Integrated sustainability analysis of innovative uses of forest biomass.

Bio-oil as an energy vector.

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Doctoral thesis

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A thesis submitted in fulfilment of the requirements
for the Doctoral degree in Environmental Sciences

SosteniPrA research group

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By

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The present thesis entitled 'Integrated sustainability analysis of innovative uses of forest biomass: Bio-oil as an energy vector' has been carried out at the Institute of Environmental Science and Technology (ICTA) at Universitat Autònoma de Barcelona (UAB) under the supervision of Professor Jordi Bartrolí Molins from the ICTA and the Department of Chemistry at the UAB; Dr. Ramón Murillo Villuendas from the Instituto de Carboquímica (ICB) of the Spanish National Research Council (CSIC) and Dr. Joan Rieradevall Pons from the ICTA and the Department of Chemical Engineering at the UAB.

Bellaterra, July 2010

Jordi Bartrolí Molins
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A	Acidification
A_i	pre-exponential factor (s^{-1})
AD	Abiotic Depletion
BEP	Break-even point
CF_n	fraction of constituent *n*
CHP	Combined Heat and Power
CIEMAT	Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas
C_0	minimum fuel consumption equivalent to an empty load (litres km-1)
C_p	fuel consumption of the vehicle when it carries the maximum load (litres km-1)
Q_t	the maximum load which a vehicle can carry (ton)
C_{xt}	total fuel consumption of the vehicle when a load (litres km-1)
C_{xta}	total fuel consumption of the vehicle when travelling the outgoing and the incoming routes (litres)
D	Depreciation or amortization
DAEM	Distributed Activation Energy Model
db	Dry basis
E	Eutrophication
E_i	specific activation energy (kJ/kg)
$F_{p,T}$	Fuel costs (€)
F	Financial Charges (€)
F_k	Cash-flow (€)
FC	Fixed Carbon
$f_{i,0}$	fraction of M_0 which decomposes with a specific activation energy, dimensionless
fu	Functional unit
GC/MS	Gas Chromatography/Mass Spectrometry
GW	Global Warming
h	Annual hours
H	Lifetime of the machinery (hours)
HHV	High Heating Value
HT	Human Toxicity
i	number of reactions describing the process
I_0	Investment cost (€)
i_A	Average interest (per unit)
ir	Annual interest rate (per unit)
IA	Integrated Assessment
IA-FGs	Integrated assessment- focus groups
IEA	Integrated Environmental Assessment
IL	Ionic Liquid
IRR	Internal Rate of Return
ISA	Integrated Sustainability Assessment
ISO	International Organization for Standardization
IT	Insurance and Taxes costs
k	Number of years
k_i	rate coefficient
k_{0i}	pre-exponential or frequency factor (s^{-1})
K_0	Distance traveled when the vehicle is empty (km)
K_x	Distance traveled when the vehicle is loaded. (km)
L	Length of the auger reactor (m)

LCA	Life Cycle Assessment
LCIA	Life Cycle Impact Assessment
LCI	Life Cycle Inventory
LHV	Low Heating Value
$M(t)$	mass of the sample at time t (kg)
M_0	initial mass of the sample (kg)
m	mass of volatile matter (kg)
n	number of constituents in the sample
M	Maintenance
MS	Mass Spectrometry
MW	Molecular Weight
N	Lifetime of the machinery (years)
NIST	National Institute of Standards and Technology
NPV	Net Present Value
NREL	National Renewable Energy Laboratory
ODP	Ozone Layer Depletion
O&M	Operation and Maintenance
p	Gasoline price (€/l)
p*	Gasoil price (€/l)
P	Purchase price (€)
PIA	Participatory integrated assessment
PL	Pitch of the auger reactor (m)
Q_h	mass flow rate of prepared wood feed into the reactor (odt/h)
Qt	Maximum load transported by the vehicle (ton)
Qx	Load transported by the vehicle(ton)
R	ideal gas constant (kJ/mol·K)
rpm	Revolutions per minute (r min-1)
Rt	Retention time (min)
RV	Revenues (€)
S	Spare pieces (€)
SETAC	Society of Environmental Toxicology and Chemistry
t	Time
T	Temperature (K)
TC	Total costs (€)
TCD	Thermal Conductivity Detector
TIC	Total Ion Chromatogram
TGA	Thermogravimetric analysis
toe	ton of oil equivalent (1 toe = 41.87 GJ)
TPC	total plant cost (€)
TFC	Fixed Costs (€)
TVC	Variable Costs (€)
t_r	Solid residence time (s)
V^*_i	initial mass for reaction *i*
$V_i(t)$	mass fraction for the *i*th constituent
VM	Volatile Matter
%wt	Weight percentage
w	Fraction w of inert material
X	fraction of mass remaining

