatures and catalysts in the vapors upgrading reactor are the following:

- The carbon content decreases and the hydrogen and others (mainly oxygen) contents increase when the pyrolysis heating rate is lowered, the vapors upgrading temperature is increased and catalysts are used.
- The water content of the aqueous phase increases and the organics content decreases when the pyrolysis heating rate is lowered, the vapors upgrading temperature is increased and catalysts are used.
- The water content with respect to biomass increases when temperature is increased, but it decreases when the heating rate is lowered and catalysts are used, due to the lower liquid yields obtained at those conditions.
- Both the effect of low heating rates and high temperatures not only avoids tar formation, but also reduces the organics content in the aqueous fraction. With 3 °C min^{-1} and 900 °C in the second reactor no tars and almost no organics in the aqueous phase are obtained.

Although as a general rule the tars obtained in the pyrolysis experiments were not analyzed, since were obtained in a very low proportion and was very difficult to collect them, in order to get some insight of its nature, special effort was made in some experiments to collect them and analyze by GC/MS. The results are presented in Table 4.12 and correspond to two pyrolysis experiments carried out with olives 1 (thin branches) sample at 20 °C min^{-1} with the pyrolysis reactor at 750 °C and the second reactor at 900 °C and without catalyst.

Even though there are significant differences among the tars obtained at both temperatures, it can be seen that they are mainly composed of phenolic compounds, furan- and cyclopentenone- derivates and some polycyclic compounds as naphtalenes, anthracene, etc. There is also some water contained in the tars. Many of these products, such as phenol and polycyclic aromatics, are solid at room temperature, which justifies the highly viscous and sticky nature of the tars obtained.

Table 4.12. GC/MS analysis of the organic liquid products (olives 1: thin branches sample)

Identified organic compounds (area%)	Without catalyst	
	600 °C	900 °C
Water	8.4	3.2
Furfural	2.0	-
Dianhydromannitol	0.7	3.2
2-Furanmethanol	0.4	-
1-(2-furanyl)-ethanone	1.1	-
5-Methyl-2-furancarboxaldehyde	2.1	-
2-Cyclopenten-1-one	0.7	-
Methyl-2-Cyclopenten-1-one	3.1	-
2,3-Dimethyl-2-cyclopenten-1-one	1.8	-
2-Hydroxy-3-methyl-2-cyclopenten-1-one	2.0	-
3-Methyl-1,2-cyclopentanedione	1.2	-
Phenol	8.1	7.5
Methyl-phenol	23.6	10.4
2-Methoxy-phenol	1.0	-
Dimethyl-phenol	4.2	-
Ethyl-phenol	8.9	0.9
2,6-Dimethoxy-phenol	0.4	1.1
3-Ethyl-5-methyl-phenol	1.0	-
2-Methoxy-4-(1-propenyl)-,(E)-phenol	1.2	-
Trimethyl-phenol	0.9	-
1-Ethyl-4-methoxy-benzene	1.2	-
Indole	-	1.5
Naphthalene	2.2	9.7
2-Naphthalenol	-	5.0
Methyl-naphthalene	2.4	7.2
2-Ethenyl-naphthalene	-	3.9
Biphenylene	-	7.7
Fluorene	-	5.2
Phenanthrene	1.2	10.3
Anthracene	1.0	-
n-Hexadecanoic acid	1.6	3.9
Total identified organics	82.4	80.7
Not identified	17.6	19.3

- not detected

Regarding the effect of temperature Table 4.12 shows that at 900 °C much less phenolic compounds and cyclopentanone-derivates, while much more polycyclic condensed aromatics, like naphthalene-derivates, fluorene, phenantrene, anthracene, etc., are obtained. This may be due to the fact that at higher temperatures a stronger thermal cracking of pyrolysis vapors is produced, and more radicals are generated and at higher speed. These free radicals tend to stabilize capturing H^+ from nearby molecules leaving the latter H-depleted and unstable, so that they tend to combine with each other yielding products of higher aromaticity and with a greater number of rings.

If the products contained in tars are compared to those that were obtained by Py-GC/MS-FID (Table 4.3, page 88), it can be seen that they are widely different. This is because Py-GC/MS-FID is like a flash pyrolysis in which the fragments cracked from the biomass are immediately analyzed by GC/MS-FID before they suffer any kind of recombination or reaction; therefore, they contain the organic structures of biomass (guaiacols, syringols) and have a significant amount of non-aromatic compounds. On the contrary, tars have been produced in slow pyrolysis experiments, and therefore, the biomass derived fragments initially formed can be further cracked, stabilized with protons, or/and combined with other fragments, yielding gases, coke and tars. As a consequence, tars do contain neither the original structure derived from biomass (guaiacols, syringols) nor aliphatic compounds. Anyhow, Py-GC/MS-FID products and tars obviously have some common features such as the high amounts of oxygenated compounds, the high proportion of aromatics and the presence of some common products as phenol, naphthalene, cyclopentenone and furan.

Since one of the objectives of this thesis was to avoid tar promotion, and as has been proved no tars are obtained if the appropriate operating conditions and catalysts are used, the discussion of tar composition does not deserve any more discussion in this thesis.

4.3.5. Characterization of the Pyrolysis Solids (Biocokes)

The characteristics of the solids obtained in the pyrolysis experiments are obviously not influenced by the conditions (temperature or catalyst) used in the second vapor upgrading reactor. The pyrolysis solids can only be influenced by the operating conditions of the first pyrolysis reactor.

The characterization results of the solids obtained at different heating rates are presented in Table 4.13. It has to be mentioned that the solids were characterized in all the experiments, even though the conditions of the second reactor did not modify their characteristics. The results presented in Table 4.13 are the mean value of the characteristics of all the pyrolysis solids obtained at each heating rate regardless the temperature and catalyst used in the second reactor. The characterization has been performed following the analytical techniques explained in section 3.5.2 (page 65). All the results presented in Table 4.13 correspond to pyrolysis solids derived from olives 1 (thin branches) sample pyrolyzed at 750 °C.

Table 4.13. Characteristics of the pyrolysis solids obtained at different heating rates (olives 1: thin branches)

As produced basis (wt.%)		20 °C min^{-1}	15 °C min^{-1}	3 °C min^{-1}
Proximate analysis	Moisture	1.7	1.6	1.7
	Volatile matter	10.0	10.1	10.6
	Ash	9.3	10.2	9.2
	Fixed Carbon[1]	79.0	78.1	78.5
Ultimate analysis	C	84.0	81.7	84.1
	H	1.0	1.3	1.0
	N	1.1	1.3	1.2
	Others[1,2]	2.9	3.9	2.8
HHV (MJ kg^{-1})		28.3	27.1	29.0

[1]By difference; [2]Others=100-C-H-N-H_2O-Ash

Table 4.13 shows that the pyrolysis solids are mainly composed of carbon, with elemental carbon contents around 85 wt.%. The moisture content is rather low (≈1.7 wt.%), the volatiles content is quite low (≈10 wt.%) and the ash content is around 9-10 wt.% which is coherent with the ash content of the original biomass sample (which remains in the solid) and the solid yields obtained.

Table 4.13 shows that there is no influence of heating rate in the composition of pyrolysis solids. Although it is a well-known fact that decreasing heating rates intensifies the carbonization process giving rise to more carbon-rich products. This tendency is not observed in the results of Table 4.13. The reason for this may be that 20 °C min^{-1} is a heating rate slow enough to produce a well carbonized product at 750 °C, so that slower heating rates do not further promote carbonization at such temperature.

Regarding the HHV of the pyrolysis solids it can be seen that it was rather high (≈28 MJ kg^{-1}) which is in the range of the HHV of commonly used solid fossil fuels, such as bituminous coals (Centre Flow, 2011).

On view of the characteristics of olives pyrolysis solids many potential applications for them can be proposed. It can be used as a rather good quality solid fuel (high HHV, low pollutants (S, N) content and low ash contents compared to fossil fuels), or as sorbent material provided that it is firstly activated or as soil amendment agent. However, the objective of this thesis was to obtain a solid product useful as reducing agent for metallurgical purposes.

It is a well-known fact that the use of charcoal as top charge with the iron oxides burden in blast furnaces instead of bituminous coal derived coke is not possible due to the lack of compressive strength of charcoal. Therefore, the use of charcoal would only be possible in mini blast furnaces of a reduced height (Agirre et al., 2013) or replacing the reducing agents which are tuyére-injected (oil, pulverized coal, natural gas) in the lower part of the furnace to provide heat and a reducing atmosphere (Suopajärvi et al., 2013).

It has been reported that charcoals obtained by fast pyrolysis of corn cob, with ash contents ≈13 wt.% and carbon contents ≈77 wt.%, are in the range of suitable blast furnace reducing agent injected feeds (Babich et al., 2010; Suopajärvi et al., 2013).

Alternatively charcoal may be used in the non-ferrous industry where no mechanical strength is required. Agirre et al., (2013) have reported that the requirements for charcoals as chemical reducers in metal processing are fixed carbon contents ≈85 wt.% as well as volatiles content lower than 10 wt.%.

The results presented in Table 4.13 show that the biocokes obtained in this thesis are close to fulfill the requirements reported by the above mentioned authors to be used as reducing agent, either injected in iron blast furnaces, or in the non-ferrous metal industry. The use of temperatures higher than 750 °C in the first pyrolysis reactor could probably produce a charcoal with lower volatile matter and higher fixed carbon contents. However this could not be proved since 750 °C is the maximum allowable temperature of the pyrolysis reactor used in the experiments. A more thorough study of the characteristics of pyrolysis solids as reducing agents, as well as its comparison with industrial commercial reducing agents used in non-ferrous metallurgical processes is presented in section 4.6 (page 138).

4.4. Study of Catalysts for Pyrolysis Vapors Upgrading

In this section a study of the effectiveness of different catalysts for upgrading the pyrolysis vapors obtained in biocoke production is presented. This study was performed with two different biomass samples, olives 2 (thick branches) and eucalyptus. The study could not be continued with the olives 1 sample because it had come to an end and a new olives shipment, which turned out to be somewhat different to the first one, was received.

All the catalysts were tested with the operating conditions which had given the best results in the previous studies (sections 4.3.2 and 4.3.3): 750 °C and 3 °C min^{-1} in the first pyrolysis reactor and 900 °C in the second vapors upgrading reactor.

4.4.1. Comparison of Catalysts with the olives 2 (thick branches) sample

Olives thick branches were pyrolyzed using the following commercial catalysts: two zeolites (HY and HZSM5) doped with nickel and a nickel containing commercial catalyst (Katalco 57-4Q). Surface area and porosity of the fresh catalysts have been presented in section 4.2 (page 93).

The pyrolysis yields and gas compositions obtained with all the catalysts are presented in Table 4.14.

Table 4.14. Effect of the catalysts in the pyrolysis yields and gas compositions of the olives 2 (thick branches) sample

	Without catalyst	HY+Ni	HZSM5+Ni	Katalco 57-4Q
Pyrolysis yields (wt.%)				
Solids	24.0	24.4	23.6	23.8
Liquids[2]	28.0	26.5	17.9	19.2
Gases[1]	48.0	49.1	58.5	57.0
Pyrolysis gases (vol.%) and HHV (MJ m^{-3})				
H_2	34.6	37.5	49.5	47.8
CO	29.6	28.0	27.6	28.1
CO_2	19.9	17.7	13.7	13.5
CH_4	13.1	14.5	8.1	9.7
C_2H_4	0.0	0.0	0.0	0.0
C_2H_6	2.8	2.3	1.1	0.9
C3	0.0	0.0	0.0	0.0
C4	0.0	0.0	0.0	0.0
C5	0.0	0.0	0.0	0.0
C6	0.0	0.0	0.0	0.0
HHV	13.9	14.3	12.6	12.9

[1]By difference; [2]No organic phase (tars) obtained

First of all it has to be mentioned that the same as it occurred in the previous catalytic experiments, there is obviously no influence of catalysts on the solid yield. It has also to be mentioned that since a very low heating rate (3 °C min^{-1}) and high temperatures (900 °C) in the catalytic reactor are used, no tars are produced and the liquids are only composed of aqueous phase.

Concerning the influence of the catalysts in **liquid and gas yields**, Table 4.14 shows that there is an important decrease of liquid yields (≈9-10 points) and a corresponding increase in gas yields with HZSM5+Ni and with Katalco 57-4Q catalysts, but a rather low effect with the zeolite HY+Ni.

Regarding gas composition, Table 4.14 shows a similar trend. HZSM5+Ni and Katalco 57-4Q catalysts exert a significant effect increasing H_2 from 34 to 48-49 vol.% and decreasing CO, CH_4 and C_2H_6, while the effect of HY+Ni is rather slight. The decrease of CH_4 and C_2H_6 is a clear sign that catalysts promote reforming reactions (hydrocarbons + water $\leftrightarrow$ CO, CO_2 and H_2); at the same time, the increase of CO_2 and

H_2 may promote the reverse water gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) which justifies the decrease of CO_2.

The reason why HY+Ni is less effective than HZSM5+Ni and Katalco 57-4Q may be the fact that the HY zeolite has smaller average pore diameter than the other two catalysts (Table 4.5, page 94) and therefore, the greater biomass derived molecules may block the catalyst pores hindering the access of smaller molecules and reducing the efficiency of the catalyst. Another reason may be that this zeolite is even more acidic than HZSM5 (Table 3.1, page 48) and therefore may be earlier deactivated by coke deposition. It has been reported that the use of catalysts based on zeolites with high SiO_2/Al_2O_3 ratio is a suitable strategy for obtaining stable catalysts (Gayubo et al., 2011; Valle et al., 2010). These zeolites are more stable because, although they have low density of acid sites, they have a homogeneous and moderate acid strength with the enough total activity required for its catalytic activity. The zeolites used in this thesis have a SiO_2/Al_2O_3 ratio of 5.1 for HY and of 50 for HZSM5. For these materials, the SiO_2/Al_2O_3 ratio also represents a relationship between the hydrophobic character and the acidity (Ni and Meunier, 2007). Hydrophobic structures avoid the absorption of the water byproduct, which leads to deactivation. As high SiO_2/Al_2O_3 ratios correspond to a loss of the acidic properties, zeolites with high SiO_2/Al_2O_3 ratios absorb few water and are less deactivated than zeolites with low SiO_2/Al_2O_3 ratios, which easily absorb water at the surface, blocking the access to the pores (Coman and Parvulescu, 2013).

If the results obtained with olives 2 sample are compared to those obtained with olives 1 sample (Table 4.10, page 109), it can be seen that surprisingly, even though both samples come from the same vegetal specie, there are significant differences in the results. On the one hand when no catalyst is used, olives 1 gives rise to noticeable lower liquid yields and higher H_2 contents than olives 2 sample. On the other hand, the effect of the catalysts is much less pronounced with olives 1 than with olives 2 sample. Although strictly speaking, the results obtained with catalysts with both olive samples cannot be compared since not the same catalysts were tested with both samples, it is worth mentioning that the best results obtained with both olive samples, each with its most effective catalyst, are quite similar (olives 1 with Ni/CeO_2-Al_2O_3 yielded 18 wt.% liquids and 46.6 vol.% and olives 2 with HZSM5+Ni yielded 17.9 wt.% liquids and 49.5 vol.% H_2).

On view of these results, a rigorous comparison of the effectiveness of the catalysts tested in this section with those tested with olives 1 sample (section 4.3.3, page 108) cannot be obviously done.

Supplementary tests with the olives 2 sample testing again the Ni/CeO_2-Al_2O_3 and HZSM5 catalysts could neither be carried out since this sample came also to an end. Therefore, it was decided to test again all those catalysts, which based on the results obtained with olives 1 and olives 2 samples, considered more promising with a new homogeneous and abundant enough sample, the eucalyptus sample. The results are presented in the following section.

4.4.2. Comparison of Catalysts with the eucalyptus sample

This section is devoted again to a comparative study of the effect of catalysts in biomass pyrolysis but now using the eucalyptus sample. Those catalysts that were considered more promising in the previous studies were again tested and compared.

Based on the results of the previous sections, the catalysts that were not included in this study were the Ni/ZrO_2-Al_2O_3 catalyst, since it proved to be similar to the homemade Ni/CeO_2-Al_2O_3 catalyst but it gave worse results (section 4.3.2, page 103), and the HY+Ni zeolite, since it proved to have rather poorer effectiveness than the other catalysts tested with the olives 1 (thin branches) sample (section 4.4.1, page 123).

The catalysts tested in this section were HZSM5 zeolite with and without Ni, in order to evaluate the beneficial effect of nickel, the Ni/CeO_2-Al_2O_3 catalyst prepared in our laboratories, and the commercial steam reforming catalyst Katalco 57-4Q. The textural characterization of these fresh catalysts has been presented in section 4.2 (page 93).

As in the previous study of the catalysts, the pyrolysis experiments were carried out with 3 °C min^{-1} heating rate and at 750 °C the first reactor and 900 °C the catalytic reactor. The pyrolysis yields and gas compositions obtained in the tests are presented in Table 4.15.

Table 4.15. Effect of the catalysts in the pyrolysis yields and gas compositions of the eucalyptus sample

	Without catalyst	HZSM5	HZSM5+Ni	Katalco 57-4Q	Ni/CeO_2-Al_2O_3
Pyrolysis yields (wt.%)					
Solids	26.0	26.0	26.1	26.3	26.0
Liquids[2]	31.0	29.8	26.2	25.8	24.7
Gases[1]	43.0	44.2	47.7	47.9	49.3
Pyrolysis gases (vol.%) and HHV (MJ m^{-3})					
H_2	28.0	34.8	42.6	43.4	45.2
CO	30.7	26.7	25.6	28.2	26.7
CO_2	22.9	22.9	20.4	17.8	17.5
CH_4	14.6	12.4	9.5	9.1	8.9
C_2H_4	0.3	0.3	0.1	0.0	0.0
C_2H_6	3.3	2.5	1.6	1.4	1.4
C3	0.1	0.1	0.0	0.0	0.0
C4	0.0	0.1	0.0	0.0	0.0
C5	0.0	0.0	0.0	0.0	0.0
C6	0.1	0.2	0.2	0.1	0.3
HHV	14.6	14.0	12.7	12.6	12.9

[1]By difference; [2]No organic phase obtained

First of all, it has to be mentioned that as in the previous study of catalysts with the olives 2 (thick branches) sample, the solid yields are obviously not affected by the catalysts, and that the liquid products are only composed of aqueous phase (no tars) since a low heating rate (3 °C min^{-1}) in the pyrolysis reactor and a high temperature (900 °C) in the catalytic reactor were used.

Concerning pyrolysis yields, once more it can be seen that the catalysts decrease liquid yields and increase gas yields, and regarding gas composition, the effect is to promote hydrogen formation while CO, CO_2, CH_4 and C_2H_6 decrease. The most effective catalyst, as far as both pyrolysis yields and gas compositions is concerned, is the homemade Ni/CeO_2-Al_2O_3 catalyst followed by the commercial Katalco 57-4Q catalyst, and this one closely followed by the HZSM5+Ni zeolite. The least effective catalyst is the HZSM5 zeolite, which shows a noticeable lower effect than the Ni added zeolite. Therefore it is demonstrated that doping the HZSM5 zeolite with nickel is beneficial for reducing liquid yields and for upgrading (H_2 increasing) the biomass pyrolysis gases.

The zeolite is more acidic than the other catalysts used in this study. Therefore, it has a great tendency to deactivate by the deposition of coke. The modification of zeolites with nickel is a suitable strategy for obtaining stable catalysts (Valle et al., 2010). The addition of nickel to the zeolite partially reduces its acidity because the nickel replaces some of the protons of the zeolite. Therefore, the deactivation tendency may be somewhat reduced. This may be the reason why the performance of the zeolite with nickel is better than that of the zeolite alone.

Comparing the results obtained with the olives 2 (thick branches) sample (Table 4.14, page 124) and with the eucalyptus sample, it can be seen that, both with and without catalysts, the eucalyptus sample yields more solids and liquids and less gases than the olives 2 sample. Concerning the effect of catalysts, there are some differences. On the one hand, with olives 2 sample HZSM5+Ni was somewhat more effective than Katalco 57-4Q. On the other hand, the liquid yield reduction caused by the above mentioned catalysts (HZSM5+Ni and Katalco 57-4Q) was more pronounced with the olives 2 sample (≈9-10 points) than with the eucalyptus sample (≈5 points), while the H_2 increase was similar with both biomass samples (≈15-15 points).

The main conclusions that can be drawn from the comparative study of the effect of catalysts are the following:

- The most effective catalyst is the homemade Ni/CeO_2-Al_2O_3 catalyst, closely followed by Katalco 57-4Q and HZSM5+Ni.
- The addition of Ni to HZSM5 zeolite enhances its effectiveness for biomass vapors upgrading.
- There are significant differences among the results obtained with the different lignocellulosic biomass samples, not only between different species (olives vs. eucalyptus) but also between different shipments or parts of the very same species (olives 1 vs. olives 2). Therefore, it was decided to carry out a study, which is presented in the following section, to compare all the biomass samples and try

to draw conclusions concerning the influence of the type of biomass. Since both the olives 1 and olives 2 samples had come to an end a new olives sample was acquired (olives 3). The results obtained with this third sample will also be discussed in the following section.