Acknowledgments

During this dissertation, due to its multidisciplinarity, I had the opportunity to work with different research groups. I am very grateful to all colleagues from SosteniPrA research group for the years and good times we had. Special thanks to Dr. Joan David Tàbara for his assistance in organizing the focus groups and his contribution to the social assessment. I am also thankful to Dr. Ramon Alibés and his research group, from the section of Organic Chemistry of the Department of Chemistry at Universitat Autònoma de Barcelona, for their contribution and help during the lab work; and Dr. Geoff Fowler and his research group at Imperial College London for the months we could work together. I also want to express my gratitude to all the people from the Energy and Environment Department at Instituto de Carboquímica (ICB-CSIC) for the intense and hard-working months we enjoyed.

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Summary

During the past decades, forest management in Mediterranean countries has been constantly diminishing. Recently, an increase of the forest area and its neglectfulness is accounted to these regions due to economy tertiarization and lack of profitability, among other factors. The main objective of this dissertation is to provide an alternative to Mediterranean forests and specifically in the case of Catalonia, a region located in the northeast of Spain that has a forested area of 1.930.481 ha, representing 60.1% of its total surface area.

This context gives raise to concerns such as the lack of full operational biomass systems in Mediterranean countries and the necessity to improve this current circumstance. To answer these questions, a multidisciplinary perspective (social, environmental and technological) is approached. First, an integrated assessment of biomass systems by means of focus groups methodology is carried out in order to identify what political, social and environmental barriers have prevented integrated forest biomass systems to be further developed in a Mediterranean context such as Catalonia. Results showed that while the opportunities and stakes are high, in Mediterranean countries, specific socio-ecologic factors need to be taken into account if forest biomass is to contribute decisively to securing renewable sources of energy in Europe, integrating landscape planning with resource policies or mitigating climate change. Among these key factors identified are property regimes, low productivity of Mediterranean forests and weak institutional capacity. Other elements such as logistics and supply difficulties and the lack of economic profitability of forest products constitute limitations identified in the implementation of bioenergy systems.

The state-of-the-art of the different biomass conversion technologies showed that combustion is the most extended biomass conversion process, gasification is in a commercial stage and pyrolysis is under important research, development and demonstration. Since gasification process offers higher energy efficiency compared to combustion, a life cycle assessment of a bioenergy system based on gasification of two different biomass sources was performed in order to compare different biomass supply chains and logistics: forest biomass and post-consumer wood. This study showed that forest biomass needs higher energy requirements due to mainly an additional drying stage in order to comply with the gasification demands. This fact raised uncertainties about one of the biggest issues in forest biomass systems, the energy demands and costs of the pre-treatment and transport stages. Regarding this aspect, biomass pyrolysis offers significant advantages for the multiple value-added products obtainable, from liquid fuels to chemicals. Pyrolysis yields to liquid, solid and gas fractions, and the pyrolysis liquids, known as bio-oil, represent an alternative way to reduce the high transport costs of biomass.