4.5. Comparison of the pyrolysis results of the different biomass samples

In this section a comparison of the pyrolysis results obtained with six different olives samples as well as with the eucalyptus sample is presented. Additionally, one of the olives sample was tested both dry and with its original moisture. As has been previously mentioned, the reason for carrying out this study was that it had been observed that there were significant differences between the pyrolysis yields obtained with the different olives samples shipments received in our laboratory, even they came from the same origin. Therefore, the objective of this study was to evaluate such differences and try to find out the reasons for their occurrence.

4.5.1. Dry versus moist olives samples

All the pyrolysis experiments carried out in this thesis (except the few fast runs described in section 4.3.1, page 95) can be categorized as slow pyrolysis experiments. It was observed that in all the experiments the liquids were composed of a majority aqueous phase and that this phase was much greater than the original moisture of the biomass sample, so some water was formed during the pyrolysis process. Therefore, with the operating conditions used in this thesis (slow high temperature pyrolysis), which aim to obtain metallurgical grade biochar, the liquids obtained are a useless product mainly composed of water. For this reason, it was considered that if moisture were eliminated from the original biomass, very few liquid products would be obtained. That is why it was decided to carry out pyrolysis experiments with a sample of dry biomass.

The experiment was carried out with the olives 1 (thin branches), 3 °C min^{-1}, 750/900 °C and the Ni/CeO_2-Al_2O_3 catalyst. The pyrolysis yields obtained with the dry and the original olives 1 sample are presented in Table 4.16. Since all the pyrolysis experiments of this thesis were carried out with 100 g of sample, the dry sample was prepared starting from 100 grams of the original sample and drying it overnight at 105 °C. The amount of dried sample which was pyrolyzed was 91.2 g. The pyrolysis yields of the original sample, calculated in dry basis, have also been included in Table 4.16.

Table 4.16. Effect of the moisture content in the pyrolysis yields

	Original sample (8.8 wt.% moisture)		Dry sample
	As pyrolyzed basis	Dry basis	(as pyrolyzed basis)
Pyrolysis yields (wt.%)			
Solids	24.6	27.0	27.8
Liquids[2]	17.8	9.9	20.4
Gases[1]	57.6	63.1	51.8
Pyrolysis gases (vol.%) and HHV (MJ m^{-3})			
H_2	46.6		44.3
CO	29.3		34.1
CO_2	13.4		10.3
CH_4	9.6		10.2
C_2H_4	0.0		0.0
C_2H_6	1.1		1.1
C3	0.0		0.0
C4	0.0		0.0
C5	0.0		0.0
C6	0.0		0.0
HHV (MJ m^{-3})	13.0		13.5

[1] *By difference;* [2] *No organic phase obtained*

The liquid yield obtained with the original biomass was 17.8 wt.% and was only composed of aqueous phase. Since the original sample has a moisture content of 8.8 wt.% a liquid yield of about 9.9 wt.% [(17.8-8.8)/(100-8.8)] was expected for the dry biomass. Surprisingly the liquid yield obtained was much higher (20.4 wt.%).

Several approaches have been considered to understand these results. On the first place, it was considered that it could be possible that the original moisture was not condensed with the pyrolysis liquids, and it evolved as vapor in the first stage of the process and is collected with the pyrolysis gases in the plastic bags. Therefore, the amount of water vapor that can be contained in the gases at ambient temperature was estimated: it was assumed that it is an ideal gas and follows the ideal gas law ($P_{H2O}·V=n_{H2O}·R·T$). The saturation pressure at 20 °C is 0.02 atm, so the saturation limit of the water would be 0.015 g L^{-1}. The size of the plastic bags used to collect the pyrolysis gases is 25 L, and assuming that all the moisture is collected in the first gas-bag, the maximum amount of water in the plastic bag would be just 0.37 g. Water contents higher than 0.37 g would imply the condensation of water drops inside the plastic bags and this was not observed. Since 100 g of biomass which contained 8.8 wt.% moisture were pyrolyzed, it is obvious that such a high amount is not contained in the gas product. A second approach was to consider that the moisture could be retained in the active carbon column of the pyrolysis installation; however the weight increase of the carbon column with the original biomass was 3.70 g while with the dry biomass was 2.75 g. Therefore, this reasoning neither justifies that the moisture of the sample were not collected with the liquid pyrolysis products.

So, the conclusion is that the moisture of the biomass sample ends mixed with the pyrolysis liquids or is involved in pyrolysis reactions. As a matter of fact, on view of the results of Table 4.16 (dry biomass liquid yield > original biomass liquid yield dry basis), it may be concluded that since the biomass moisture is present from the beginning of the process, it participates in reactions with the biomass derived vapors and gases formed in the initial stages of the process, while when dry biomass is pyrolyzed, the reactions that involve water molecules, such as reforming reactions or water gas shift reactions, only take place at later stages of the process when pyrolytic water has been formed. Moreover, the fact that in some stages of the process there is no water available for water consuming reactions, equilibriums may shift towards water generation.

As a matter of fact, Table 4.16 shows that the gases obtained with the moist sample contains more H_2 and less CH_4 than those obtained with the dry sample, which may be attributed to the production of the water gas shift reaction to a further extent ($CH_4 + H_2O \rightarrow CO/CO_2 + H_2$).

However, this reasoning is yet to be definitively proved. It has not been possible to find in the scientific literature any clarifying reference to prove or explain this anomalous behavior of water in the dry/moist biomass pyrolysis experiments carried out in this thesis.

4.5.2. Comparison of the different olives derived samples and the eucalyptus sample

In this section a comparison of the behavior in pyrolysis of all the biomass samples studied in this thesis is presented. The samples included are the eucalyptus sample and six olive samples, three coming from three different shipments (olives 1, 2 and 3) and the other three derived from the olives 3 sample, by manual screening to separate soil, twigs and leaves.

Table 4.17 summarizes the pyrolysis yields and gas compositions obtained with all the samples pyrolyzed at 3 °C min^{-1} and 750 °C and treating the vapors at 900 °C without catalyst.

Table 4.17 shows that the amount of pyrolysis solids is in the range 24-26 wt.% for all the samples, except for the olives 3 (twigs + leaves + soil) sample (32.7 wt.%), for which is significantly higher due to the greater ash content of this sample. Olives 3.3 (leaves) sample, which present also a high ash content in their initial composition (Table 4.1, page 81), does not yield more solid fraction than the other samples, so if the solid ash free yields were considered, the olives 3.3 sample would yield the lowest solid fraction. This may be because leaves have the lowest lignin content of the studied samples in this thesis, and it has been reported that lignin gives raise to higher char yields than carbohydrates (cellulose and hemicellulose) (Cagnon et al., 2009; Demirbas, 2004). Besides, the leaves sample also has the highest extractives content, which contain many aliphatic compounds (waxes, fats, proteins, oils, etc.), that have no tendency to carbonize. The greatest char yields are obtained with olives 1 (thin branches) and eucalyptus (26 wt.%).

Table 4.17. Pyrolysis yields and gas compositions of the different biomass samples

	Olives 1 Thin Branches	**Olives 2** Thick Branches	**Olives 3** Twigs + Leaves + Soil	**Olives 3.1** Twigs + Leaves	**Olives 3.2** Twigs	**Olives 3.3** Leaves	**Eucalyptus**
Pyrolysis yields (wt.%)							
Solids	26.1	24.0	32.7	24.7	24.4	24.0	26.0
Liquids	19.7	28.1	23.1	27.0	26.9	27.3	31.1
Gases[1]	54.2	47.9	44.2	48.3	48.7	48.7	42.9
Pyrolysis gases (vol.%) and HHV (MJ m^{-3})							
H_2	40.8	34.6	39.1	40.6	37.2	38.4	28.0
CO	27.3	29.6	24.9	18.2	28.0	21.7	30.7
CO_2	17.0	19.9	18.5	21.7	19.3	18.6	22.9
CH_4	12.1	13.1	13.8	15.2	12.6	16.0	14.6
C_2H_4	0.0	0.0	0.0	0.0	0.0	0.0	0.3
C_2H_6	2.7	2.8	3.7	4.3	2.9	5.3	3.3
C3	0.0	0.0	0.0	0.0	0.0	0.0	0.1
C4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C6	0.1	0.0	0.0	0.0	0.0	0.0	0.1
HHV (MJ m^{-3})	14.0	13.9	14.6	14.9	13.9	15.9	14.6

[1] *By difference*

All the pyrolysis liquid yields are in the range of 26-28 wt.% except olives 1 (thin branches), which present an unexpected lower liquid yield (19.7 wt.%), eucalyptus, which shows a somewhat higher liquid yield (31.1 wt.%), and olives 3 (twigs + leaves + soil) sample, which has a somewhat lower liquid yield (23.1 wt.%). The highest liquid yield of the eucalyptus may be attributed to the highest lignin content of this sample, since in the pyrolysis process, lignin molecules are reduced to heavy organic compounds that condense to liquids or char, while, on the contrary, hemicellulose generates lighter molecules, among them gases. On the other hand, it has to be mentioned that no explanation has been found to justify the low liquid yield obtained with the olives 1 sample. The lower liquid yield of the olives 3 sample is not real since due to the higher ash content of this sample, and the consequently greater solid yield, both liquid and gas yields seem lower. However, if the yields were analyzed on ash free basis, the results would be similar to those obtained with the other woody olives samples.

Regarding gas yields, Table 4.17 shows that they are around 48 wt.% with the same two exceptions considered for liquid yields. This time olives 1 (thin branches) presents the highest gas yield (54.2 wt.%) and eucalyptus the lowest gas yield (43.0 wt.%). Olives 3 sample also has a comparatively low gas yield (44.0 wt.%).

Concerning the influence of the type of biomass on gas composition, the most worth mentioning facts are the following: (1) the eucalyptus pyrolysis gases contain less H_2 than the other gases, which may be attributed to the fact that the eucalyptus sample contains the lowest H content and a significantly lower H/C ratio than the other samples, and (2) the olives 3.3 (leaves) sample gives rise to the highest methane and ethylene yields. This may be because leaves have somewhat different composition and nature compared to the other wood samples: they have the lowest C/N ratio, which entails that it is more easily degradable, and it has by far the highest extractives content; it has been reported (Mészáros et al., 2007) that among the extractives some of them evolve at lower temperatures than cellulose and lignin derived products and give rise to additional products, therefore it is plausible that more light products derived from extractives, such as methane and ethylene are formed at the beginning of the pyrolysis process.

Concerning higher heating values, most of them are ≈14 MJ m^{-3}, except olives 3.3 (leaves) which has a somewhat higher HHV that is due to its higher methane content.

The proximate and ultimate analyses of the pyrolysis biocokes produced with the different biomass samples are presented in Table 4.18 in an ash free (af) basis and in an as produced (ap) basis in Table 4.19. The characterizations data are reported in the both mentioned basis in order to better discuss the results.

Table 4.18 shows that the biocokes derived from olives 3 (twigs + leaves + soil) and olives 3.3 (leaves) samples differ significantly from the rest of the samples. Both samples have the highest ash content, which is due to the high ash contents of the corresponding original samples. These high ash contents are the cause of the low fixed carbon and elemental carbon contents, as well as the low HHV of the biocokes derived from such samples. This is rather inconvenient for the use of biocokes as metallurgical reducing agents, not only because of its lower HHV and carbon content, but also because it introduces different ash elements that can be detrimental for the metallurgical process.

In order to evaluate the characteristics of the real biocokes produced avoiding the distortion that the ash content causes in the analytical data, all the results included in Table 4.19 (ash free) should be considered.

Table 4.18. Proximate and ultimate analyses of the different biomass samples (as produced basis)

As produced basis (wt.%)		**Olives 1** Thin branches	**Olives 2** Thick branches	**Olives 3** Twigs + Leaves + Soil	**Olives 3.1** Twigs + Leaves	**Olives 3.2** Twigs	**Olives 3.3** Leaves	**Eucalyptus**
Proximate analysis	Moisture	1.7	1.7	1.3	1.6	2.5	0.2	1.4
	Volatile matter	10.6	8.3	9.6	10.5	10.5	13.3	8.0
	Ash	9.2	3.6	37.2	8.7	5.2	19.2	5.3
	Fixed Carbon[1]	78.5	86.4	51.9	79.2	82.1	67.3	85.3
Ultimate analysis	C	84.1	88.7	55.8	84.2	88.1	69.3	89.6
	H	1.0	1.0	0.9	1.1	1.2	1.3	1.0
	N	1.2	0.9	1.1	1.4	0.8	2.0	0.8
	Others[1, 2]	2.8	4.1	3.7	3.0	2.2	8.0	1.9
HHV (MJ kg^{-1})		29.0	31.7	18.7	29.1	30.5	24.5	31.2

[1]By difference; [2]Others=100-C-H-N-H_2O-Ash

Table 4.19. Proximate and ultimate analyses of the different biomass samples (ash free basis)

Ash free basis (wt.%)		**Olives 1** Thin branches	**Olives 2** Thick branches	**Olives 3** Twigs + Leaves + Soil	**Olives 3.1** Twigs + Leaves	**Olives 3.2** Twigs	**Olives 3.3** Leaves	**Eucalyptus**
	Ash (ap)	9.2	3.6	37.2	8.7	5.2	19.2	5.3
Proximate analysis	Moisture	1.9	1.8	2.1	1.8	2.6	0.2	1.5
	Volatile matter	11.6	8.6	15.3	11.5	10.8	16.5	8.5
	Fixed Carbon[1]	86.5	89.6	82.6	86.7	86.6	83.3	90.0
Ultimate analysis	C	92.6	92.0	88.9	92.2	92.9	85.8	94.7
	H	1.1	1.1	1.4	1.2	1.3	1.6	1.0
	N	1.3	0.9	1.8	1.5	0.8	2.5	0.8
	Others[1, 2]	3.1	4.2	5.8	3.3	2.4	9.9	2.0
HHV (ap) (MJ kg^{-1})		29.0	31.7	18.7	29.1	30.5	24.5	31.2

[1]By difference; [2]Others=100-C-H-N-H_2O

Biocokes have a fixed carbon content in the range of 86.5-90.9 wt.% and a volatile matter content in the range of 8.5-11.6 wt.% (except those derived from olives 3 and olives 3.3 (leaves) samples). These ranges are quite close to the requirements for charcoals to be useful as reducing agent in metallurgical processes (Griessacher et al., 2012). So it is concluded that in order to obtain a metallurgical grade biochar, on the one hand the contamination of biomass with inorganics such as soil or dirt should be avoided, and on the other hand the leaves content should be reduced as much as possible.

Concerning the ultimate analysis, the elemental carbon follows a similar tendency as that of the fixed carbon. For the rest of the elements, the results are quite similar in most of the samples; it only stands out the olives 3.3 (leaves) derived char, which is the one richest in hydrogen and also in nitrogen, as was expected considering the elemental compositions of the original samples (Table 4.1, page 81). The nitrogen content, of the biocokes is higher than that of the original biomass samples. Comparing both N contents (biomass vs. biocokes) it can be inferred that most of the N remains in the pyrolysis solids.

Olives 2 (thick branches) and eucalyptus samples have the highest fixed carbon amounts. These are also the samples with the lowest volatile matter contents, and the highest HHV.

Therefore, the best quality biocokes, as far as both fixed carbon and elemental carbon are concerned, are obtained with olives 2 (thick branches) and eucalyptus samples since both are clean wood samples without soil and leaves, and with little bark content.

4.6. Pyrolysis solids as reducing agents: comparison with commercial reducing agents

Since one of the objectives of this thesis was to produce a high grade biochar able to substitute reducing agents in the metallurgical industry, in this section a study of the characteristics of the pyrolysis solids focused on the suitability to be used as reducing agents is presented.

As has been previously mentioned in section 4.3.5 (page 120), biomass derived cokes have no mechanical strength and therefore cannot be used in blast furnaces as top charge, but as has been reported by other authors, they can be used as reducing agent injected at the bottom of the furnaces in replacement of fossil fuel reducers (pulverized coal, oil, etc.) (Suopajärvi et al., 2013). Alternatively, they can be used as reducers in rotary kilns for non-ferrous materials recycling such as Zn or Cu recycling processes. In this section, the characteristics of pyrolysis solids are compared to those of commercial reducing agents used in the Zn recycling Waelz process. The commercial reducers tested were metallurgical coke, petroleum coke and anthracite, which were provided by Befesa Zinc Aser S.A. (a company belonging to Befesa Steel R&D S.L.) located in Erandio (Biscay – Spain).

In this section, the chemical composition, the surface area and porosity, and the CO_2 reactivity measurements of the commercial reducers and of the biomass derived reducers are presented.

4.6.1. Proximate and ultimate analysis

In this section, the proximate and ultimate analyses of the commercial reducing agents and of two of the biocokes obtained in this thesis are discussed. The detailed specifications that Befesa Zinc Aser S.A. requires from their providers of reducing agents are presented in Table 4.20. The specifications in dry basis which are also included in the table, have been calculated considering that the moisture content were

20 wt.%, which is the maximum allowable moisture specified by Befesa; these data in dry basis reflect the allowable values if the sample did not contain moisture.

Table 4.20. Quality requirements for process materials analyzed in laboratory. Befesa Zinc Aser S.A. 2013

Material	Parameter	Befesa Zinc Aser technical specifications (wt.%)	Specifications in dry basis (wt.%)[1]
Metallurgical coke	Granulometry	> 10 mm: ≤ 20 % < 2 mm: ≤ 40 % on daily sample	
	Dry ashes	≤ 20 % on monthly sample	≤ 20 %
	Moisture	≤ 20 % on daily sample	
	Volatile matter	≤ 7 % on monthly sample	≤ 8.75 %
	Sulfur	≤ 3 % on monthly sample	≤ 3.75 %
Petroleum coke	Granulometry	< 2 mm: > 30 % > 10 mm: ≤ 20 % on diary sample	
	Dry ashes	≤ 20 % on monthly sample	≤ 20 %
	Moisture	≤ 20 % on daily sample	
	Volatile matter	≤ 15 % on monthly sample	≤ 18.75 %
	Sulfur	≤ 3 % on monthly sample	≤ 3.75 %
Anthracite	Granulometry	< 2 mm: > 30 % > 10 mm: ≤ 20 % on diary sample	
	Dry ashes	≤ 20 % on monthly sample	≤ 20 %
	Moisture	≤ 20 % on daily sample	
	Volatile matter	≤ 7 % on monthly sample	≤ 8.75 %
	Sulfur	≤ 3 % on monthly sample	≤ 3.75 %

[1] *Calculated assuming that the moisture content was 20 wt.%*

Table 4.21 presents the characterization of the commercial reducing agents. For comparative purposes and for the sake of reduction, this table only includes the compositions of the two biocokes that presented more promising results as bioreducers, which as has already been indicated in section 4.4.2 (page 126), are olives 2 (thick branches) and eucalyptus biocokes, both obtained at 750 °C and with 3 °C min^{-1} heating rate. For better analyzing the results, the Befesa specifications have been included in brackets in Table 4.21.

Table 4.21. Proximate and ultimate analyses of the commercial reducers and two of the bioreducers obtained in this thesis (as received basis)

As received basis (wt.%)		Commercial reducers			Bioreducers	
		Metallurgical coke	Petroleum coke	Anthracite	Olives 2 Thick branches	Eucalyp.
Proximate analysis	Moisture	11.4 *(<20)*	6.4 *(<20)*	18.0 *(<20)*	1.7	1.4
	Volatile matter	3.5 *(<7)*	9.4 *(<15)*	5.9 *(<7)*	8.3	8.0
	Ash	11.0	1.8	9.2	3.6	5.3
	Fixed carbon^1	74.1	82.2	66.9	86.4	85.3
Ultimate analysis	C	74.8	78.1	71.0	88.7	89.6
	H	1.7	3.3	2.5	1.0	1.0
	N	0.9	1.2	0.8	0.9	0.8
	S	0.8 *(<3)*	5.2 *(<3)*	0.5 *(<3)*	<0.05	<0.05
	Others^{1,2}	10.4	3.9	7.2	4.1	1.9
HHV (MJ kg^{-1})		26.0	33.6	25.5	31.7	31.2

^{1}*By difference;* ^{2}*Others includes ashes; (#) Befesa specifications*

Table 4.22. Proximate and ultimate analyses of the commercial reducers and two of the bioreducers obtained in this thesis (dry basis)

Dry basis (wt.%)		Commercial reducers			Bioreducers	
		Metallurgical coke	Petroleum coke	Anthracite	Olives 2 Thick branches	Eucalyp.
Proximate analysis	Volatile matter	3.9 (<8.75)	10.1 (<18.75)	7.2 (<8.75)	8.4	8.1
	Ash	12.5 (<20)	2.0 (<20)	11.2 (<20)	3.7	5.4
	Fixed carbon^1	83.6	87.9	81.6	87.9	86.5
Ultimate analysis	C	84.4	83.5	86.6	90.2	90.9
	H	0.5	2.8	0.6	1.0	1.0
	N	1.0	1.3	1.0	0.9	0.8
	S	0.9 (<3.75)	5.6 (<3.75)	0.6 (<3.75)	<0.05	<0.05
	Others^1	0.8	4.9	0.0	4.2	1.9
HHV (MJ kg^{-1})		29.3	35.9	31.1	32.2	31.6

^{1}*By difference; (#) Befesa specifications*

First of all, it has to be mentioned that although the commercial reducers were provided by Befesa Zinc Aser S.A. itself, one of them (petroleum coke) does not totally fulfill the quality requirements specified by Befesa since it contains more sulfur (5.6 wt.%) than that specified one in Table 4.20 (< 3 wt.%). Secondly, it is a significant fact the high moisture contents of the commercial reducers. Such contents do for sure not correspond to the natural inherent moisture of these materials, but it must be accidental moisture incorporated to the sample during the transport and/or storage. As a matter of fact, water drops were able to be seen in the containers in which were provided the commercial reducers. Therefore, in order to more fairly compare the intrinsic properties of the commercial and the biomass derived reducers, regardless of the moisture content, the proximate and ultimate analyses in dry basis are presented in Table 4.22.