Moreover, in recent years this interest has increased with the possibility of performing pyrolysis processes in remote locations, which represent a major opportunity to process diverse biomass feedstock from forests or agricultural land, due to its dispersion and its seasonal production. Lignocellulosic energy crops can also represent a good opportunity to foster bioenergy systems while maintaining the mosaic landscape, lost during the last decades due to agricultural land converted to forest. In addition, the solid fraction, known as char, has de potential to provide an important carbon sink and to reduce environmental pollution by fertilizers. For this reason, biomass pyrolysis was studied as a local strategy to make use of forest biomass as feedstock. First of all, an application of the Distributed Activation Energy Model (DAEM) to biomass and biomass constituents' devolatilisation was performed to study the thermal decomposition of biomass. Second, biomass pyrolysis was performed in an auger reactor pilot plant (10 kg/h) in order to study the optimal operation conditions (different reaction temperatures, different solid residence times and different mass flow rates) and to characterize the properties of the products obtained. Auger reactors offer numerous advantages such as their compact design and low maintenance operations, which allow them to convert them into a mobile plant. The novelty of this approach is the use of pine woodchips (up to 20 mm of nominal size) as raw material, instead of small particle size feedstock, with the objective of avoiding energy intensive pre-treatment. Results showed that complete pyrolysis of the woodchips could be achieved in the auger reactor. Pyrolysis temperature is the process variable that most influences the products yield and the physicochemical composition of bio-oil. It was also found that the greatest yields for liquid production (59%) and optimum product characterisation were obtained at the lowest temperature studied (773 K) and applying solid residence times longer than 2 minutes. Regarding to the bio-oils properties, GC/MS qualitative identification showed that the most abundant compounds are volatile polar compounds, phenols and benzenediols and very few differences could be observed in the physical properties of the bio-oil samples regardless of the pyrolysis operating conditions. The bio-oil produced in this auger reactor is similar to the bio-oil obtained in other auger reactors; except for that it has less water and oxygen content. On the whole, experimental results demonstrated that complete reaction could be achieved in an auger reactor in most of the experimental conditions tested. This allowed performing simulation processes to assess the mass and energy balances of the pyrolysis process in the pilot plant and in a scaled up auger reactor (1500 kg/h). From this study, it could be demonstrated that a drying unit and a char combustor were needed if the pyrolysis had to be performed in situ, even though the process is energy-independent when moisture content is lower than 6%. An economic assessment also showed that these mobile pyrolysis plants offer advantages in a local scenario in terms of an energy vector. The total costs of producing bio-oil in the scaled-up pilot plant is between 269 and 289 €/m^3 depending on the biomass cost (40-50€/ton). The break-even point of the pyrolysis plant is 116 €/barrel when the biomass is purchased at 50 €/ton and 108 €/barrel when the biomass cost is 40 €/ton. In the long term, bio-oil offers great potential in a biorefinery scenario. In addition, in order to study other greener processing technologies than pyrolysis, a novel approach by means of microwave-assisted dissolution of wood in ionic liquids was performed.

In conclusion, this research offers a multidisciplinary approach to study different novel uses of forest biomass and a development of an integrated study from the standpoint of environmental, social, economic and technological using the different tools such as IA-Focus Groups, LCA and experimental pilot plant. These novel uses offer great opportunity for the Mediterranean forestry sector, since they offer value-added products such as the bio-oil. Bio-oil represents a new energy carrier, which is as versatile as oil and which may be the basis for a new generation of second-generation biofuels and, in turn, raw material for biorefineries. This dissertation is also related to social sustainability by suggesting actions and proposals related to local development and the network economy, as well as facilitating decision-making processes, which help to make a step forward to a global and integral knowledge of sustainability.

Preface

This dissertation is the result of a multidisciplinary approach to answer a question raised for the currently neglected Mediterranean forests and the need to seek for different potential value-added outputs.

Such concerns derived from two projects funded by Abertis Foundation entitled: *Biomass as a source of raw materials and energy: Feasibility Study of the Montseny and Montnegre-Corridor* (2005) and *Sustainable development of Mediterranean forests. Forestry Centre in Sant Celoni* (2007), carried out by Universitat Autònoma de Barcelona and Universitat de Girona. In these studies, several significant factors emerged relating mainly to forest management and biomass conversion technologies. These factors have led to the subsequent research of this dissertation, which resulted in the opening of a new line of research on novel uses of biomass in the Institute of Environmental Science and Technology (ICTA) and the Department of Chemistry of the Universitat Autònoma de Barcelona, currently ongoing.