Comparing the results (ar basis) of the commercial reducers and the bioreducers, the following advantages of the bioreducers can be mentioned:

- The bioreducers have much lower moisture contents than any of the commercial reducers.
- The bioreducers have significantly lower ash contents than the metallurgical coke and the anthracite.
- The bioreducers have significantly lower sulfur contents than any of the commercial reducers.
- The bioreducers have higher fixed carbon and elemental carbon contents than any of the commercial reducers.

The only somewhat critical aspect of the bioreducers is that they have a volatiles content that does not meet the specifications of metallurgical coke and anthracite, though it does meet the petroleum coke specification.

If the results on dry basis are compared, it can be seen that on the one hand, the fixed carbon and elemental carbon contents of the commercial reducers are much closer to those of the bioreducers. On the other hand, the volatiles contents of the bioreducers now do meet the corrected volatiles specifications of all the commercial reducers.

Therefore, it can be concluded that as far as composition is concerned, the olives 2 and eucalyptus derived reducers can replace the commercial reducers with the great advantage of having much lower ash and sulfur contents.

4.6.2. Real density, specific surface area and porosity measurements

In this section the real density, specific surface area and porosity of all the pyrolysis solids obtained in this thesis are presented. Such parameters were determined according to the analytical techniques explained in section 3.5.2.4 (page 65). The results have been organized in three subsections. In the first one, the biocokes obtained at different heating rates and temperatures are compared. The second one includes the biocokes obtained at 750 °C and 3 °C min^{-1} from all the different biomass samples tested in this thesis, and in the third subsection, the commercial reducing agents are compared to the two biocokes considered most promising based on the results of section 4.5.2 (olives 2 and eucalyptus).

4.6.2.1. Biocokes obtained at different heating rates and temperatures

In Table 4.23 and Figure 4.4, the results obtained in the textural characterization of the pyrolysis solids obtained with olives 1 (thin branches) and eucalyptus samples at 750 °C and with different heating rates are presented.

Table 4.23. Effect of heating rate in textural characterization of the biocokes obtained at 750 °C from the olives 1 and eucalyptus samples

	Heating rate (°C min^{-1})	Real density (g cm^{-3})	Micropore volume (cm^{3} g^{-1})	Micropore equivalent surface area (m^{2} g^{-1})
Olives 1 Thin branches	20	1.926	0.16	375
	15	1.867	0.15	362
	3	1.871	0.15	363
Eucalyptus	20	1.849	0.20	476
	3	1.830	0.21	501

The CO_2 adsorption isotherms presented in Figure 4.4 show the CO_2 volume adsorbed (cm^{3} g^{-1}) against the relative pressure (P/P_0). The CO_2 adsorption isotherms are clearly of Type I that are typical of microporous materials. Although there is some controversy, it is frequently considered that the micropores volume determined by CO_2 adsorption corresponds to narrow micropores (< 0.7 nm). The pore size distributions of the biocoke samples calculated by NL-DFT method are presented in Figure 4.5, which show that the biocokes do not have micropores greater than such size, therefore, the micropores volume determined corresponds to the total pores volume.

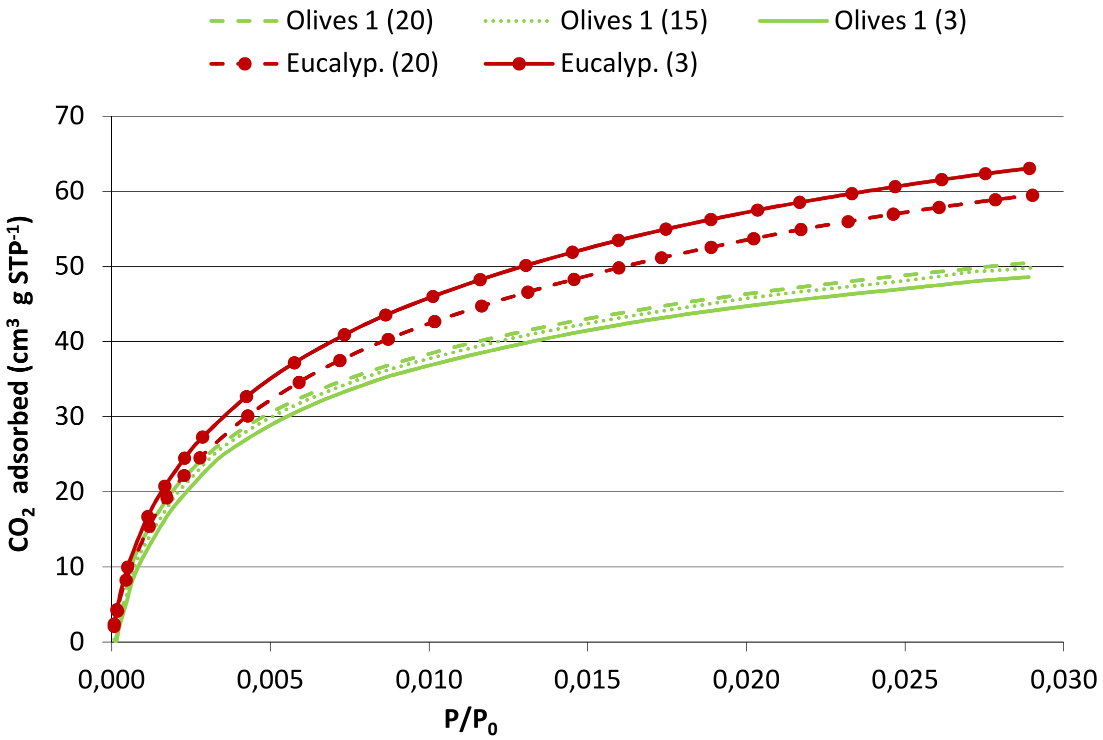


Figure 4.4. Effect of heating rate on CO_2 *adsorption isotherms of the biocokes obtained at 750 °C from the olives 1 and eucalyptus samples*

Concerning the **effect of the heating rate**, Table 4.23 as well as Figure 4.4 and Figure 4.5, show that there is not a clear influence of heating rate on the textural properties. Considering olives 1 results it seems that the real density, micropore volume and surface area somewhat decreases with the decrease in the heating rate, but in the case of the eucalyptus sample the density also decreases but the micropore volume and surface area somewhat increase. It has been reported that the longer the char residence time, the greater its surface area (Dutta et al., 2012; Hasan Khan Tushar et al., 2012). This has not been the case in this thesis, which may be due to the fact that 20 °C min^{-1} is a low enough heating rate under which no further increase in surface area is produced.

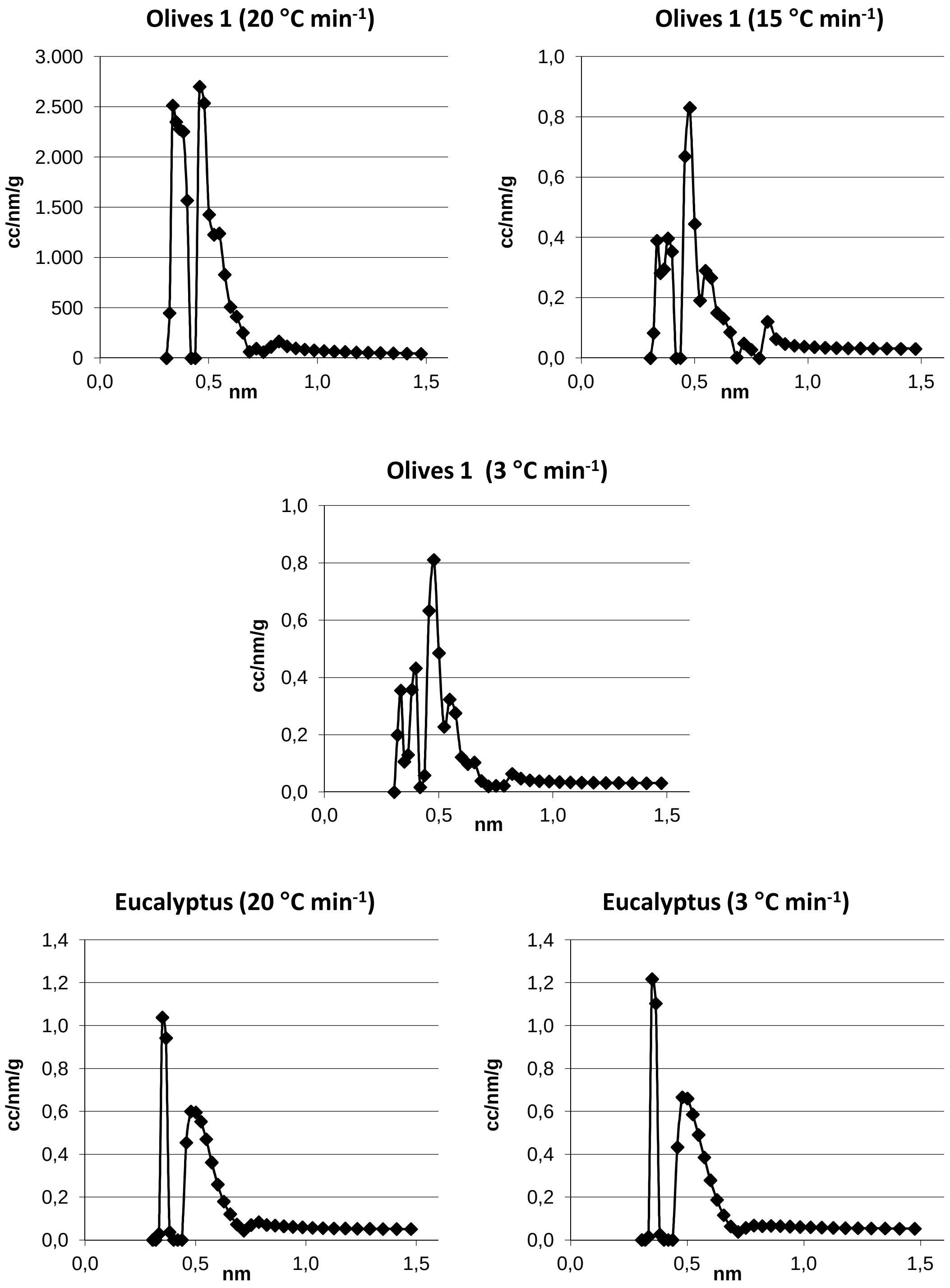


Figure 4.5. Effect of heating rate in pore size distribution of the biocokes obtained at 750 °C from the olives 1 and eucalyptus samples

In Table 4.24, Figure 4.6 and Figure 4.7, the results obtained in the textural characterization of the pyrolysis solids obtained with olives 1 (thin branches) and eucalyptus samples at 20 °C min^{-1} and different pyrolysis temperatures are presented.

Table 4.24. Effect of the temperature in the textural characterization of the biocokes obtained at 20 °C min^{-1} from olives 1 and eucalyptus samples

	Temperature (°C)	Real density (g cm^{-3})	Micropore volume (cm^3 g^{-1})	Micropore equivalent surface area (m^2 g^{-1})
Olives 1 Thin branches	600	1.669	0.15	360
	750	1.926	0.16	375
Eucalyptus	600	1.622	0.19	444
	750	1.849	0.20	476

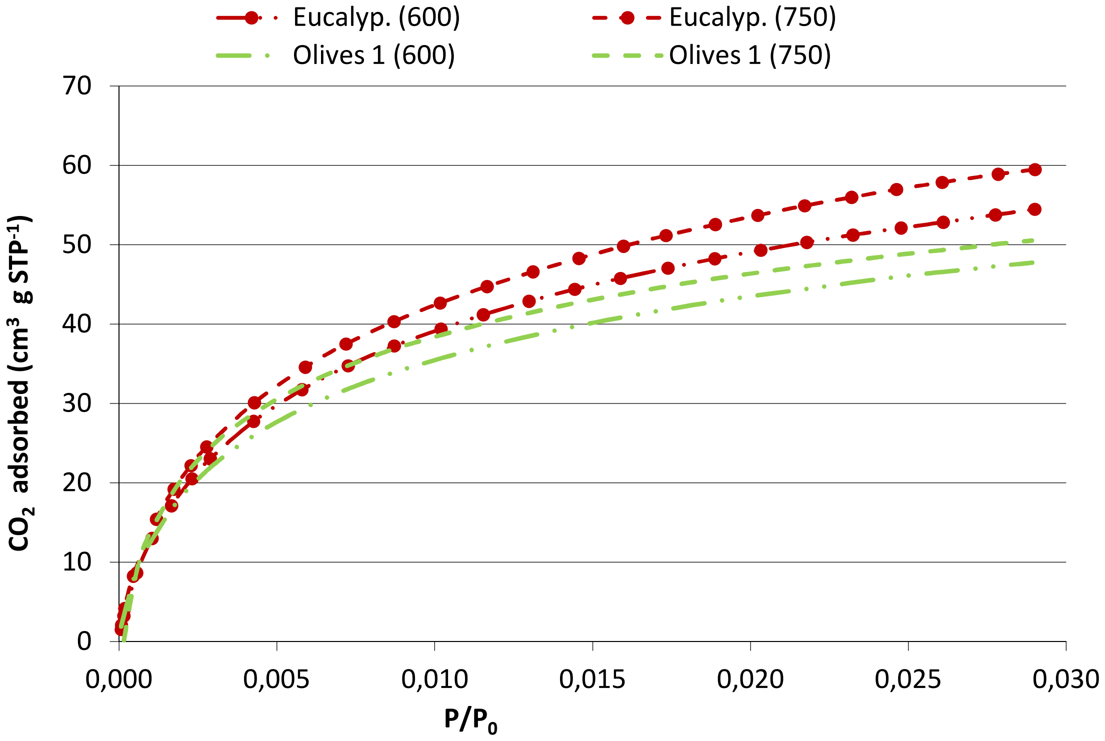


Figure 4.6. Effect of temperature on CO$_2$ adsorption isotherms of the biocokes obtained at 20 °C min^{-1} from olives 1 and eucalyptus samples

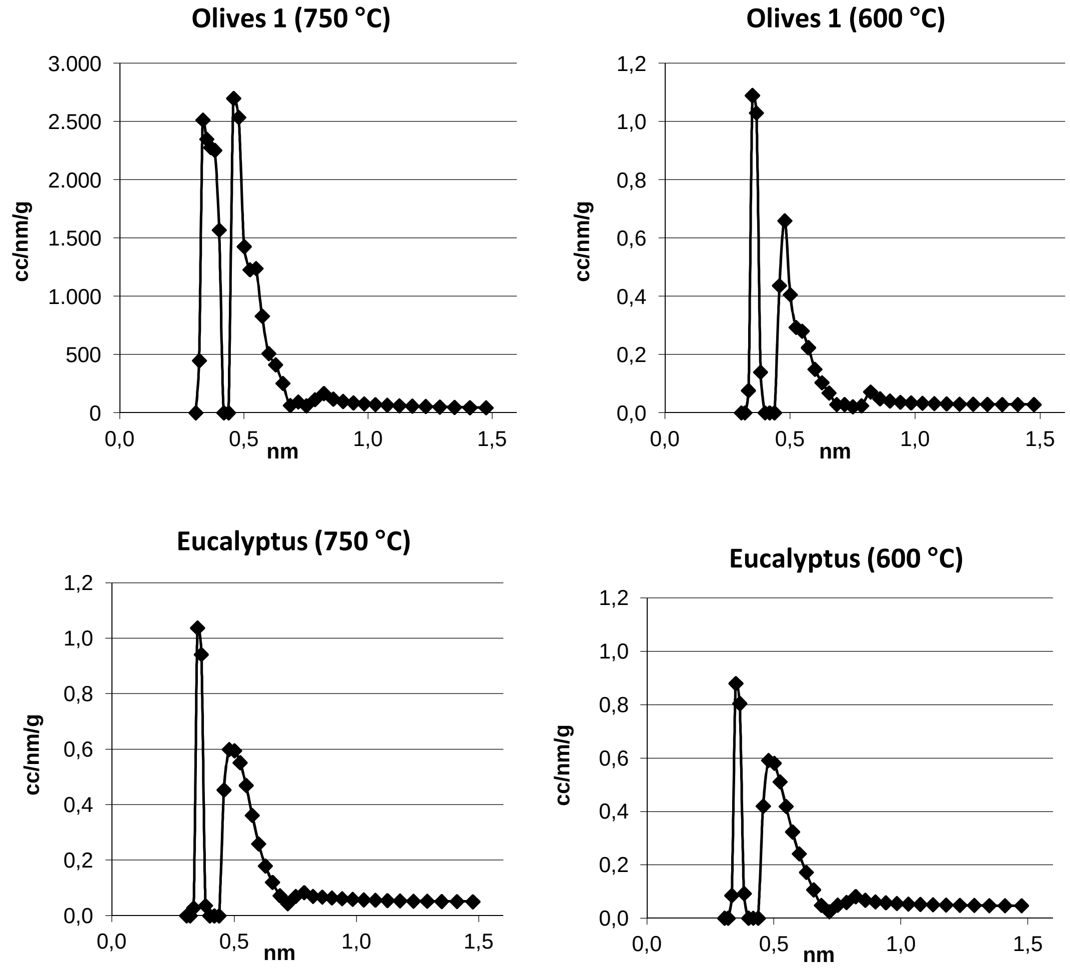


Figure 4.7. Effect of temperature in pore size distribution of the biocokes obtained at 20 °C min^{-1} from olives 1 and eucalyptus samples

Concerning the **effect of the pyrolysis temperature**, it can be seen that the real density clearly increases as the temperature is raised from 600 °C to 750 °C, while the micropore volume and surface area also increases but very slightly, as it happened to other authors (Fu et al., 2012).

The increase of micropore surface area is contrary to what has been observed by Burhenne et al., (2013) who reported a decrease in char surface area when the pyrolysis temperature was raised from 500 to 800 °C. This discrepancy may be due to differences in the surface area determination methods, N_2 (used by Burhenne) versus CO_2 adsorption (used in this thesis). Burhenne reasoning is that at higher temperature an occlusion of most micropores occurs; however it is plausible that what is happening is that at higher pyrolysis temperature, narrower micropores are produced, and this, as will be explained next, are difficult to be measured with liquid N_2.

Agirre et al., (2013) also obtained that the surface area increases when the pyrolysis temperature is increased. The reason for the increase of surface area with temperature may be that at higher temperatures more volatiles are driven out, giving rise to more micropores.

If the surface areas of the biocokes are compared to those presented in the literature, it can be seen that there are very great differences. Very low charcoal surface areas have been reported by several authors: Huo et al., (2014) reported N_2 BET area < 9 m^2 g^{-1} for chars obtained at 900 °C from saw dust and straw, Burhenne et al., (2013) reported N_2 BET area ≈1 m^2 g^{-1} for spruce wood chars obtained at 800 °C (and BET area 200-400 m^2 g^{-1} for chars obtained at 500 °C), Senneca (2007) also reported N_2 BET areas < 1 m^2 g^{-1} for char samples obtained from pine wood at 850 °C.

On the contrary, other authors report surface areas in the range of those obtained in this thesis. Rösler et al., (2012) obtained surface areas (measured by CO_2 adsorption) between 325 and 425 m^2 g^{-1} for biochars obtained at 750 °C, and Carrier et al., (2012) reported a N_2 BET area of 259 m^2 g^{-1} for char obtained from sugarcane bagasse at 460 °C and 350-450 m^2 g^{-1} for that same char but after heating it to 800 °C and 900 °C in N_2 atmosphere, and 440-570 m^2 g^{-1} after activating the char with steam at 700-900 °C.