The dissertation is based partly on the following published papers in peer-reviewed journals:

- Puy N, Tàbara D, Bartrolí Molins J, Bartrolí Almera J, Rieradevall J. Integrated Assessment of forest bioenergy systems in Mediterranean basin areas: The case of Catalonia and the use of participatory IA-focus groups. Renewable and Sustainable Energy Reviews 2008;12:1451-1464.
- Puy N, Rieradevall J, Bartrolí J. Environmental assessment of post-consumer wood and forest residues gasification: The case study of Barcelona metropolitan area. Biomass and Bioenergy In Press, Corrected Proof. doi:10.1016/j.biombioe.2010.04.009
- Navarro MV, Puy N, Murillo R, Mastral AM, Bartroli J. Application of the Distributed Activation Energy Model to Biomass and Biomass Constituents Devolatilization. AIChE Journal 2009;55:2700-2715.
- Puy N, Murillo R, Navarro MV, Aranguren N, López JM, Rieradevall J, et al. Valorisation of forestry waste by pyrolysis in an auger reactor. Waste Management (accepted).

In addition to these peer-reviewed papers and several conference contributions, the following article has been published by invitation in a journal specialized in environmental and forest issues, where the different issues and concerns raised in this dissertation are addressed:

- Puy N, Alier S, Bartrolí J. The use of biomass and the managements of forests. Medi Ambient. Tecnologia i Cultura 2009;44:133-138.

The structure of the dissertation is organized in five main chapters:

(I) Introduction and methodology;
(II) Social tool: Integrated assessment of forest bioenergy systems;
(III) Environmental assessment of a gasification bioenergy system;
(IV) Technological assessment: experimental, simulation and economic study on biomass pyrolysis, along with a green chemistry approach in the biorefinery context for processing biomass; and
(V) Conclusions and future research

Chapter I provides an overview of biomass as energy source, the context of this dissertation, followed by the motivation and objectives of this thesis. Afterwards, the methodologies used in this work are presented that consist of sustainability assessment tools and the experimental section.

Chapter II presents an integrated assessment of forest bioenergy systems. It contains the description, analysis and results obtained in the participatory sessions by means of focus groups methodology.

In Chapter III the life cycle assessment of post-consumer wood and forest residues gasification is disclosed.

Chapter IV shows the results, analyses and posterior simulations of the experimental work carried out. It includes the application of the Distributed Activation Energy Model to biomass, the performance of the auger reactor pilot plant, and the characterisation of the products obtained from the pyrolysis products. Moreover, a simulation process to assess the mass and energy balance of the auger reactor pilot plant and of a scaled-up pilot plant is presented. In addition, an economic assessment is carried out with the intention of evaluating the feasibility of mobile pyrolysis plants to produce bio-oil. Furthermore, a novel approach to green chemistry is presented, where a prospective study of liquefaction of biomass using ionic liquids is presented.

Finally, in Chapter V the conclusions and proposals for future improvement and research are addressed.

I

Introduction and methodology

1. Introduction

In Mediterranean countries there is the social perception that forest management is declining, which is especially relevant since the eighties. In recent years, socioeconomic changes have played a leading role in these countries' economy tertiarization, causing a decrease of forest biomass harvesting, which, in turn, resulted in an increase of the forest area and its neglectfulness. The importance of forests is tied largely to its use as a source of natural resources and its role as an ecological system and landscape. In this sense, biomass has the potential to become one of the major renewable primary energy sources and forest biomass in particular has an important role to play in the landscape management and in the climate policy domain during the present century. In fact, integrated bioenergy systems are suggested to be important contributors to ensure future supply of energy [1,2]. On the other hand, there are national, regional and European plans and policies that encourage the use of renewable energies, within which forest biomass plays an important role. However, in Mediterranean areas the use of biomass as energy source is not extended, and thus missing an opportunity to develop forest centred economies and, at the same time, causing negative side effects, such as an rise in forest fire risk.

This context arises two main questions: why biomass systems are not fully in operation in Mediterranean countries and how could this situation, which is not optimal, be improved. Such concerns triggered the beginning of this work and marked the starting point for the successive stages of the research.

1.1. Overview of biomass as energy source

The term biomass refers to the set of organic matter of vegetable or animal origin. This broad definition includes from forest residues to animal residues such as meat and bone meal. However, in this dissertation the term biomass is referred to forest biomass, known as well as lignocellulosic biomass.

The following section provides an outline and description of lignocellulosic biomass and biomass conversion processes.

1.1.1. Lignocellulosic biomass

Lignocellulosic biomass comprises three main polymeric components: cellulose, hemicellulose and lignin. They constitute 97-99% of the total dry mass of wood, of which 65-75% are polysaccharides. Typically, woody materials consist of 40-60% cellulose; 20-40%

hemicellulose and 10-25% lignin on dry basis [3]. The rest of the components are inorganic minerals and organic extractives, which comprise a large variety of chemical substances, such as terpenoids, fats and waxes, various types of phenolic compounds, as well as n-alkanes and can comprise usually between the 4 and 10% of the total wood [4]. Cellulose is a highmolecular-weight lineal polymer of β-(1→4)-D-glucopyranose units (see Figure 1). Hemicellulose is the second major wood chemical constituent and has lower molecular weights than cellulose and it comprises mainly glucose, galactose, mannose, xylose, arabinose and glucuronic acid. Lignin is a three dimensional, highly branched, polyphenolic substance that consists of phenylpropane units, which exhibit the p-coumaryl, coniferyl and sinapyl structures (see Figure 1).