The reason for these differences in the surface areas reported is the determination method used. As has been mentioned before in section 3.5.2.4 (page 65), it is difficult to obtain reliable results with N_2 adsorption methods with carbonaceous materials, since it is carried at -196 °C and at such a low temperature N_2 has diffusion problems in the narrow micropores and therefore, it may take a long time to reach the thermodynamic adsorption equilibrium, it may last (if reached) even weeks. Another reason for erroneous BET area measurements with liquid N_2 that has been reported in the literature (Jones, 2013), is that there can be pore shrinkage, so that the measured surface areas are apparent not real. In this thesis it was at first tried to determine the surface areas by liquid N_2 adsorption but for most of the biocokes samples the equilibrium was not reached, even after a week, and in those samples that reached equilibrium, the BET area obtained was very low 7-15 m^2 g^{-1}.

The biocokes obtained in this thesis have surface areas comparables to those reported by Carrier et al., (2012) for sugarcane bagasse char activated with steam (440-570 m^2 g^{-1}). In particular, the eucalyptus derived biocoke presents surface areas (476-501 m^2 g^{-1}) equivalent to the reported by Carrier et al., (2012) for sugarcane derived chars activated with steam at 700-900 °C for 1 hour. Therefore, the eucalyptus biocoke could be used as a sorbent material without needing to be activated. However, it has to be mentioned that the surface area of the eucalyptus biocoke, the same as that of Carrier et al., (2012) activated chars, are well below commercial activated carbon values (BET area ≈1000 m^2 g^{-1}).

4.6.2.2. Biocokes obtained from the different biomass samples

The results obtained in the textural characterization of the pyrolysis solids obtained with all the olives derived biomass samples and the eucalyptus sample obtained at 750 °C and 3 °C min^{-1} are presented in Table 4.25, Figure 4.8 and Figure 4.9.

Table 4.25. Textural characterization of pyrolysis biocokes obtained at 750 °C and 3 °C min^{-1}

	Real density ($g\ cm^{-3}$)	Micropore volume ($cm^3\ g^{-1}$)	Micropore equivalent surface area ($m^2\ g^{-1}$)
Olives 1: thin branches	1.871	0.15	363
Olives 2: thick branches	1.796	0.19	454
Olives 3.1: twigs + leaves	1.810	0.17	398
Olives 3.2: twigs	1.842	0.17	418
Olives 3.3: leaves	1.829	0.14	339
Eucalyptus	1.830	0.21	501

Table 4.25 shows that there are not clear differences neither among the densities of the olives derived biocokes, nor between those and the eucalyptus derived biocoke. As it has been previously mentioned when talking about the effect of heating rate and temperature on biocokes textural properties, what is measured by CO_2 adsorption is

the narrow micropores volume, and as the pore size distribution curves show (Figure 4.9), there are no micropores greater than 0.7 nm. Therefore, the measured volume is the total pore volume.

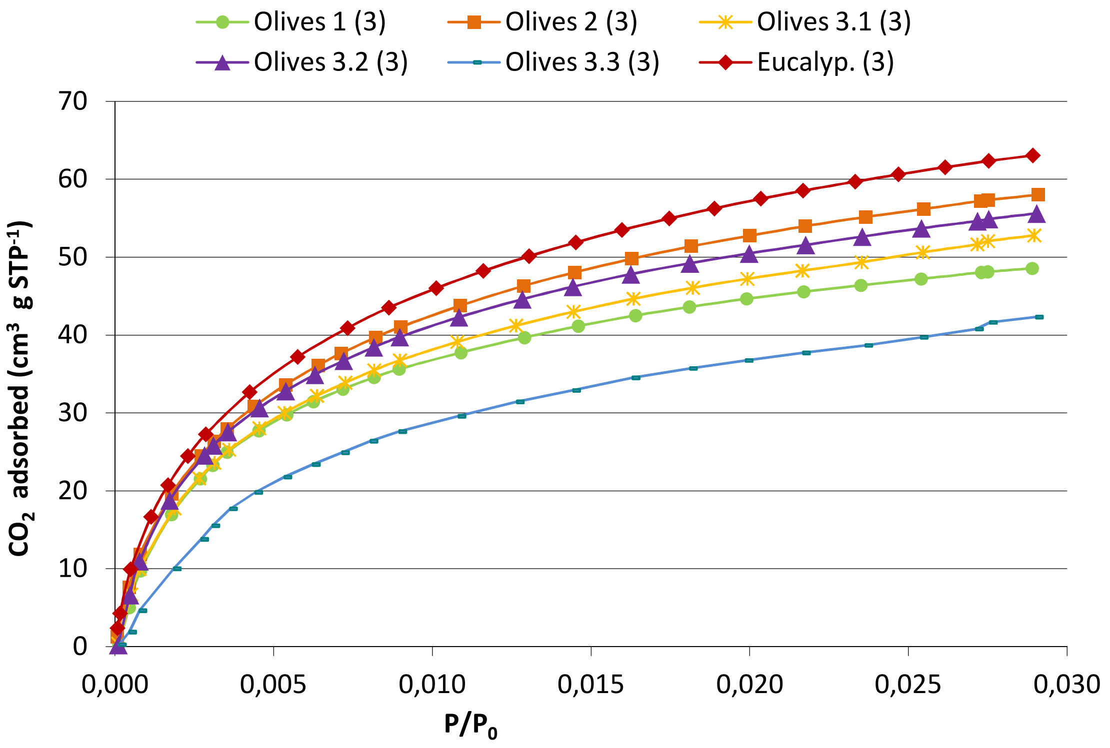


Figure 4.8. CO_2 adsorption isotherms of pyrolysis biocokes obtained at 750 °C and 3 °C min^{-1}

The samples that have greater surface areas and micropore volumes are olives 2 (thick branches) and eucalyptus. This may be due to the less bark content of these two samples compared to the others. Lee et al., (2013) have reported N_2 BET surface areas of wood stem and wood bark, showing that wood bark surface areas are significantly lower than wood stem surface areas.

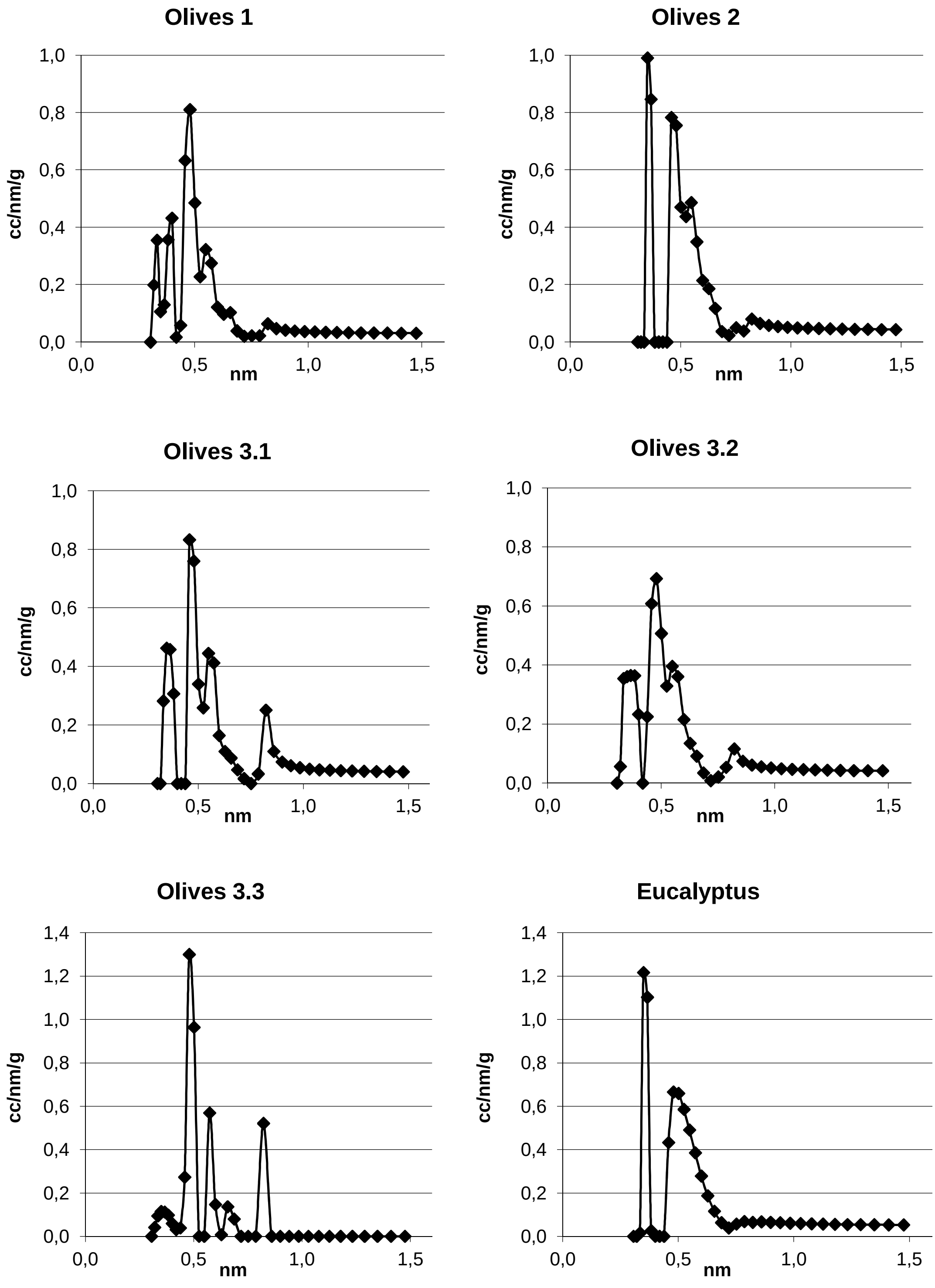


Figure 4.9. Pore size distribution of pyrolysis biocokes obtained at 750 °C and 3 °C min^{-1}

Besides, it has been reported (Carrier et al., 2013) that there is a correlation between the cellulose content and the micropore area; the higher the cellulose content, the greater the micropores surface area. The biocoke with the lowest surface area is the one obtained from olives 3.3 (leaves), which is fact is the one that lowest cellulose content has (Table 4.1, page 81), what is in agreement with Carrier et al., (2013) findings.

On the other hand, as might have been expected, the textural properties of the olives 3.1 (twigs + leaves) sample lay between those from olives 3.2 (twigs) and olives 3.3 (leaves) samples.

4.6.2.3. Biocokes compared to commercial reducing agents

In Table 4.26, the textural properties of the three commercial reducing agents and of the pyrolysis solids obtained from olives 2 (thick branches) and eucalyptus samples at 750 °C and 3 °C min^{-1} are presented.

Table 4.26. Textural characterization of commercial reducers and olives 2 (thick branches) and eucalyptus bioreducers

	Real density (g cm^{-3})	Micropore volume (cm^3 g^{-1})	Micropore equivalent surface area (m^2 g^{-1})	N_2 BET area (m^2 g^{-1})
Olives 2: thick branches	1.796	0.19	454	-
Eucalyptus	1.830	0.21	501	412
Metallurgical coke	1.916	0.01	24	3
Petroleum coke	1.389	0.07	156	1
Anthracite	1.793	0.05	122	10

Concerning the real density, Table 4.26 shows that the bioreducers are comparable to metallurgical coke and anthracite, while petroleum coke has a significantly lower real density. This may be attributed to the lower ash content and the higher micropore volume of the petroleum coke.

With respect to surface area, in Table 4.26 the N_2 BET areas have been included for those samples for which the equilibrium in the adsorption was reached in less than one week. It can be seen, as has been previously mentioned, that the N_2 BET surface area is much lower (specially that of the commercial reducers) than the corresponding surface area determined by CO_2 adsorption, due to difficulty of liquid N_2 to diffuse in the narrow micropores of the material. Comparing the bioreducers with the commercial reducers, it can be seen that the former's surface areas are much greater than those of the latter. Therefore, a higher reactivity of the bioreducers might be expected (this will be analyzed in the following section).

Figure 4.10 shows the CO_2 absorption isotherms of the three commercial reducing agents (left axis) and of the pyrolysis solids obtained from olives 2 (thick branches) and eucalyptus samples at 750 °C and 3 °C min^{-1} (right axis).

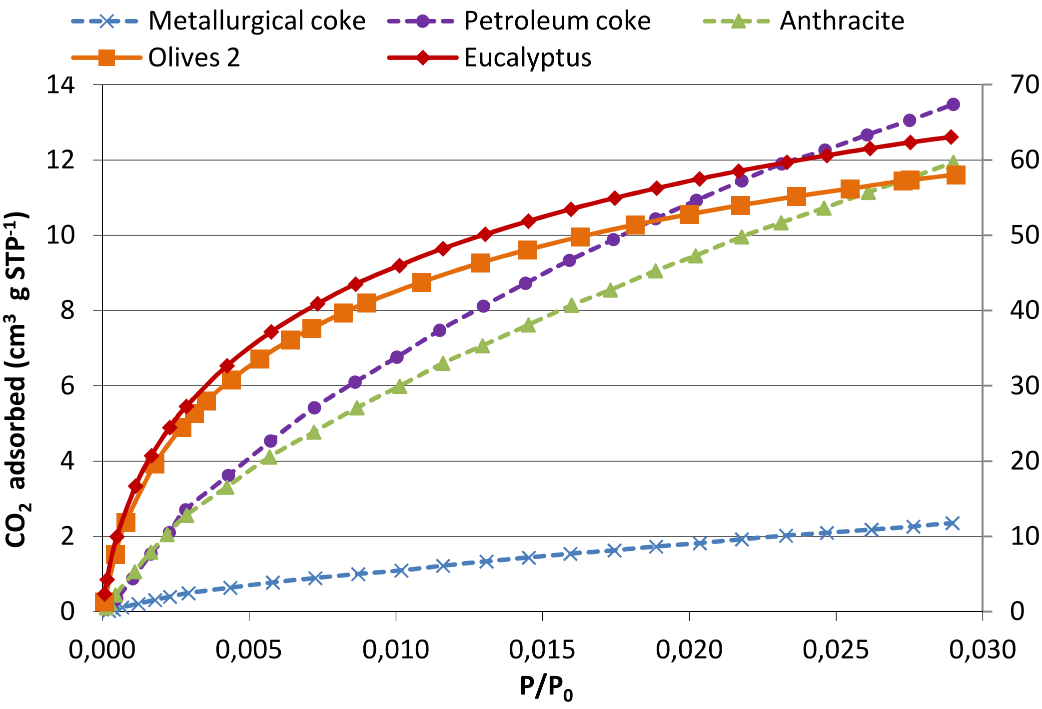


Figure 4.10. CO_2 adsorption isotherms of commercial reducers and olives 2 (thick branches) and eucalyptus bioreducers

It can be seen that the commercial reducers isotherms are also Type I, which is typical of microporous materials. However, accordingly to the surface area data, the commercial reducers' curves are much lower than those of the biocokes.

The pore size distributions of the biocokes and the commercial reducing agents calculated by NL-DFT method are presented in Figure 4.11.

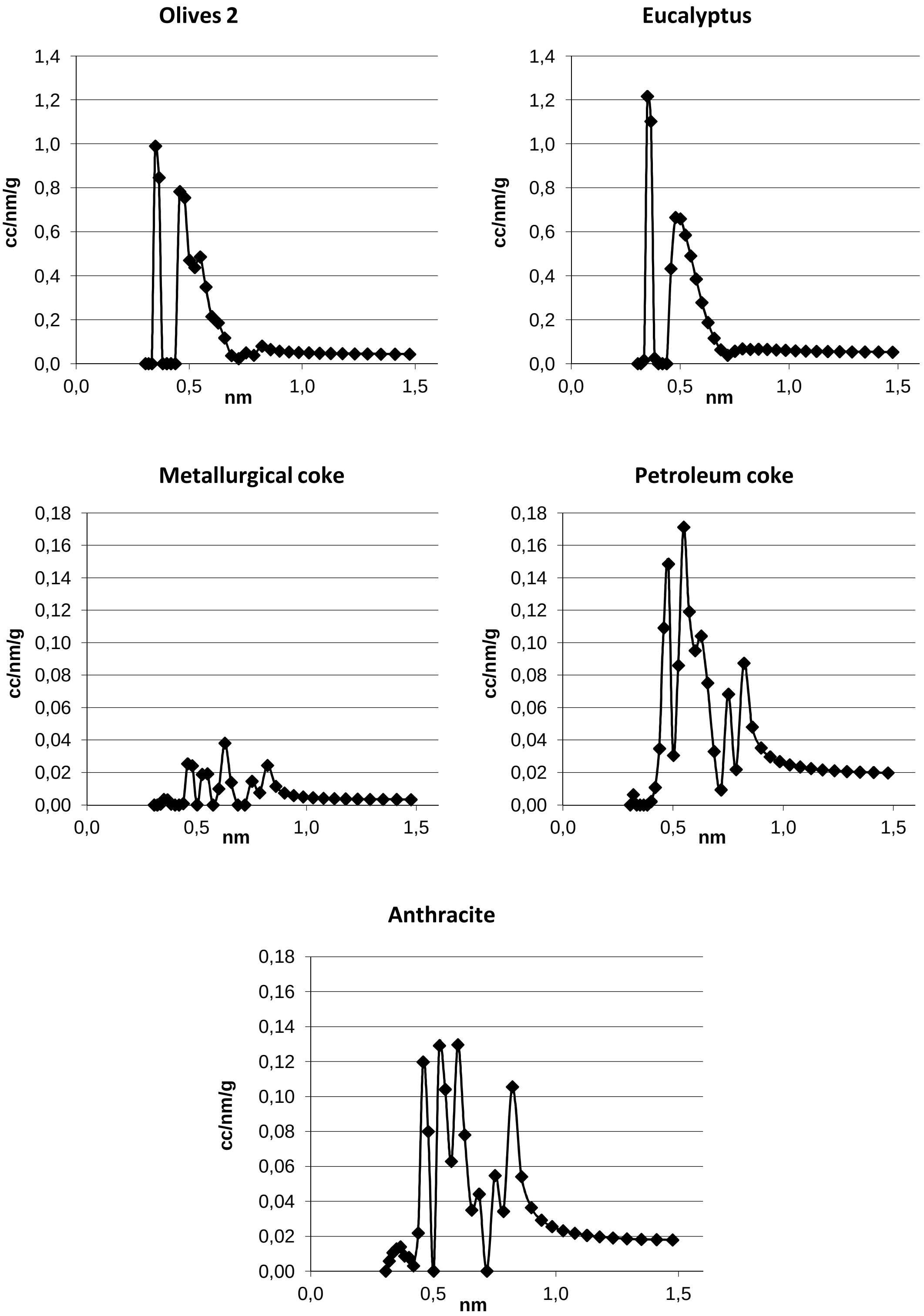


Figure 4.11. Pore size distribution of commercial reducers and olives 2 (thick branches) and eucalyptus bioreducers

It can be seen that there are important differences between the curves that correspond to the commercial reducers and the pore size distribution of the biocokes.

First of all, the amount of pore of each size is much smaller with the commercial reducers than with the biocokes. It has to be born in mind that the y-axis scale is about 10 times lower in the petroleum coke and anthracite graphs and about 40 times lower in the metallurgical coke graph than in biocokes graphs.

On the other hand, it seems that the commercial reducers, although have much lower pore volume than the biocokes, they have some pores of a greater size (near 1 nm) than the biocokes.

To summarize, the main conclusion concerning the comparison of the biocokes with the commercial reducing agents is that, although in terms of comparison (proximate and ultimate analyses) both types of reducing agents are quite similar, even better the biocokes, in terms of surface area and porosity, are very different, and this bring about, as will be seen in the following section, different reactivity behaviors.

4.6.3. Reactivity

In order to evaluate the suitability of the pyrolysis solids as alternative reducing agents in metallurgy, it is essential to investigate its reactivity with CO_2. There are standardized reactivity measurements like the ASTM D 5314-99 standard which were developed, and have been traditionally used, for evaluating the quality of metallurgical cokes. In this thesis, reactivity measurements of the commercial reducing agents and of some of the pyrolysis solids have been carried out. The procedure used, which has been described in section 3.4, page 55, is based in the ASTM D 5314-99 standard. However, to meet the specifications of this standard, a specific large equipment and a great amount of sample (250 g) is required. Since neither of them was available, an adaptation of the ASTM method had to be carried out trying to keep the different operational parameter as close as possible to the specifications of the ASTM standard. Since a significantly lower amount of sample than 250 g had to be used, the amount of sample/CO_2 flow ratio was kept equivalent to the one specified in the ASTM standard.