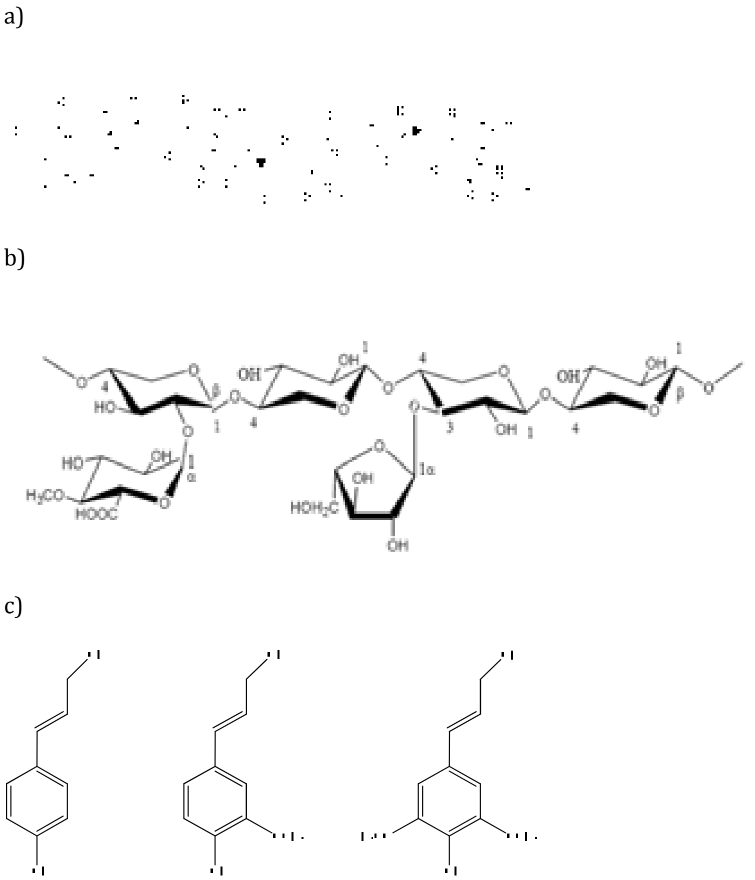
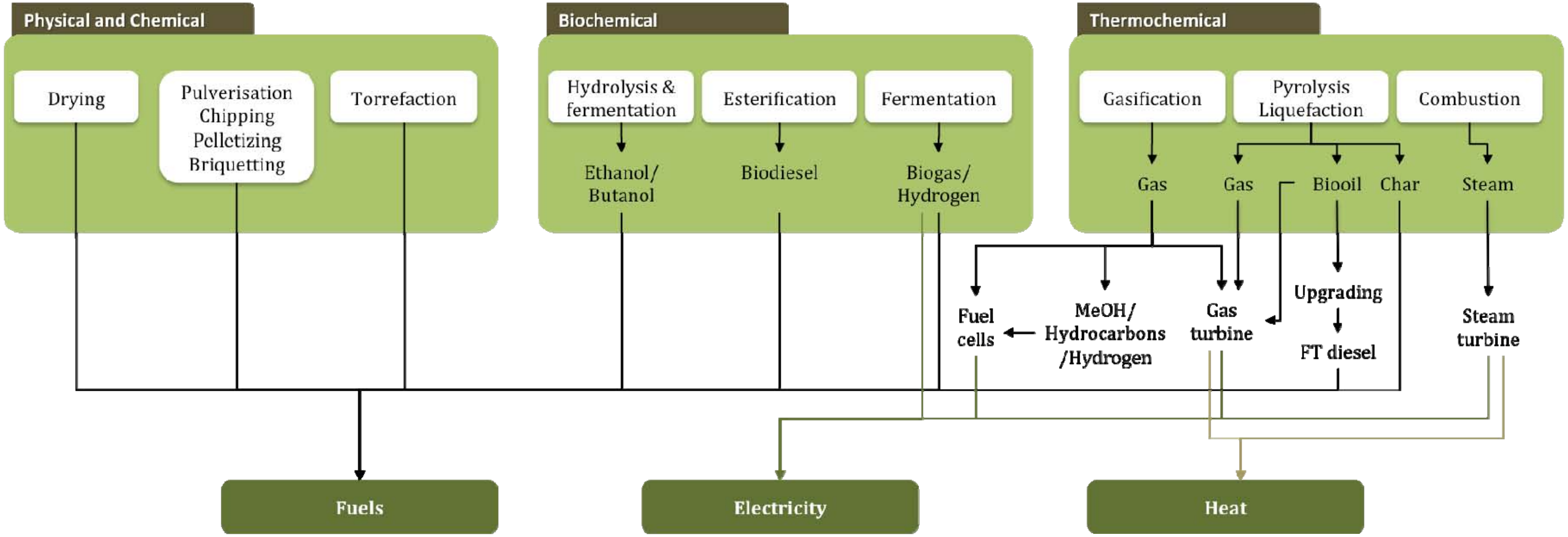


Figure 1. Structures of (a) cellulose polymer linked by β-Glycosidic linkages; (b) hemicellulose; and (c) p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol units present in lignin.

1.1.2. Biomass conversion technologies

Biomass can be converted into solid, liquid or gaseous fuels by means of different thermochemical, biological, chemical and physical upgrading processes [5-7]. Thermochemical processes can be divided into several main groups: (i) combustion, carried out in the presence of air to convert the chemical energy to power; (ii) gasification, which converts biomass to different gaseous hydrocarbons, (iii) direct liquefaction, which can be performed by high temperature pyrolysis or high pressure liquefaction; and (iv) pyrolysis, which is the heating of biomass in absence of oxygen to produce solid, liquid and gaseous products. Biological and chemical processes consist of hydrolysis to obtain products such as methanol or butanol; fermentation to produce biogas or hydrogen; and esterification in order to generate biodiesel.

Physical upgrading processes are generally needed to process biomass, which involve reducing the particle size (chipping, pulverisation, briquetting or pelletizing), drying and torrefaction. Torrefaction processes are included in this classification, although some chemical transformation occurs. The main processes and the products obtained for biomass conversion can be observed in Figure 2 and in Table 1.



Source: Adapted from [8].

Figure 2. Biomass conversion processes to secondary energy carriers.

Modern applications of biomass embrace the above-mentioned technologies for: household applications (e.g. improved cooking stoves); small cottage industrial applications (e.g. hospitals, swimming pools); and large industrial applications (e.g. CHP, electricity generation) [5].