The parameters determined in the reactivity tests are CRI and R factor (Eq. 4.1 and Eq. 4.2).

$$\mathrm{CRI}_{\mathrm{sample}}\,(\%) = \frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} * 100 \qquad \text{Eq. 4.1}$$

$$\text{R factor}\,(\%) = \frac{\mathrm{CO}}{\mathrm{CO_2} + \mathrm{CO}/2} * 100 \qquad \text{Eq. 4.2}$$

The first one is the mass weight loss or the degree of conversion (wt.%) and the second one is the amount of CO in the gas stream after reaction (vol.% with respect to the original existing CO_2). High values of both parameters indicate high reactivity of the coke.

The reactivity experiments carried out in this thesis were the following:

- Reactivity tests with the three commercial reducers (metallurgical coke, petroleum coke and anthracite) using 50 g of sample and 1375 mL min^{-1} CO_2 flow.
- Reactivity tests with metallurgical coke using different amounts of sample and CO_2 flow ratios.
- Reactivity tests with two of the bioreducers obtained in this thesis (olives 1: thin branches and olives 2: thick branches).

4.6.3.1. Reactivity tests with the commercial reducers (50 g sample – 1375 mL min^{-1} CO_2)

The objective of these first set of reactivity tests was to determine the reactivity behavior of the reducing agents used and provided by Befesa Zinc Aser S.A. (metallurgical coke, petroleum coke and anthracite). The amount of sample/CO_2 flow ratio used in these tests was equivalent to that specified in ASTM D 5314-99 standard.

The results obtained of both, CRI and R factor, are presented in Table 4.27.

Table 4.27. Reactivity results of commercial reducing agents

	Metallurgical coke	Petroleum coke	Anthracite
CRI (%)	30.9	16.5	31.6
R factor (%)	47.4	20.0	47.4

It can be seen that the metallurgical coke and anthracite have similar reactivities according to both, its CRI and R factor, while the both parameters are significantly lower for the petroleum coke. Agirre et al., (2013) have reported CRI and R values for a typical commercial petroleum coke comparable and somewhat lower than those obtained in this thesis (13.7 % and 16.5 % respectively). Other authors have also observed that petroleum cokes have lower reactivities than metallurgical cokes (Menéndez et al., 1995). It has been reported that this may be because petroleum coke has somewhat more crystalline structures which are less reactive (Ruiz et al., 1990).

After this first set of reactivity tests, it was tried to determine the reactivity of the pyrolysis solids. However, due to the lower apparent density of these solids, it was not possible to introduce 50 g of sample in the tubular reactor. Therefore, it was decided to carry out some experiments to investigate if the amount of sample used could have an influence on the results obtained on the reactivity tests. The results are presented in the following section.

4.6.3.2. Reactivity tests with different amounts of sample and different CO_2 flows (metallurgical coke)

The CRI and R factor obtained with the metallurgical coke using different amounts of sample and different CO_2 flows are presented in Table 4.28.

Table 4.28. Reactivity results of metallurgical coke

	1375 mL min^{-1}			750 mL min^{-1}
	50 g	30 g	15 g	30 g
CRI (%)	30.9	43.5	41.0	34.5
R factor (%)	47.4	27.0	9.8	45.9

Analyzing the reactivity results obtained with the same CO_2 flow used before (1375 mL min^{-1}) but with different amounts of sample, it can be seen that the CRI content significantly increases from 50 to 30 g, but then from 30 g to 15 g, it can be considered that it has stabilized. The explanation to this fact may be the following. As greater is the amount of sample, larger is the height occupied by it inside the tubular reactor. The CO_2 stream is fed into the reactor through the bottom, therefore it starts reacting with coke, and as it goes up through the char bed it is impoverished in CO_2, leading to a lower reaction rate at the upper part of the reactor. This effect is almost not observed from the 30 to the 15 g tests because probably with smaller column heights the CO_2 decrease is not enough to produce a negative effect.

Regarding the R factor, it clearly decreases in the whole mass sample range when the amount of sample is reduced. This was obviously the expected trend, since as less sample is used, less total CO is produced, and consequently, for the same CO_2 flow lower is the CO/CO_2 ratio and therefore, the R factor.

Comparing the results obtained with 30 g of sample at the two different CO_2 flows, it is observed that the CRI decreases while the R factor increases as the CO_2 flow decreases. This was to be expected since, if there is less CO_2 available for the same amount of sample, on the one hand, less coke reacts and therefore, the weight loss is smaller, and consequently the CRI decreases. On the other hand, since the CO_2 concentration is much lower, even though less CO has been produced, the CO/CO_2 ratio increases, and consequently, the R factor increases.

If the results obtained with 30 g and 750 mL min^{-1} are compared with those obtained with 50 g and 1375 mL min^{-1}, it can be seen that they are quite similar, which is attributed to the fact that in both cases the amount of sample/CO_2 flow ratio is quite similar (≈26).

Therefore, it is demonstrated that in the reactivity tests the amount of sample used plays a very important role, but that if the amount of sample/CO_2 flow is kept constant, the influence of the amount of sample can be neglected.

4.6.3.3. Reactivity tests with the biocokes (30 g sample – 750 mL min^{-1} CO$_2$)

Finally, the reactivity tests of the pyrolysis solids obtained in this thesis (olives 1: thin branches and olives 2: thick branches) were carried out using 30 g and 750 mL min^{-1} CO$_2$. The results are included in Table 4.29.

Table 4.29. Reactivity results of pyrolysis biocokes

	Olives 1 Thin branches			Olives 2 Thick branches
	20 °C min^{-1}	15 °C min^{-1}	3 °C min^{-1}	3 °C min^{-1}
CRI (%)	87.8	86.8	86.1	88.9
R factor (%)	81.3	82.4	74.4	93.0

Table 4.29 shows that the reactivity of the bioreducers is very high. The CRI values are around 87 %, therefore only a 13 % of the initial mass has been left after the experiment. Taking into account that the ash contents of the bioreducers from olives 1 (thin branches) is close to 10 % (Table 4.18, page 136) it has to be mentioned that the samples have almost completely reacted with CO$_2$, therefore, the values in Table 4.29 came to be the maximum achievable reactivities. For this reason, a discussion of the influence of the heating rate or type of sample on the reactivity results does not deserve any attention.

Compared to metallurgical coke, the reactivity of bioreducers is far higher. Huo et al., (2014) also obtained much higher reactivities of biocokes than of petroleum coke or anthracite, and they also reported that there is a relationship between reactivity and surface area. This is in agreement with the results obtained in this thesis, since the surface areas of the commercial reducers were much lower (24 - 156 m^2 g^{-1}) than those of the bioreducers derived from olives 1 and olives 2 samples (363 - 454 m^2 g^{-1}). Burhenne et al., (2013) also obtained almost 100 % reactivity of spruce wood derived char in tests carried out both in TGA at 800 °C for 3-5 h and in a fixed bed reactor at 800 °C for 30 min.

On the contrary, biocokes obtained by pyrolysis of fruit tree cuttings at 900 °C by Agirre et al., (2013), have CRI values in the range of 20-50 % and R factor 35-70 %, both values much lower than those obtained in this thesis, and comparables to those of commercial reducing agents. There are several reasons that can explain these differences. (1) On the one hand, the equipment used for reactivity measurements is very different from the one used in this thesis; it is a horizontal tubular furnace and the sample is placed in a crucible inside the reactor, therefore the CO_2 stream is only in contact with the upper surface of the sample, while in this thesis, the CO_2 stream goes through the whole char bed. (2) The reaction time one reached the reaction temperature (1000 °C), was only 15 min instead of 2 h which is the time specified in the ASTM D 5341-99 and the one used in the reactivity tests of this thesis. (3) The type of original biomass from which chars were derived was different (fruit tree cuttings vs. olive tree cuttings).

It is worth mentioning that there are three roles that coke plays in the metallurgical processes:

1. It has to provide heat or energy.
2. It has to provide a reducing atmosphere by means of the reaction: $C + CO_2 \leftrightarrow 2\,CO$.
3. It has to act as a support medium for the burden if the process is carried out in a blast furnace.

The first two requirements are well fulfilled by the bioreducers obtained in this thesis; they have rather high heating values (≈30 MJ kg^{-1}) and they are fully reactive. However, bioreducers cannot fulfill the third requirement, and therefore, due to its missing strength and too its high reactivity, cannot be used in blast furnaces as support medium, but it do can be used tuyére-injected in the lower part of the blast furnaces in substitution of typically used fossil fuels (pulverized carbon, oils, natural gas). On the other hand, bioreducers can also be used in the non-ferrous metal industry since no mechanical strength is required, because frequently rotator kilns, where the burden is mixed and rotates with the coke, are used.

It has been shown in this section that concerning proximate and ultimate analysis, the bioreducers produced in this thesis are comparable, and in some aspects even better, than commercial fossil derived reducers (metallurgical coke, petroleum coke and anthracite) since, the former contain less ash and sulfur, and the HHV is also comparable or higher than that of commercial reducers. The great difference between bio- and commercial- reducers is its surface area and reactivity, both much higher in the bioreducers. As a consequence, the final decision to determine the suitability of bioreducers for the non-ferrous metallurgical industry depends on the specific characteristics of the process itself. Metal reduction experiments should be carried out with the bioreducers in order to determine if the high reactivities could be a handicap for the process, and such kind of experiments were beyond the scope of this thesis. However, it has been found in the literature experiments of reduction of electric arc furnace dusts carried out with charcoal which show that bioreducers achieve higher zinc volatilization and iron oxide reduction in comparison to the fossil cokes normally used in industry (Griessacher et al., 2012).

CHAPTER 5

CONCLUSIONS

5. CONCLUSIONS

The main conclusions that can be drawn from this PhD thesis devoted to the optimization of the biomass pyrolysis process for the simultaneous production of bio-reducing agents and high value gases are the following:

Conclusions concerning the operating conditions of the pyrolysis process:

- In order to obtain pyrolysis solids suitable to be used as reducing agents in metallurgical processes, high temperatures (≥ 750 °C) and slow heating rates (≤ 20 °C min^{-1}) have to be used, and in order to optimize the pyrolysis gases, avoiding tar formation and increasing hydrogen production, a second high temperature (900 °C) catalytic step is required.
- In high temperature slow pyrolysis processes liquids should be minimized since they are mainly composed of an aqueous phase together with a small amount of an organic phase (tars), and therefore, are useless byproducts which should be treated before being discharged.
- The increase of the temperature of the vapors catalytic treatment decreases total liquids as well as tar yields, and increases gas yields and the H_2 content of the gases, while reduces the CO_2 content, so that a more valuable gas is obtained.
- The use of very low heating rates is highly recommended not only because the amount and quality of the biocoke is enhanced, but also because the vapor upgrading step is much more effective, due to the slower flow of the vapors through the catalytic bed.
- As lower is the heating rate, higher are the gas yields and its hydrogen content, and lower is the total liquid yield, as well as the aqueous fraction yield, tars yield and the organic compounds contained in the aqueous phase.

- With 3 °C min^{-1} low heating rate, 750 °C pyrolysis temperature and 900 °C catalytic treatment, tars formation is avoided and the aqueous phase is composed of more than 99 area% of water.
- Comparing the one step pyrolysis with the two steps process using the best operating conditions (3 °C min^{-1} and 750 °C in the 1st reactor and 900 °C in the 2nd reactor) and the most effective catalyst (the homemade Ni/CeO_2-Al_2O_3 catalyst) total liquid yield is reduced in a 60 % (from 45.4 to 17.8 wt.%), tars are not produced (from 16.8 to 0 wt.%), gas yield is increased in a 70 % (from 33.2 to 57.6 wt.%) and the hydrogen content of the gases is increased more than four times (from 11.5 to 46.6 vol.%).

Conclusions concerning the comparison of the catalysts at the best operating conditions (3 °C min^{-1}, 750 °C in the 1st reactor and 900 °C in the 2nd reactor):

- The use of appropriate catalysts reduces total liquids (aqueous fraction) yields and increases the gas yield. The hydrogen content in the gases is increased, while the CO, CH_4 and C_2H_6 contents are reduced.
- Nickel containing catalysts have proved to be appropriate catalysts for upgrading biomass pyrolysis vapors. The best results concerning both pyrolysis yields and gas compositions are obtained with the homemade Ni/CeO_2-Al_2O_3 catalyst followed by the commercial Katalco 57-4Q catalyst which is also a Ni based catalyst.
- Concerning the homemade catalysts, the addition of the CeO_2 promoter enhances the performance of the catalyst more than ZrO_2.
- The addition of Ni to the HZSM5 zeolite enhances its effectiveness for biomass pyrolysis vapors upgrading.
- HY zeolite has proved to be much less effective for biomass pyrolysis vapors upgrading than HZSM5 zeolite, even though the HY zeolite was also doped with Ni.

Conclusions concerning the potential uses of the pyrolysis products obtained (gases and solids):

- The pyrolysis upgraded gases obtained with the best operating conditions (3 °C min^{-1} and 750 °C in the 1st reactor and 900 °C in the 2nd reactor) and the most effective catalysts, contain 45-50 vol.% H_2 and 70-75 vol.% CO+H_2. Therefore, they are high value gases which can be used as source of hydrogen, as synthesis gas or as reducing agent, apart from the conventional use as fuel.

- The solids obtained in slow high temperature pyrolysis are high carbon containing materials (84 wt.%) with low volatile matter contents (10 wt.%) and high HHV (29 MJ kg^{-1}), porosity (0.15 cm^3 g^{-1}) and surface areas (363 m^2 g^{-1}). They can therefore be used as high quality fuels, as sorbents or as reducing agents.

Conclusions concerning the comparison of the different biomass samples:

- The presence of equilibrium moisture in the biomass is beneficial for upgrading the pyrolysis vapors since it promotes water involving reactions, such as reforming reactions, which increase H_2 production, and so, the amount and quality of pyrolysis gases is enhanced. Drying the sample prior to pyrolysis not only does not reduce liquid yields but also decrease the H_2 production.

- The pyrolysis products and yields are influenced by the type of biomass, even when different shipments of the same biomass species are compared. Leaves, bark and the inner wood have different proximate, ultimate and constituents analyses; therefore, the biomass sample thickness has an influence on the process.

- Both leaves and bark have higher ash contents and therefore give rise to higher biocoke yields but of worse quality.

- Leaves have a very high extractives content and very low lignin content, and consequently, are less prone to carbonize.

- Eucalyptus, which is softwood biomass, has higher lignin contents than olives, which are hardwoods; as a consequence, eucalyptus gives rise to higher biocoke yields.

Conclusions concerning the comparison of the biocokes with typical commercial reducing agents:

- The biocokes obtained in this thesis have no mechanical strength and present extremely high reactivity (close to 100 %) with CO_2. Therefore, they cannot be used as top burden in blast furnaces, but they can be used as fuel and reducing agent either tuyére-injected at the lower part of the blast furnace or in non-ferrous metallurgical processes where no mechanical strength is needed, like in rotary kilns.

- In order to enhance the quality of the biocokes, the amount of leaves, bark and, most of all, soil and dirtiness that may accompany the biomass should be minimized.

- As far as proximate an ultimate analyses is concerned, the biocokes obtained are of better quality than typical commercial reducing agents used in non-ferrous processes (metallurgical coke, petroleum coke, anthracite), since the former have lower ash and sulfur contents.

- The surface area and porosity of the biocokes obtained (454-501 $m^2\ g^{-1}$ and 0.19-0.21 $cm^3\ g^{-1}$ respectively) are much higher than those of the typical commercial reducing agents (24-156 $m^2\ g^{-1}$ and 0.01-0.07 $cm^3\ g^{-1}$ respectively), and in both, the total pore volume corresponds to micropores (< 1 nm).

- The determination of the surfaces areas of the biocokes by liquid N_2 adsorption is rather difficult and may lead to erroneous results, due to the low diffusivity of liquid N_2 in the narrow micropores of these materials. The determination of surface areas by CO_2 adsorption does not present such problem, and is therefore the recommended method for these carbonaceous materials.

- The biocokes reactivity measurements with CO_2 are very much conditioned by the experimental procedure used. If the ASTM D 5314-99 standard procedure cannot be strictly followed due to sample shortage, a CO_2-flow/mass sample ratio equivalent to that of the ASTM standard should be used.

CHAPTER 6

FUTURE RESEARCH LINES

6. FUTURE RESEARCH LINES

This PhD thesis provides the opportunity to work in complementary, parallel or in new research lines. Some of them are presented below.

Further study of the optimization of the pyrolysis process for the production of bioreducers in a plant which resembles a potential real industrial plant (with pyrolysis and vapors upgrading step) and with the following characteristics:

- Continuous operation (both continuous pyrolysis and continuous online vapor upgrading).
- Higher temperatures (up to 1000 °C).
- Variation of the residence time.

Complementary study of the influence of the temperature, both in fast and slow pyrolysis, at lower temperatures (450-500 °C) for further scientific understanding.

More in-depth study of the behavior of the catalysts:

- Lifetime.
- Coke deposition.
- Further characterization.

Further investigation concerning the suitability of bioreducers as reducing agents:

- Achievement of bioreducers of lower reactivity by means of increasing pyrolysis temperature and feedstock particle size.
- Adaptation of the ASTM D 5314-99 standard for measuring coke reactivity in a thermogravimetric analyzer (TGA).
- Metal reduction experiments in order to determine the range of reactivities that would be suitable for the process.

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7. REFERENCES

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LIST OF TABLES

8. LIST OF TABLES

LIST OF FIGURES

9. LIST OF FIGURES

LYST OF ACRONYMS

10. LIST OF ACRONYMS

ASAP	Accelerated Surface Area and Porosimetry System
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CENER	Centro de Energías Renovables = Renewable Energy Centre
COP	Conference of Parties
CRI	Coke Reactivity Index
CSIC	Consejo Superior de Investigaciones Científicas = Spanish National Research Council
DOE/EERE	Department of Energy’s Office of Energy Efficiency and Renewable Energy
DR	Dubinin-Radushkevich
DTG	Derivative Thermogravimetry
EPA	Environmental Protection Agency
ESYRCE	Encuesta de Superficies Y Rendimientos de Cultivos = Crop areas and yields survey
FCC	Fluid Catalytic Cracking
FID	Flame Ionization Detector
GC	Gas Chromatography
GHG	Greenhouse gases
ha	Hectare
HAA	Hydroxyacetaldehyde
HHV	Higher Heating Value
HPLC	High Performance Liquid Chromatography
HZSM5	Hydrogen Zeolite Socony Mobil-5
ICP-AES	Inductively Coupled Plasma Atomic Emission System
IEA	International Energy Agency
INCAR	Instituto Nacional del Carbón = Spanish National Institute of Coal

IUPAC	International Union of Pure and Applied Chemistry
IWI	Incipient Wetness Impregnation
JM	Johnson Matthey
LG	Levoglucosan
MS	Mass Spectrometry
MTG	Methanol to Gasoline
NABC	National Advanced Biofuels Consortium
NIST	National Institute Standards Technology
NL-DFT	Non-Local Density Functional Theory
NREL	National Renewable Energy Laboratory
ppm	parts per million
Py	Pyrolysis
R&D	Research and Development
S.A.	Sociedad Anónima = Public Limited Company (PLC)
SDTA	Simultaneous Differential Thermal Analysis
S.L	Sociedad Limitada = Limited (Ltd)
TCD	Thermal Conductivity Detector
Tg	Teragram
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
TPR	Temperature Programmed Reduction
TWC	Three Way Catalyst
WGS	Water Gas Shift

APPENDIX A:

PUBLICATIONS RELATED TO THE DOCTORAL THESIS

11. APPENDIX A: Publications related to the Doctoral Thesis

In the present Appendix the contributions to different international conferences, as well as the published and sent articles related to the present doctoral thesis are shown.

A.1. Contributions to international conferences

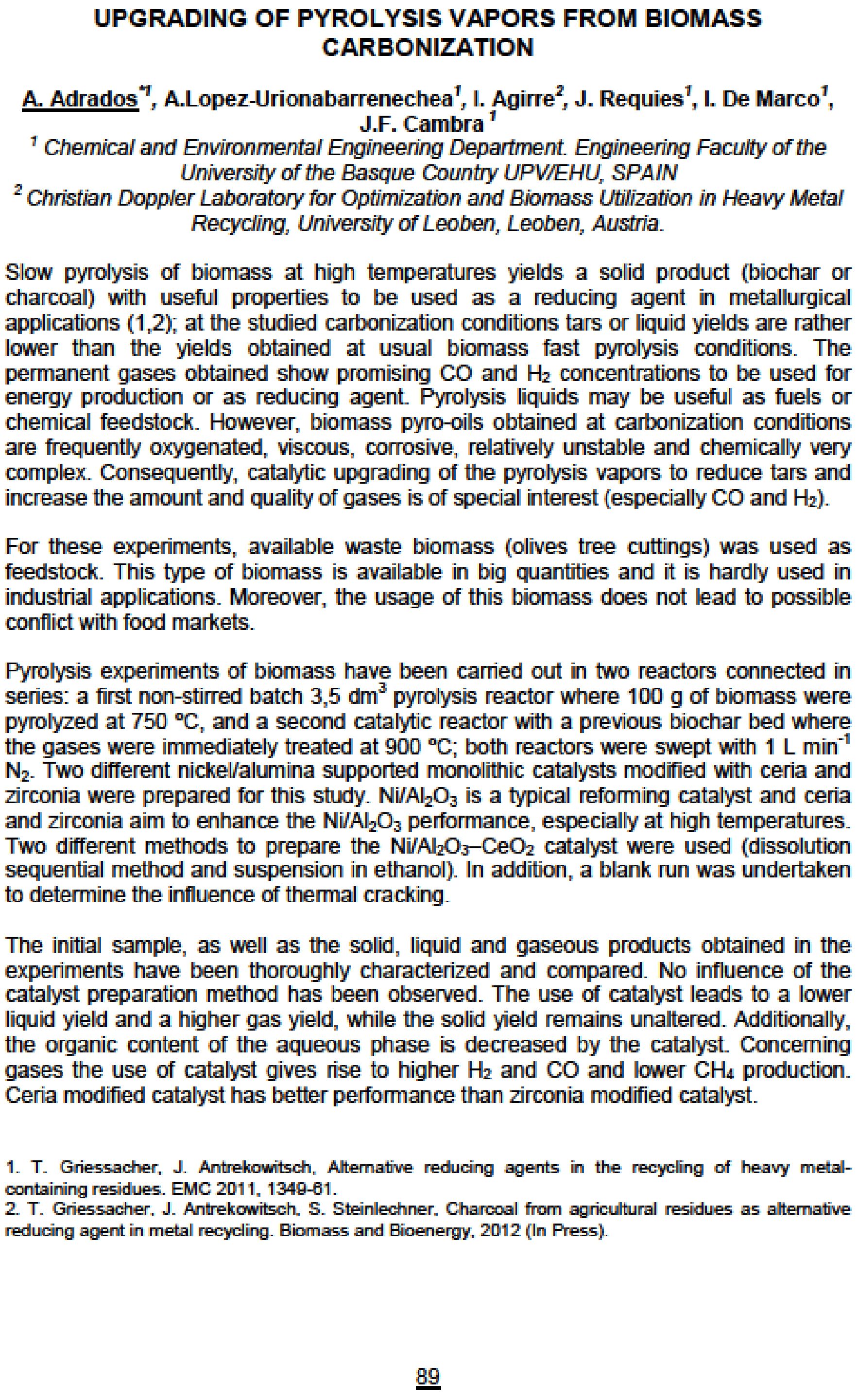
Authors: A. Adrados, A. López, I. de Marco, B.M. Caballero, M.F. Laresgoiti

Title: Upgrading of pyrolysis vapors from biomass carbonization

Congress: 19th International Symposium on Analytical and Applied Pyrolysis

Publication: Book of abstracts PYRO 2012 **Type of participation:** Oral

Place: Linz, Austria **Date:** May 2012



UPGRADING OF PYROLYSIS VAPORS FROM BIOMASS CARBONIZATION

A. Adrados*[1], **A.Lopez-Urionabarrenechea**[1], **I. Agirre**[2], **J. Requies**[1], **I. De Marco**[1], **J.F. Cambra**[1]

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Slow pyrolysis of biomass at high temperatures yields a solid product (biochar or charcoal) with useful properties to be used as a reducing agent in metallurgical applications (1,2); at the studied carbonization conditions tars or liquid yields are rather lower than the yields obtained at usual biomass fast pyrolysis conditions. The permanent gases obtained show promising CO and H_2 concentrations to be used for energy production or as reducing agent. Pyrolysis liquids may be useful as fuels or chemical feedstock. However, biomass pyro-oils obtained at carbonization conditions are frequently oxygenated, viscous, corrosive, relatively unstable and chemically very complex. Consequently, catalytic upgrading of the pyrolysis vapors to reduce tars and increase the amount and quality of gases is of special interest (especially CO and H_2).

For these experiments, available waste biomass (olives tree cuttings) was used as feedstock. This type of biomass is available in big quantities and it is hardly used in industrial applications. Moreover, the usage of this biomass does not lead to possible conflict with food markets.

Pyrolysis experiments of biomass have been carried out in two reactors connected in series: a first non-stirred batch 3,5 dm^3 pyrolysis reactor where 100 g of biomass were pyrolyzed at 750 °C, and a second catalytic reactor with a previous biochar bed where the gases were immediately treated at 900 °C; both reactors were swept with 1 L min^{-1} N_2. Two different nickel/alumina supported monolithic catalysts modified with ceria and zirconia were prepared for this study. Ni/Al_2O_3 is a typical reforming catalyst and ceria and zirconia aim to enhance the Ni/Al_2O_3 performance, especially at high temperatures. Two different methods to prepare the $Ni/Al_2O_3–CeO_2$ catalyst were used (dissolution sequential method and suspension in ethanol). In addition, a blank run was undertaken to determine the influence of thermal cracking.

The initial sample, as well as the solid, liquid and gaseous products obtained in the experiments have been thoroughly characterized and compared. No influence of the catalyst preparation method has been observed. The use of catalyst leads to a lower liquid yield and a higher gas yield, while the solid yield remains unaltered. Additionally, the organic content of the aqueous phase is decreased by the catalyst. Concerning gases the use of catalyst gives rise to higher H_2 and CO and lower CH_4 production. Ceria modified catalyst has better performance than zirconia modified catalyst.

1. T. Griessacher, J. Antrekowitsch, Alternative reducing agents in the recycling of heavy metal-containing residues. EMC 2011, 1349-61.
2. T. Griessacher, J. Antrekowitsch, S. Steinlechner, Charcoal from agricultural residues as alternative reducing agent in metal recycling. Biomass and Bioenergy, 2012 (In Press).

Authors: A. Lopez-Urionabarrenechea, I. de Marco, A. Adrados, B.M. Caballero, M.F. Laresgoiti

Title: A comparison between biomass and plastic waste pyrolysis processes

Congress: 4th International Conference on Engineering for Waste and Biomass Valorisation (WASTENG 2012) **Type of participation:** Oral

Publication: Book of abstracts of WasteEng 2012 (ISBN: 979-10-91526-00-5)

Place: Oporto, Portugal **Date:** September 2012

4th International Conference on Engineering for Waste and Biomass Valorisation September 10-13, 2012 – Porto, Portugal

A COMPARISON BETWEEN BIOMASS AND PLASTIC WASTE PYROLYSIS PROCESSES

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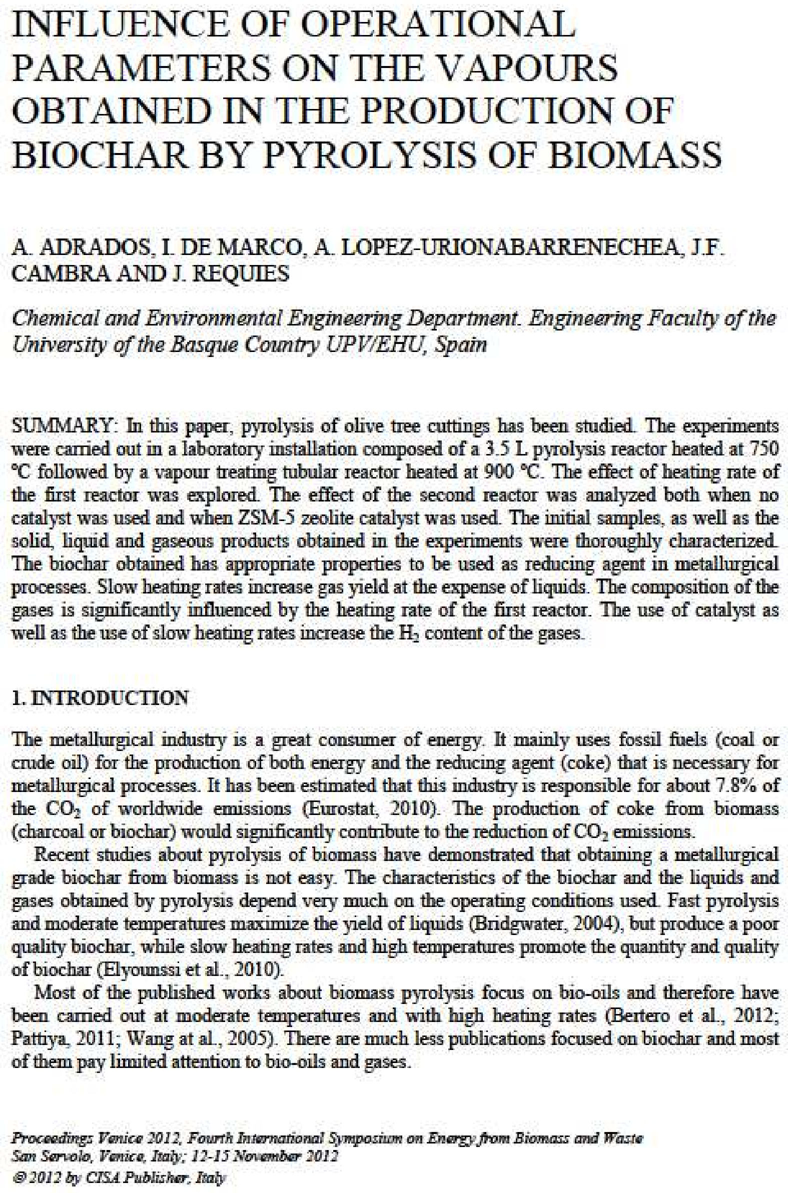
Keywords: pyrolysis, packaging waste, plastic waste, biomass, feedstock recycling, bio-oil, bio-char.

Abstract

Plastic waste pyrolysis and biomass pyrolysis have been compared carrying out pyrolysis experiments in a lab-scale installation in semi-batch operation at different temperatures for 30 min. The results show that the quantity and characteristics of the products obtained in the process strongly depend on the nature of the sample pyrolysed. When the plastic waste sample is the raw material, the liquid and gaseous fractions are the main products of the process; the liquid fraction is an organic liquid (oil) mainly composed of un-substituted hydrocarbons, the gaseous product is mainly composed of C1-C6 hydrocarbons and has high HHV, and the solid is the minority product and is composed of char and the inorganic material of the original sample. When biomass is pyrolysed, the solid fraction is much more important; the liquid product (bio-oil) is mainly an aqueous liquid containing a low proportion of water soluble oxygenated hydrocarbons mixed with a minority tar-like fraction, the gaseous fraction is mainly composed of H_2, CO, CO_2 and CH_4, and the solid fraction (bio-char) is a coke-like product, which can be used as reducing agent in metallurgical processes. Therefore, in plastic waste pyrolysis, gases and liquids are the valuable products and should be the objective of the process, while in biomass pyrolysis the solid and gaseous products are the valuable and more ready to use products, since the usefulness of the liquid product is rather questionable.

Authors:	A. Adrados, I. de Marco, A. Lopez-Urionabarrenechea, J.F. Cambra, J. Requies		
Title:	Influence of operational parameters on the vapours obtained in the production of biochar by pyrolysis of biomass		
Congress:	4th International Symposium on Energy from Biomass and Waste (VENICE 2012)	**Type of participation:**	Oral
Publication:	CD of the congress Venice 2012 (ISBN: 978-88-6265-006-9)		
Place:	Venice, Italy	**Date:**	November 2012



INFLUENCE OF OPERATIONAL PARAMETERS ON THE VAPOURS OBTAINED IN THE PRODUCTION OF BIOCHAR BY PYROLYSIS OF BIOMASS

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SUMMARY: In this paper, pyrolysis of olive tree cuttings has been studied. The experiments were carried out in a laboratory installation composed of a 3.5 L pyrolysis reactor heated at 750 °C followed by a vapour treating tubular reactor heated at 900 °C. The effect of heating rate of the first reactor was explored. The effect of the second reactor was analyzed both when no catalyst was used and when ZSM-5 zeolite catalyst was used. The initial samples, as well as the solid, liquid and gaseous products obtained in the experiments were thoroughly characterized. The biochar obtained has appropriate properties to be used as reducing agent in metallurgical processes. Slow heating rates increase gas yield at the expense of liquids. The composition of the gases is significantly influenced by the heating rate of the first reactor. The use of catalyst as well as the use of slow heating rates increase the H_2 content of the gases.

1. INTRODUCTION

The metallurgical industry is a great consumer of energy. It mainly uses fossil fuels (coal or crude oil) for the production of both energy and the reducing agent (coke) that is necessary for metallurgical processes. It has been estimated that this industry is responsible for about 7.8% of the CO_2 of worldwide emissions (Eurostat, 2010). The production of coke from biomass (charcoal or biochar) would significantly contribute to the reduction of CO_2 emissions.

Recent studies about pyrolysis of biomass have demonstrated that obtaining a metallurgical grade biochar from biomass is not easy. The characteristics of the biochar and the liquids and gases obtained by pyrolysis depend very much on the operating conditions used. Fast pyrolysis and moderate temperatures maximize the yield of liquids (Bridgwater, 2004), but produce a poor quality biochar, while slow heating rates and high temperatures promote the quantity and quality of biochar (Elyounssi et al., 2010).

Most of the published works about biomass pyrolysis focus on bio-oils and therefore have been carried out at moderate temperatures and with high heating rates (Bertero et al., 2012; Pattiya, 2011; Wang at al., 2005). There are much less publications focused on biochar and most of them pay limited attention to bio-oils and gases.

Proceedings Venice 2012, Fourth International Symposium on Energy from Biomass and Waste
San Servolo, Venice, Italy; 12-15 November 2012

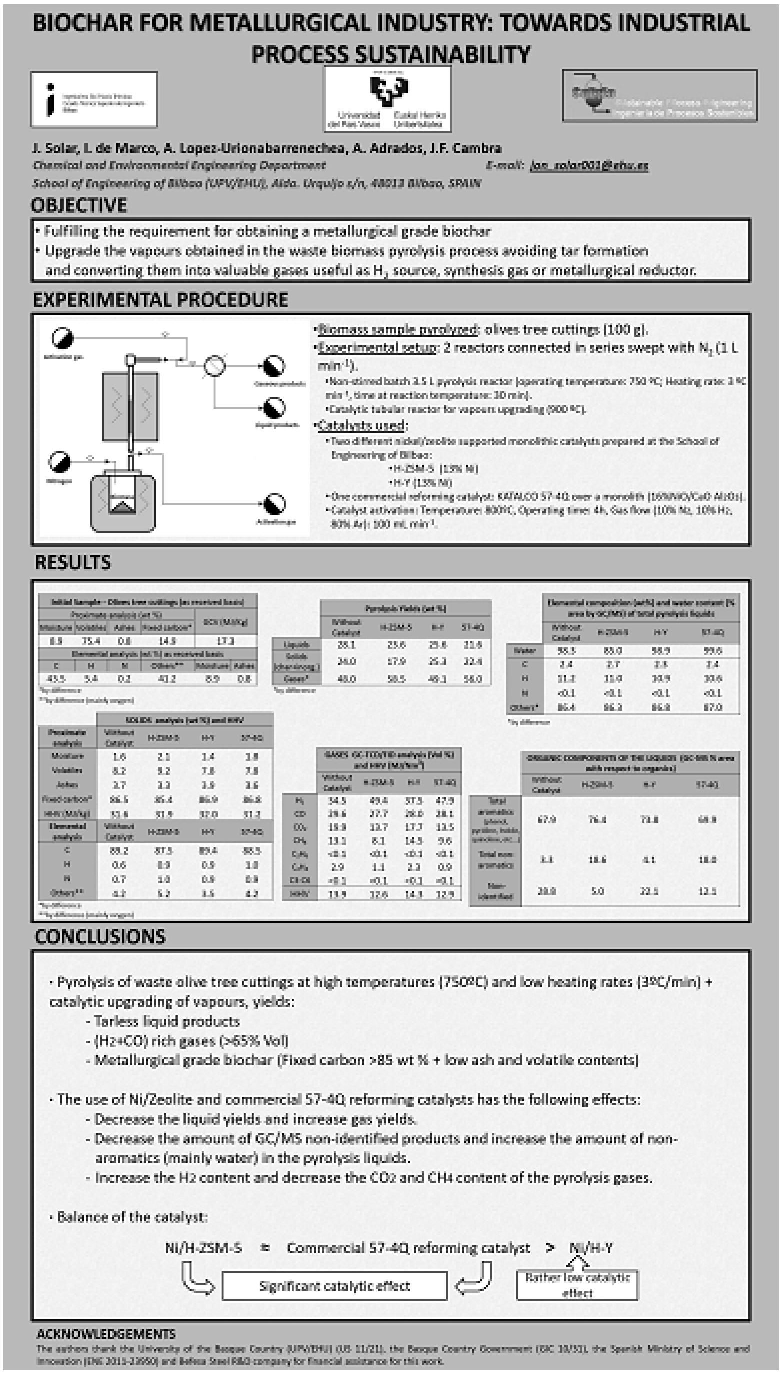
Authors: A. Adrados, I. de Marco, A. Lopez-Urionabarrenechea, J.F. Cambra, J. Solar

Title: Biochar for metallurgical industry: towards industrial process sustainability

Congress: 2^{nd} International Symposium on Green Chemistry, Renewable carbon and Eco-efficient processes

Publication: **Type of participation:** Poster

Place: La Rochelle, France **Date:** May 2013



BIOCHAR FOR METALLURGICAL INDUSTRY: TOWARDS INDUSTRIAL PROCESS SUSTAINABILITY

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OBJECTIVE

- Fulfilling the requirement for obtaining a metallurgical grade biochar
- Upgrade the vapours obtained in the waste biomass pyrolysis process avoiding tar formation and converting them into valuable gases useful as H_2 source, synthesis gas or metallurgical reductor.

EXPERIMENTAL PROCEDURE

- Biomass sample pyrolyzed: olives tree cuttings (100 g).
- Experimental setup: 2 reactors connected in series swept with N_2 (1 L min⁻¹).
  - Non-stirred batch 3.5 L pyrolysis reactor (operating temperature: 750 ºC; Heating rate: 3 ºC min⁻¹, time at reaction temperature: 30 min).
  - Catalytic tubular reactor for vapours upgrading (900 ºC).
- Catalysts used:
  - Two different nickel/zeolite supported monolithic catalysts prepared at the School of Engineering of Bilbao:
    - H-ZSM-5 (13% Ni)
    - H-Y (13% Ni)
  - One commercial reforming catalyst: KATALCO 57-4Q over a monolith (16%NiO/CaO Al_2O_3).
  - Catalyst activation: Temperature: 800ºC, Operating time: 4h, Gas flow (10% N_2, 10% H_2, 80% Ar): 100 mL min⁻¹.

RESULTS

CONCLUSIONS

- Pyrolysis of waste olive tree cuttings at high temperatures (750ºC) and low heating rates (3ºC/min) + catalytic upgrading of vapours, yields:
  - Tarless liquid products
  - (H_2+CO) rich gases (>65% Vol)
  - Metallurgical grade biochar (Fixed carbon >85 wt % + low ash and volatile contents)
- The use of Ni/Zeolite and commercial 57-4Q reforming catalysts has the following effects:
  - Decrease the liquid yields and increase gas yields.
  - Decrease the amount of GC/MS non-identified products and increase the amount of non-aromatics (mainly water) in the pyrolysis liquids.
  - Increase the H_2 content and decrease the CO_2 and CH_4 content of the pyrolysis gases.
- Balance of the catalyst:

Ni/H-ZSM-5 ≈ Commercial 57-4Q reforming catalyst > Ni/H-Y

Significant catalytic effect

Rather low catalytic effect

ACKNOWLEDGEMENTS
The authors thank the University of the Basque Country (UPV/EHU) (UFI 11/21), the Basque Country Government (GIC 10/31), the Spanish Ministry of Science and Innovation (ENE 2011-23950) and Befesa Steel R&D company for financial assistance for this work.

Authors: A. Lopez-Urionabarrenechea, I. de Marco, A. Adrados, J. Solar, B.M. Caballero, J.F. Cambra

Title: Slow pyrolysis of woody biomass waste: Influence of raw material on pyrolysis products

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Publication: Book of abstracts of CIIEM 2013 (ISBN: 978-989-98406-5-2)

Place: Lisbon, Portugal **Date:** July 2013

5th International Congress on Energy and Environment Engineering and Management / Lisbon, 17-19 July 2013

Slow pyrolysis of woody biomass waste: Influence of raw material on pyrolysis products

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1. Introduction

In the pyrolysis process of biomass three main products are obtained: bio-char, a solid product mainly composed of carbon, bio-oil, a liquid product composed of water and oxygenated organic compounds, and the pyrolysis gases, which are normally composed of carbon oxides, light hydrocarbons and hydrogen. The quality and quantity of each product depends on the operation parameters, such as temperature, heating rate and reactor design. The difference between fast and slow pyrolysis lies on the use of fast or slow heating rates in the process, which brings about different pyrolysis yields (quantity of each product) and products characteristics. Fast pyrolysis (usually at moderate temperatures) maximizes the yield of bio-oil while slow pyrolysis (usually at higher temperatures) is normally used when bio-char is the main objective of the process [1]. In such conditions, the bio-char obtained can be directly used as solid fuel, soil amender or reducing agent [2]. The influence of biomass type on the characteristics of bio-char, and also on the liquid and gaseous products, is studied in this communication.

2. Experimental

The samples pyrolysed are woody biomass waste samples coming from agricultural activities carried out in the south of Spain. More specifically, 4 samples coming from olive tree pruning (olive tree trunks, olive tree branches, olive tree leaves and olive tree branches + leaves) and 2 samples coming from the wine industry (grapevines and vine shoot) have been used for the experiments. This type of waste is available in big quantities in countries with olive and grapevine plantations like Spain, and it is at present not valorized. Pyrolysis experiments have been carried out in a pyrolysis installation equipped with two reactors connected in series: a first non-stirred batch 3,5 dm^3 pyrolysis reactor where 100 g of biomass are pyrolysed at 750 °C, and a second tubular reactor where the vapors and gases coming from the first reactor are treated at 900 °C; both reactors are swept with 1 L min^{-1} N_2.

3. Results and Discussion

Related to pyrolysis yields, the quantity of bio-char is a relatively constant value in all the experiments, ranging from 24 to 25 wt%, while the proportions of both liquids (19-30 wt%) and gases (48-55 wt%) are more influenced by the type of biomass. The type of biomass has stronger effect on the characteristics of the products; bio-chars with fixed carbon values from 67 to 86 wt% are obtained, being the elemental carbon content between 72 and 89 wt%. Concerning pyrolysis liquids, they are aqueous liquids (>95 %area water, determined by GC-MS) in all the cases but their carbon content (organic content) varies among 0.5 and 2.5 wt% depending on the feedstock used. Attending the gas characteristics, they are composed of hydrogen, carbon monoxide and dioxide, methane and low quantities of ethane and ethylene. The proportion of hydrogen is quite high in all the experiments (34-41 vol%) which indicates the potential of the pyrolysis gases as a source of hydrogen. Besides, the proportion of $H_2 + CO$ ranges from 60 to 65 vol%, which opens the possibility of using them as synthesis gas.

4. Conclusions

The results obtained indicate that the type of raw material plays an important role on the quality and quantity of the pyrolysis products. The best results are obtained when olive tree trunks are pyrolysed, since the characteristics of the bio-char are the best ones (86.4 wt% fixed carbon, 89.2 wt% elemental carbon). Working with this type of biomass and at the aforementioned operation parameters, low quantities of water-like bio-oil and high quantities of pyrolysis gas with 65 vol% $H_2 + CO$ are also obtained.

5. References

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[2] B. Xu, L. Ferrante, K. Hall, C. Briens, F. Berruti, *J. Anal. Appl. Pyrolysis*, 91 (2011) p. 55.

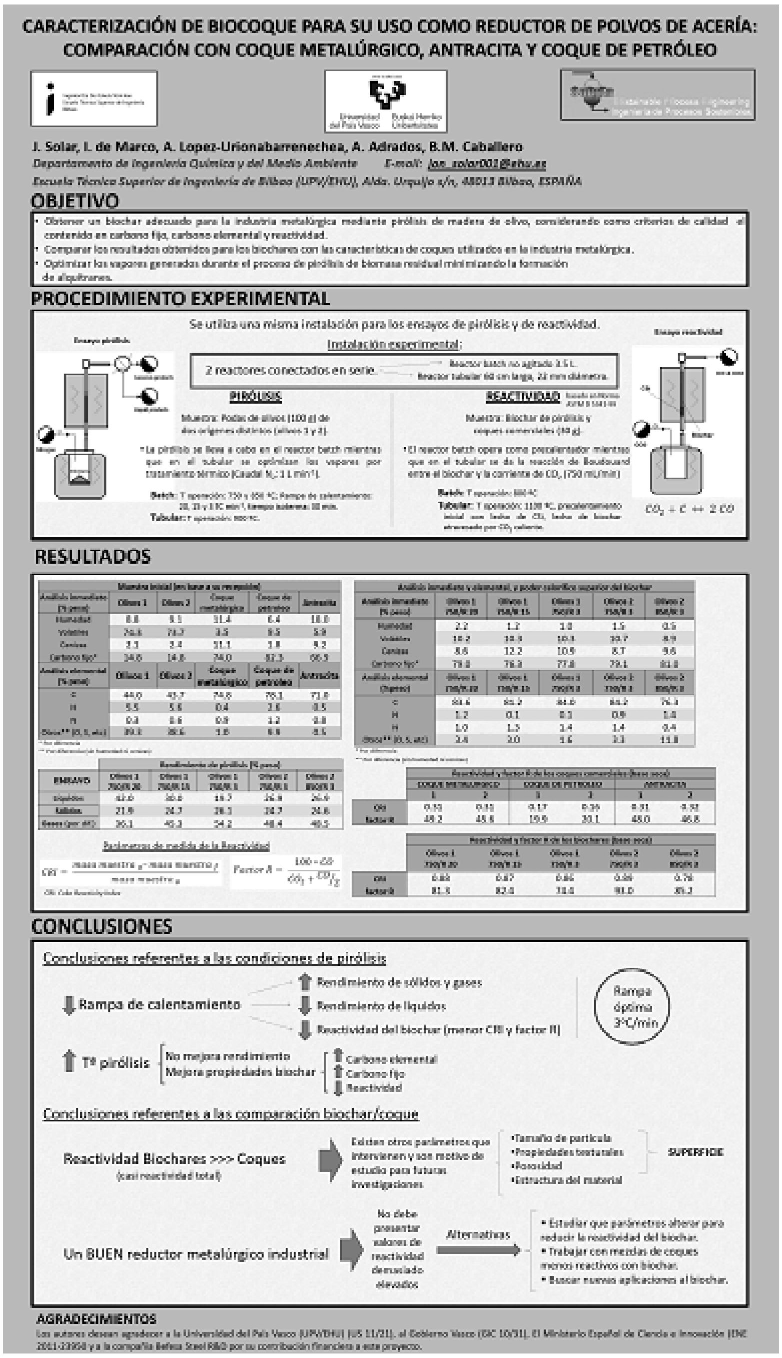
Authors: A. Lopez-Urionabarrenechea, J. Solar, I. de Marco, A. Adrados, B.M. Caballero

Title: Caracterización de biocoque para su uso como reductor de polvos de acería: comparación con coque metalúrgico, antracita y coque de petróleo **Type of participation:** Poster

Congress: XXXIV Reunión Bienal de la Real Sociedad Española de Química

Publication: Book of abstracts (ISBN: 978-84-695-8511-5)

Place: Santander, Spain **Date:** September 2013



CARACTERIZACIÓN DE BIOCOQUE PARA SU USO COMO REDUCTOR DE POLVOS DE ACERÍA: COMPARACIÓN CON COQUE METALÚRGICO, ANTRACITA Y COQUE DE PETRÓLEO

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OBJETIVO

- Obtener un biochar adecuado para la industria metalúrgica mediante pirólisis de madera de olivo, considerando como criterios de calidad el contenido en carbono fijo, carbono elemental y reactividad.
- Comparar los resultados obtenidos para los biochares con las características de coques utilizados en la industria metalúrgica.
- Optimizar los vapores generados durante el proceso de pirólisis de biomasa residual minimizando la formación de alquitranes.

PROCEDIMIENTO EXPERIMENTAL

Se utiliza una misma instalación para los ensayos de pirólisis y de reactividad.

Instalación experimental:

2 reactores conectados en serie.
- Reactor batch no agitado 3.5 L.
- Reactor tubular 60 cm largo, 22 mm diámetro.

PIRÓLISIS

Muestra: Podas de olivos (100 g) de dos orígenes distintos (olivos 1 y 2).

- La pirólisis se lleva a cabo en el reactor batch mientras que en el tubular se optimizan los vapores por tratamiento térmico (Caudal N_2: 1 L min^{-1}).

Batch: T operación: 750 y 850 °C; Rampa de calentamiento: 20, 15 y 3 °C min^{-1}, tiempo isoterma: 30 min.
Tubular: T operación: 800 °C.

REACTIVIDAD

Muestra: Biochar de pirólisis y coques comerciales (30 g).

- El reactor batch opera como precalentador mientras que en el tubular se da la reacción de Boudouard entre el biochar y la corriente de CO_2 (750 mL/min).

Batch: T operación: 800 °C
Tubular: T operación: 1100 °C, precalentamiento inicial con lecho de CO_2, lecho de biochar atravesado por CO_2 caliente.

$CO_2 + C \leftrightarrow 2\,CO$

RESULTADOS

Parámetros de medida de la Reactividad

CONCLUSIONES

Conclusiones referentes a las condiciones de pirólisis

⇩ Rampa de calentamiento
- ⇧ Rendimiento de sólidos y gases
- ⇩ Rendimiento de líquidos
- ⇩ Reactividad del biochar (menor CRI y factor R)

Rampa óptima 3°C/min

⇧ Tª pirólisis
- No mejora rendimiento
- Mejora propiedades biochar
  - ⇧ Carbono elemental
  - ⇧ Carbono fijo
  - ⇩ Reactividad

Conclusiones referentes a las comparación biochar/coque

Reactividad Biochares >>> Coques
(casi reactividad total)

Existen otros parámetros que intervienen y son motivo de estudio para futuras investigaciones
- Tamaño de partícula
- Propiedades texturales
- Porosidad
- Estructura del material

SUPERFICIE

Un BUEN reductor metalúrgico industrial

No debe presentar valores de reactividad demasiado elevados

Alternativas
- Estudiar que parámetros alterar para reducir la reactividad del biochar.
- Trabajar con mezclas de coques menos reactivos con biochar.
- Buscar nuevas aplicaciones al biochar.

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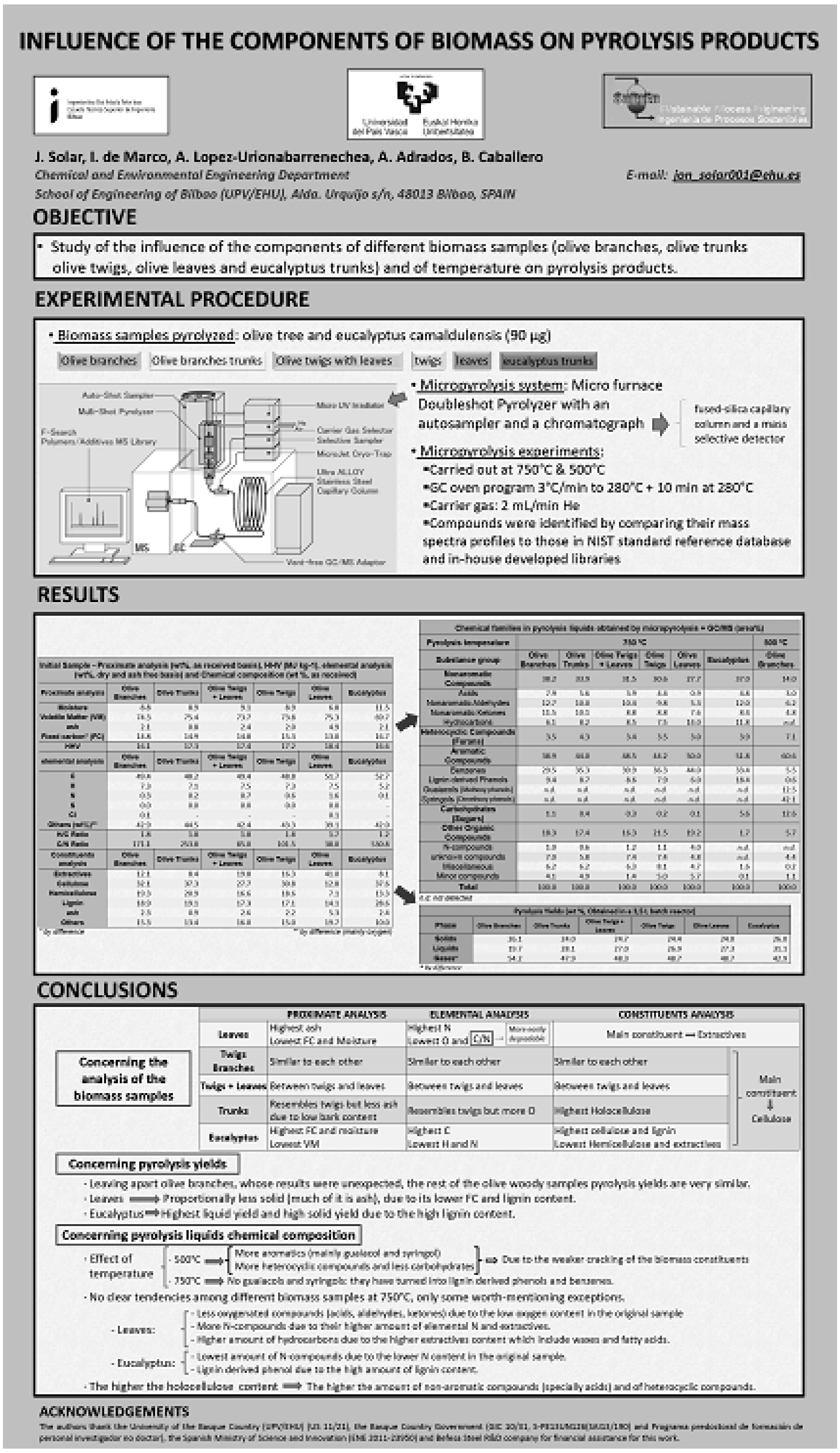
Authors: A. Adrados, I. de Marco, A. Lopez-Urionabarrenechea, J. Solar, B.M. Caballero

Title: Influence of the components of biomass on pyrolysis products

Congress: 4th International Congress on Green Process Engineering (GPE 2014)

Publication: Book of abstracts of GPE 2014 (ISBN: 978-84-15107-50-7)

Place: Seville, Spain **Date:** April 2014 **Type of participation:** Poster



INFLUENCE OF THE COMPONENTS OF BIOMASS ON PYROLYSIS PRODUCTS

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OBJECTIVE

- Study of the influence of the components of different biomass samples (olive branches, olive trunks olive twigs, olive leaves and eucalyptus trunks) and of temperature on pyrolysis products.

EXPERIMENTAL PROCEDURE

- Biomass samples pyrolyzed: olive tree and eucalyptus camaldulensis (90 µg)

Olive branches | Olive branches trunks | Olive twigs with leaves | twigs | leaves | eucalyptus trunks

- Micropyrolysis system: Micro furnace Doubleshot Pyrolyzer with an autosampler and a chromatograph ⇒ fused-silica capillary column and a mass selective detector
- Micropyrolysis experiments:
  - Carried out at 750°C & 500°C
  - GC oven program 3°C/min to 280°C + 10 min at 280°C
  - Carrier gas: 2 mL/min He
  - Compounds were identified by comparing their mass spectra profiles to those in NIST standard reference database and in-house developed libraries

RESULTS

Initial Sample – Proximate analysis (wt%, as received basis), HHV (MJ kg-1), elemental analysis (wt%, dry and ash free basis) and Chemical composition (wt %, as received)

Chemical families in pyrolysis liquids obtained by micropyrolysis + GC/MS (area%)

Pyrolysis Yields (wt %, Obtained in a 3.5 L batch reactor)

CONCLUSIONS

Concerning the analysis of the biomass samples	PROXIMATE ANALYSIS	ELEMENTAL ANALYSIS	CONSTITUENTS ANALYSIS
Leaves	Highest ash Lowest FC and Moisture	Highest N Lowest O and C/N → More easily degradable	Main constituent → Extractives
Twigs Branches	Similar to each other	Similar to each other	Similar to each other
Twigs + Leaves	Between twigs and leaves	Between twigs and leaves	Between twigs and leaves
Trunks	Resembles twigs but less ash due to low bark content	Resembles twigs but more O	Highest Holocellulose
Eucalyptus	Highest FC and moisture Lowest VM	Highest C Lowest H and N	Highest cellulose and lignin Lowest Hemicellulose and extractives

Main constituent ⇓ Cellulose

Concerning pyrolysis yields

- Leaving apart olive branches, whose results were unexpected, the rest of the olive woody samples pyrolysis yields are very similar.
- Leaves ⟹ Proportionally less solid (much of it is ash), due to its lower FC and lignin content.
- Eucalyptus ⟹ Highest liquid yield and high solid yield due to the high lignin content.

Concerning pyrolysis liquids chemical composition

- Effect of temperature
  - 500°C ⟹ More aromatics (mainly guaiacol and syringol); More heterocyclic compounds and less carbohydrates ⟹ Due to the weaker cracking of the biomass constituents
  - 750°C ⟹ No guaiacols and syringols: they have turned into lignin derived phenols and benzenes.
- No clear tendencies among different biomass samples at 750°C, only some worth-mentioning exceptions.
  - Leaves:
    - Less oxygenated compounds (acids, aldehydes, ketones) due to the low oxygen content in the original sample
    - More N-compounds due to their higher amount of elemental N and extractives.
    - Higher amount of hydrocarbons due to the higher extractives content which include waxes and fatty acids.
  - Eucalyptus:
    - Lowest amount of N-compounds due to the lower N content in the original sample.
    - Lignin derived phenol due to the high amount of lignin content.
- The higher the holocellulose content ⟹ The higher the amount of non-aromatic compounds (specially acids) and of heterocyclic compounds.

ACKNOWLEDGEMENTS

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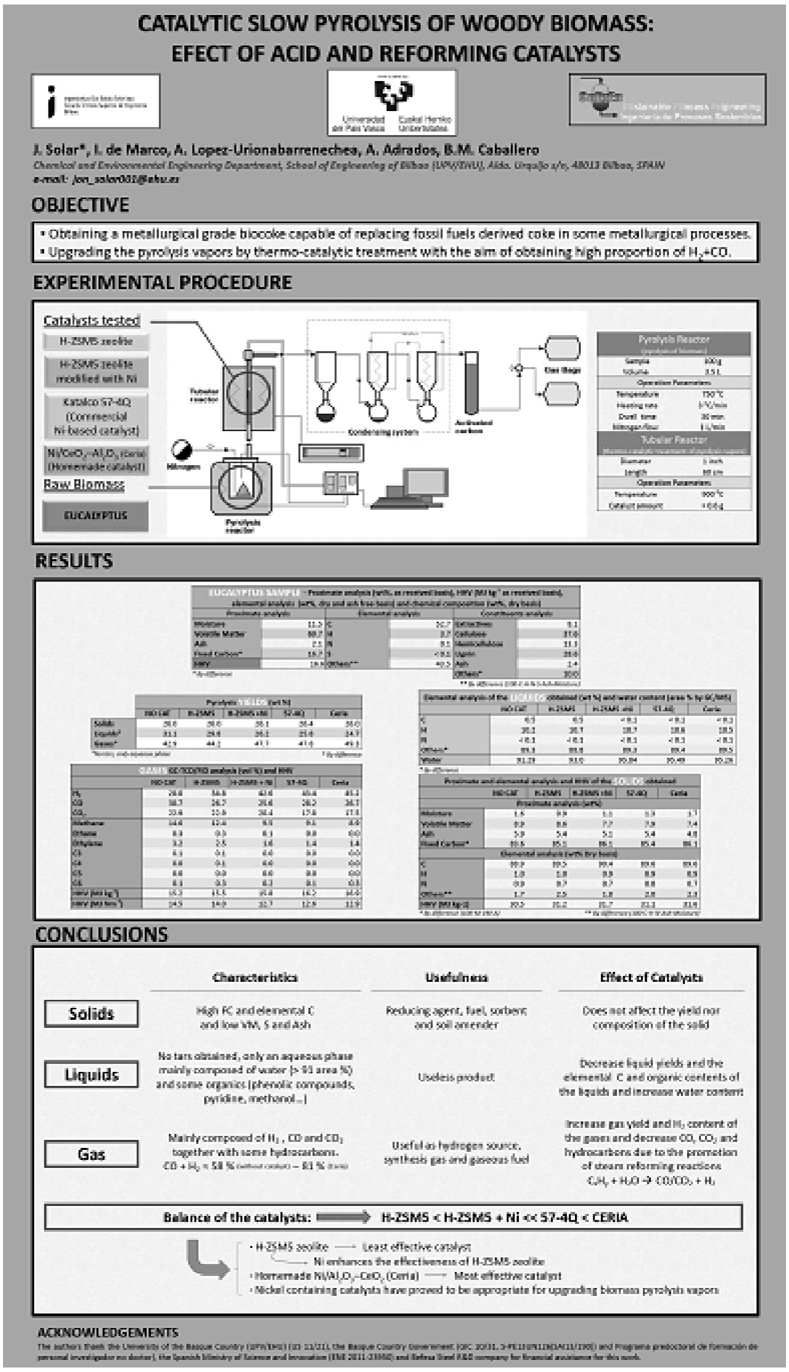
Authors: A. Adrados, I. de Marco, A. Lopez-Urionabarrenechea, J. Solar, B.M. Caballero

Title: Catalytic slow pyrolysis of woody biomass: Effect of acid and reforming catalysts

Congress: 20th International Symposium on Analytical and Applied Pyrolysis (PYRO 2014) **Type of participation:** Poster

Publication: Book of abstracts of PYRO 2014

Place: Birmingham, UK **Date:** May 2014



CATALYTIC SLOW PYROLYSIS OF WOODY BIOMASS: EFECT OF ACID AND REFORMING CATALYSTS

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OBJECTIVE

- Obtaining a metallurgical grade biocoke capable of replacing fossil fuels derived coke in some metallurgical processes.
- Upgrading the pyrolysis vapors by thermo-catalytic treatment with the aim of obtaining high proportion of H_2+CO.

EXPERIMENTAL PROCEDURE

Catalysts tested
- H-ZSM5 zeolite
- H-ZSM5 zeolite modified with Ni
- Katalco 57-4Q (Commercial Ni-based catalyst)
- $Ni/CeO_2-Al_2O_3$ (Ceria) (Homemade catalyst)

Raw Biomass
- EUCALYPTUS

RESULTS

CONCLUSIONS

	Characteristics	Usefulness	Effect of Catalysts
Solids	High FC and elemental C and low VM, S and Ash	Reducing agent, fuel, sorbent and soil amender	Does not affect the yield nor composition of the solid
Liquids	No tars obtained, only an aqueous phase mainly composed of water (> 93 area %) and some organics (phenolic compounds, pyridine, methanol…)	Useless product	Decrease liquid yields and the elemental C and organic contents of the liquids and increase water content
Gas	Mainly composed of H_2, CO and CO_2 together with some hydrocarbons. CO + H_2 ≈ 58 % (without catalyst) – 83 % (Ceria)	Useful as hydrogen source, synthesis gas and gaseous fuel	Increase gas yield and H_2 content of the gases and decrease CO, CO_2 and hydrocarbons due to the promotion of steam reforming reactions $C_xH_y + H_2O \rightarrow CO/CO_2 + H_2$

Balance of the catalysts: ⟹ H-ZSM5 < H-ZSM5 + Ni << 57-4Q < CERIA

- H-ZSM5 zeolite → Least effective catalyst
  - Ni enhances the effectiveness of H-ZSM5 zeolite
- Homemade $Ni/Al_2O_3-CeO_2$ (Ceria) → Most effective catalyst
- Nickel containing catalysts have proved to be appropriate for upgrading biomass pyrolysis vapors

ACKNOWLEDGEMENTS
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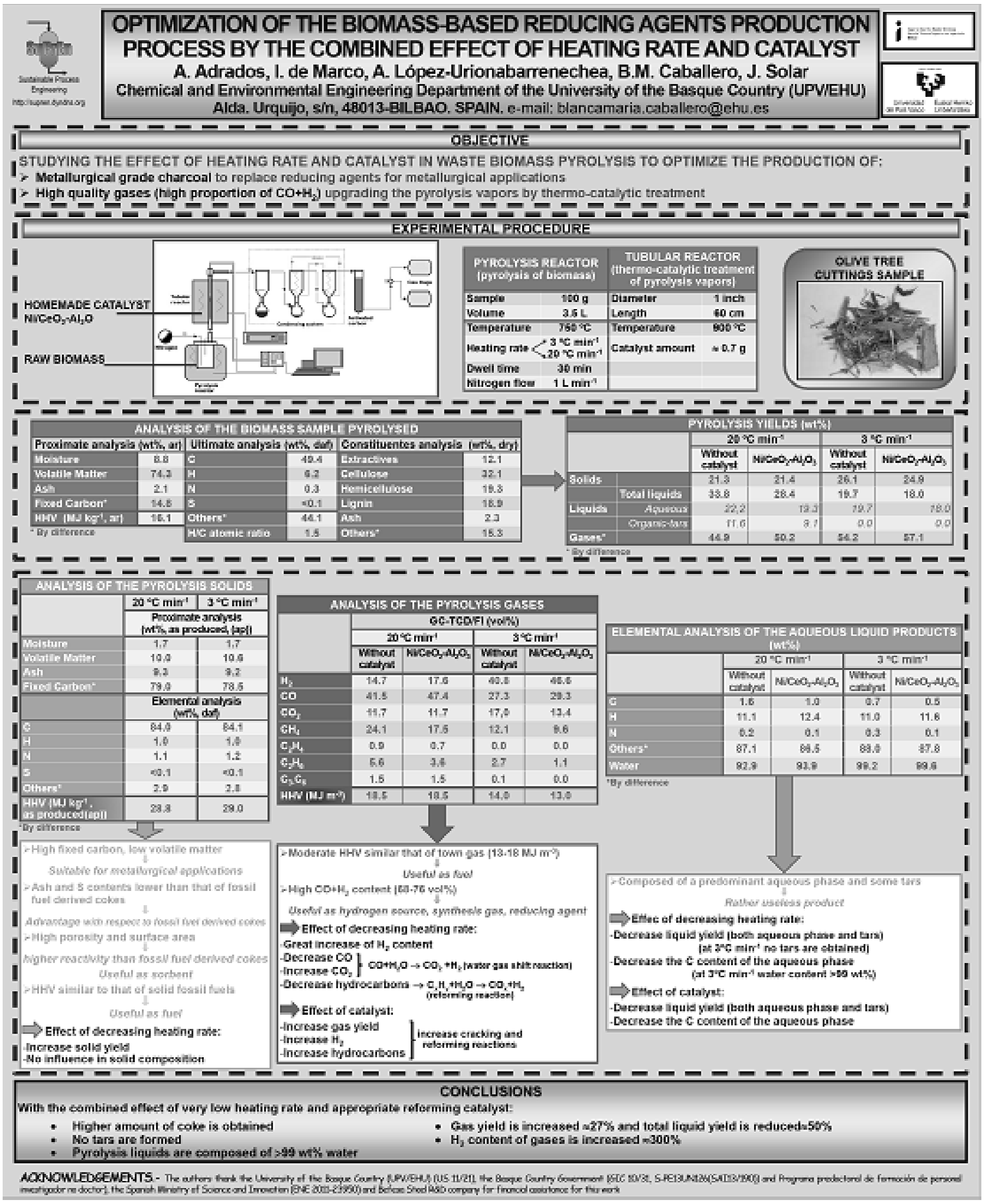
Authors: A. Adrados, I. de Marco, A. Lopez-Urionabarrenechea, B.M. Caballero, J. Solar

Title: Optimization of the biomass-based reducing agents production process by the combined effect of heating rate and catalyst

Congress: 10th International Conference on Renewable Resources and Biorefineries **Type of participation:** Poster

Publication:

Place: Valladolid, Spain **Date:** June 2014



OPTIMIZATION OF THE BIOMASS-BASED REDUCING AGENTS PRODUCTION PROCESS BY THE COMBINED EFFECT OF HEATING RATE AND CATALYST

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OBJECTIVE

STUDYING THE EFFECT OF HEATING RATE AND CATALYST IN WASTE BIOMASS PYROLYSIS TO OPTIMIZE THE PRODUCTION OF:

- **Metallurgical grade charcoal** to replace reducing agents for metallurgical applications
- **High quality gases (high proportion of CO+H_2)** upgrading the pyrolysis vapors by thermo-catalytic treatment

EXPERIMENTAL PROCEDURE

HOMEMADE CATALYST Ni/CeO_2-Al_2O

RAW BIOMASS

PYROLYSIS REACTOR (pyrolysis of biomass)		TUBULAR REACTOR (thermo-catalytic treatment of pyrolysis vapors)	
Sample	100 g	Diameter	1 inch
Volume	3.5 L	Length	60 cm
Temperature	750 °C	Temperature	900 °C
Heating rate	3 °C min^{-1} 20 °C min^{-1}	Catalyst amount	≈ 0.7 g
Dwell time	30 min		
Nitrogen flow	1 L min^{-1}		

OLIVE TREE CUTTINGS SAMPLE

ANALYSIS OF THE BIOMASS SAMPLE PYROLYSED

Proximate analysis (wt%, ar)		Ultimate analysis (wt%, daf)		Constituentes analysis (wt%, dry)	
Moisture	8.8	C	49.4	Extractives	12.1
Volatile Matter	74.3	H	6.2	Cellulose	32.1
Ash	2.1	N	0.3	Hemicellulose	19.3
Fixed Carbon*	14.8	S	<0.1	Lignin	18.9
HHV (MJ kg^{-1}, ar)	18.1	Others*	44.1	Ash	2.3
		H/C atomic ratio	1.5	Others*	15.3

* By difference

PYROLYSIS YIELDS (wt%)

		20 °C min^{-1}		3 °C min^{-1}	
		Without catalyst	$Ni/CeO_2-Al_2O_3$	Without catalyst	$Ni/CeO_2-Al_2O_3$
Solids		21.3	21.4	26.1	24.9
Liquids	Total liquids	33.8	28.4	19.7	18.0
	Aqueous	*22.2*	*19.3*	*19.7*	*18.0*
	Organic-tars	*11.6*	*9.1*	*0.0*	*0.0*
Gases*		44.9	50.2	54.2	57.1

* By difference

ANALYSIS OF THE PYROLYSIS SOLIDS

	20 °C min^{-1}	3 °C min^{-1}
	Proximate analysis (wt%, as produced, (ap))	
Moisture	1.7	1.7
Volatile Matter	10.0	10.6
Ash	9.3	9.2
Fixed Carbon*	79.0	78.5
	Elemental analysis (wt%, daf)	
C	94.0	94.1
H	1.9	1.9
N	1.1	1.2
S	<0.1	<0.1
Others*	2.9	2.8
HHV (MJ kg^{-1}, as produced(ap))	28.8	29.0

*By difference

- >High fixed carbon, low volatile matter
  ⇓
  Suitable for metallurgical applications
- >Ash and S contents lower than that of fossil fuel derived cokes
  ⇓
  Advantage with respect to fossil fuel derived cokes
- >High porosity and surface area
  ⇓
  higher reactivity than fossil fuel derived cokes
  Useful as sorbent
- >HHV similar to that of solid fossil fuels
  ⇓
  Useful as fuel

Effect of decreasing heating rate:
-Increase solid yield
-No influence in solid composition

ANALYSIS OF THE PYROLYSIS GASES

	GC-TCD/FI (vol%)			
	20 °C min^{-1}		3 °C min^{-1}	
	Without catalyst	$Ni/CeO_2-Al_2O_3$	Without catalyst	$Ni/CeO_2-Al_2O_3$
H_2	14.7	17.6	40.8	46.6
CO	41.5	47.4	27.3	29.3
CO_2	11.7	11.7	17.0	13.4
CH_4	24.1	17.5	12.1	9.6
C_2H_4	0.9	0.7	0.0	0.0
C_2H_6	5.6	3.6	2.7	1.1
C_3-C_6	1.5	1.5	0.1	0.0
HHV (MJ m^{-3})	18.5	18.5	14.0	13.0

- >Moderate HHV similar that of town gas (13-18 MJ m^{-3})
  ⇓
  Useful as fuel
- >High CO+H_2 content (56-76 vol%)
  ⇓
  Useful as hydrogen source, synthesis gas, reducing agent

Effect of decreasing heating rate:
-Great increase of H_2 content
-Decrease CO
-Increase CO_2 } $CO+H_2O \rightarrow CO_2+H_2$ (water gas shift reaction)
-Decrease hydrocarbons → $C_xH_y+H_2O \rightarrow CO_2+H_2$ (reforming reaction)

Effect of catalyst:
-Increase gas yield
-Increase H_2
-Increase hydrocarbons } increase cracking and reforming reactions

ELEMENTAL ANALYSIS OF THE AQUEOUS LIQUID PRODUCTS (wt%)

	20 °C min^{-1}		3 °C min^{-1}	
	Without catalyst	$Ni/CeO_2-Al_2O_3$	Without catalyst	$Ni/CeO_2-Al_2O_3$
C	1.6	1.0	0.7	0.5
H	11.1	12.4	11.0	11.6
N	0.2	0.1	0.3	0.1
Others*	87.1	86.5	88.0	87.8
Water	92.9	93.9	99.2	99.6

*By difference

- >Composed of a predominant aqueous phase and some tars
  ⇓
  Rather useless product

Effec of decreasing heating rate:
-Decrease liquid yield (both aqueous phase and tars)
(at 3°C min^{-1} no tars are obtained)
-Decrease the C content of the aqueous phase
(at 3°C min^{-1} water content >99 wt%)

Effect of catalyst:
-Decrease liquid yield (both aqueous phase and tars)
-Decrease the C content of the aqueous phase

CONCLUSIONS

With the combined effect of very low heating rate and appropriate reforming catalyst:

- Higher amount of coke is obtained
- No tars are formed
- Pyrolysis liquids are composed of >99 wt% water
- Gas yield is increased ≈27% and total liquid yield is reduced≈50%
- H_2 content of gases is increased ≈300%

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Authors: A. Adrados, I. De Marco, A. Lopez-Urionabarrenechea, J. Solar, D. Meier, M. Windt

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A.2. Published article

Journal: Journal of Analytical and Applied Pyrolysis

Title: Upgrading of pyrolysis vapours from biomass carbonization

Authors: A. Adrados, A. Lopez-Urionabarrenechea, J. Solar, J. Requies, I. De Marco, J.F. Cambra

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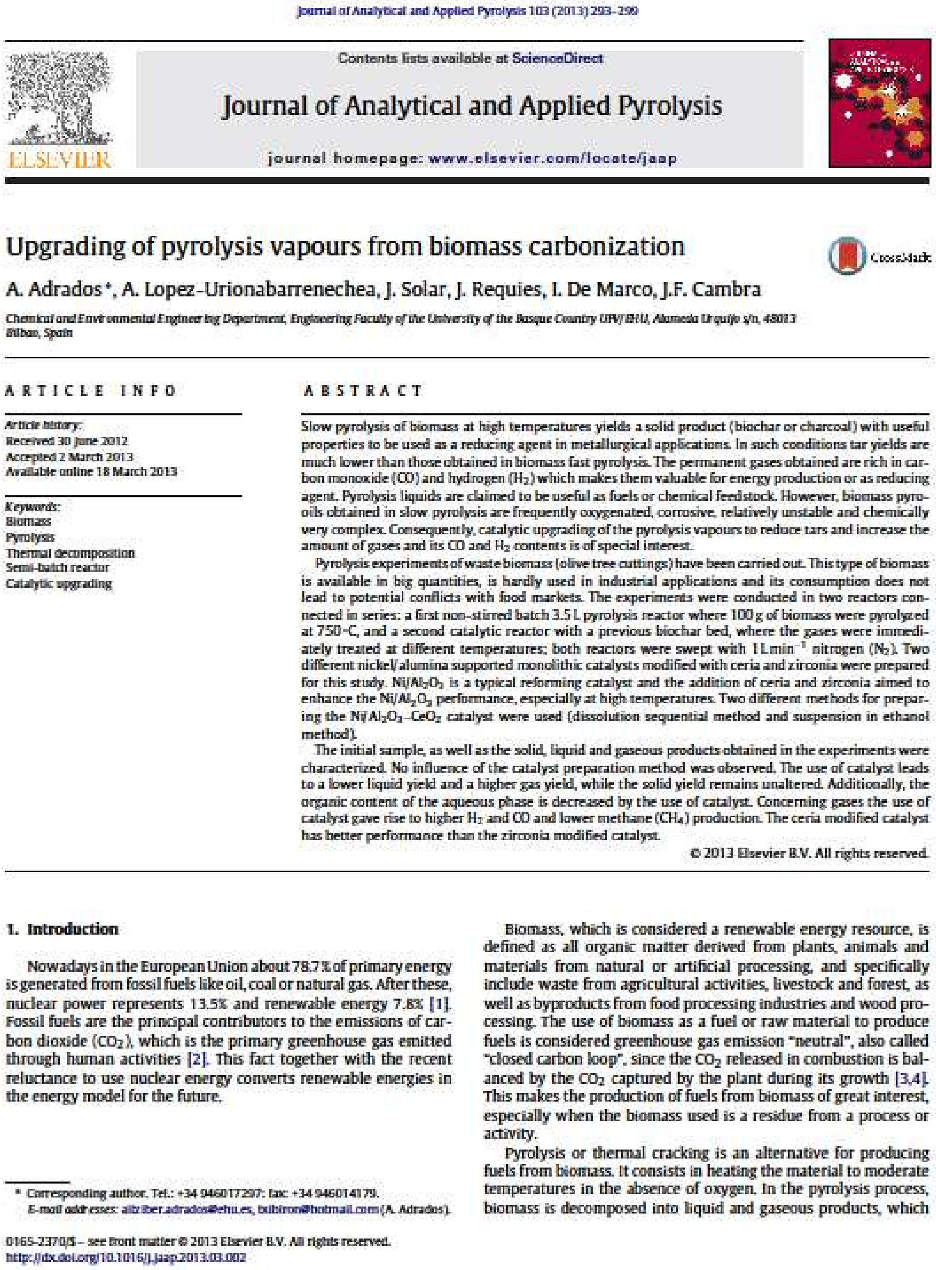

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Upgrading of pyrolysis vapours from biomass carbonization

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A B S T R A C T

Slow pyrolysis of biomass at high temperatures yields a solid product (biochar or charcoal) with useful properties to be used as a reducing agent in metallurgical applications. In such conditions tar yields are much lower than those obtained in biomass fast pyrolysis. The permanent gases obtained are rich in carbon monoxide (CO) and hydrogen (H_2) which makes them valuable for energy production or as reducing agent. Pyrolysis liquids are claimed to be useful as fuels or chemical feedstock. However, biomass pyro-oils obtained in slow pyrolysis are frequently oxygenated, corrosive, relatively unstable and chemically very complex. Consequently, catalytic upgrading of the pyrolysis vapours to reduce tars and increase the amount of gases and its CO and H_2 contents is of special interest.

Pyrolysis experiments of waste biomass (olive tree cuttings) have been carried out. This type of biomass is available in big quantities, is hardly used in industrial applications and its consumption does not lead to potential conflicts with food markets. The experiments were conducted in two reactors connected in series: a first non-stirred batch 3.5 L pyrolysis reactor where 100 g of biomass were pyrolyzed at 750 °C, and a second catalytic reactor with a previous biochar bed, where the gases were immediately treated at different temperatures; both reactors were swept with 1 L min^{-1} nitrogen (N_2). Two different nickel/alumina supported monolithic catalysts modified with ceria and zirconia were prepared for this study. Ni/Al_2O_3 is a typical reforming catalyst and the addition of ceria and zirconia aimed to enhance the Ni/Al_2O_3 performance, especially at high temperatures. Two different methods for preparing the Ni/Al_2O_3–CeO_2 catalyst were used (dissolution sequential method and suspension in ethanol method).

The initial sample, as well as the solid, liquid and gaseous products obtained in the experiments were characterized. No influence of the catalyst preparation method was observed. The use of catalyst leads to a lower liquid yield and a higher gas yield, while the solid yield remains unaltered. Additionally, the organic content of the aqueous phase is decreased by the use of catalyst. Concerning gases the use of catalyst gave rise to higher H_2 and CO and lower methane (CH_4) production. The ceria modified catalyst has better performance than the zirconia modified catalyst.

1. Introduction

Nowadays in the European Union about 78.7% of primary energy is generated from fossil fuels like oil, coal or natural gas. After these, nuclear power represents 13.5% and renewable energy 7.8% [1]. Fossil fuels are the principal contributors to the emissions of carbon dioxide (CO_2), which is the primary greenhouse gas emitted through human activities [2]. This fact together with the recent reluctance to use nuclear energy converts renewable energies in the energy model for the future.

Biomass, which is considered a renewable energy resource, is defined as all organic matter derived from plants, animals and materials from natural or artificial processing, and specifically include waste from agricultural activities, livestock and forest, as well as byproducts from food processing industries and wood processing. The use of biomass as a fuel or raw material to produce fuels is considered greenhouse gas emission "neutral", also called "closed carbon loop", since the CO_2 released in combustion is balanced by the CO_2 captured by the plant during its growth [3,4]. This makes the production of fuels from biomass of great interest, especially when the biomass used is a residue from a process or activity.

Pyrolysis or thermal cracking is an alternative for producing fuels from biomass. It consists in heating the material to moderate temperatures in the absence of oxygen. In the pyrolysis process, biomass is decomposed into liquid and gaseous products, which

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A.3. Articles sent for publication

Journal: Biomass & Bioenergy

Title: Avoiding tar formation in biocoke production from waste biomass

Authors: A. Adrados, I. De Marco, A. Lopez-Urionabarrenechea, J. Solar, B.M. Caballero

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Journal: Bioresource Technologies

Title: Slow pyrolysis of woody biomass waste: Influence of raw material on pyrolysis products

Authors: J. Solar, A. Hernandez, A. Lopez-Urionabarrenechea, I. de Marco, A. Adrados, B.M. Caballero, J.F. Cambra

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