Thermochemical processes such as combustion, pyrolysis or gasification are being extensively studied [9-11]. Combustion technologies produce about 90% of the energy from biomass, converting biomass into several forms of useful energy. It is the most extended thermochemical process since there are industrial combustion plants, which generate electricity from steam-driven turbine generations with a conversion efficiency of between 17 and 25% or, in the case of cogeneration, this efficiency is increased up to 85% [5]. Co-firing is the combustion of biomass blended with coal in differing proportions that are environmentally favourable compared to coal-only plants. Gasification is one of the most important research, development and demonstration areas in biomass for power generation, which can take advantage of advanced turbine designs and heat-recovery steam generators to achieve high energy efficiency. Combined heat and power (CHP) is a well-understood technology that is usually implemented by the addition of a heat exchanger that absorbs the exhaust heat from an existing generator to produce electricity [5]. Pyrolysis has gained and increasing interest in recent years for the multiple products obtainable, from liquid fuels to the large number of chemicals (adhesives, organic materials, etc.), even though some important challenges must be addressed for a full-operation pyrolysis plant. In fact, pyrolysis is less well developed than gasification [8]. Owing to the value-added offered by pyrolysis comparing to other technologies and the importance of this alternative in this dissertation, further information on pyrolysis is detailed below.

Table 1. Summary of the main characteristics of some biomass technologies.

Technology	Biomass type	Example of fuel used	Main product	End-use	Status
Combustion	Dry biomass	Solid biomass (wood logs, chips and pellets, etc.)	Heat	Heat and electricity (steam turbine)	Commercial
Co-firing	Dry biomass (woody and herbaceous)	Agro-forestry residues	Heat/electricity	Heat and electricity (steam turbine)	Commercial (direct combustion) Demonstration stage (advanced gasification and pyrolysis)
Gasification	Dry biomass	Woodchips, pellets	Syngas	Heat (boiler), electricity (engine, gas turbine, fuel cell, combined cycles), transport fuels (methanol, hydrogen)	Commercial stage
CHP	Dry biomass, biogas	Forest residues, straw	Heat and electricity	Combined used of heat and electric power (combustion and gasification processes)	Commercial (medium to large scale) Commercial demonstration (small scale)
Pyrolysis	Dry biomass	Woodchips, pellets	Pyrolysis oil and by-products	Heat (boiler), electricity (engine, gas turbine), liquid fuels (upgraded bio-oil)	Commercial and commercial demonstration (small scale)
Etherification/ pressing	Oleaginous crops	Oliseed rape	Biodiesel	Heat (boiler), electricity (engine), transport fuel	Commercial
Fermentation/ hydrolysis	Sugar and starches, cellulosic material	Sugarcane, corn, woody biomass	Ethanol	Liquid fuels (e.g. transport) and chemical feedstock	Commercial. Under development for cellulosic biomass
Anaerobic digestion	Wet biomass	Manure, sewage sludge	Biogas and by-products	Heat (boiler), electricity (engine, gas turbine, fuel cells)	Commercial, except fuel cells

Source: Adapted from [5].

The pyrolysis process

Pyrolysis occurs when heat is applied to a material in the absence of oxygen. It is the fundamental chemical reaction that is the first stage of both the gasification and combustion of solid fuels [7]. Liquid, solid and gas products are obtained from the pyrolysis reaction and their yields depend on the raw material and the process conditions.

Pyrolysis processes can be divided mainly by conventional pyrolysis and fast pyrolysis. Conventional pyrolysis, also sometimes known as slow pyrolysis, has been applied for the production of charcoal for thousands of years [12]. In conventional pyrolysis, biomass is heated to approximately 773 K and the heating rate is typically much slower than that used in fast pyrolysis. Fast pyrolysis is usually carried out at reaction temperatures of 773 K, where the feedstock is rapidly heated in the absence of air, vaporises and condenses to a dark brown mobile liquid which has a heating value of about half that of conventional fuel oil [13]. In Table 2 properties for bio-oils and heavy fuel oil are shown.

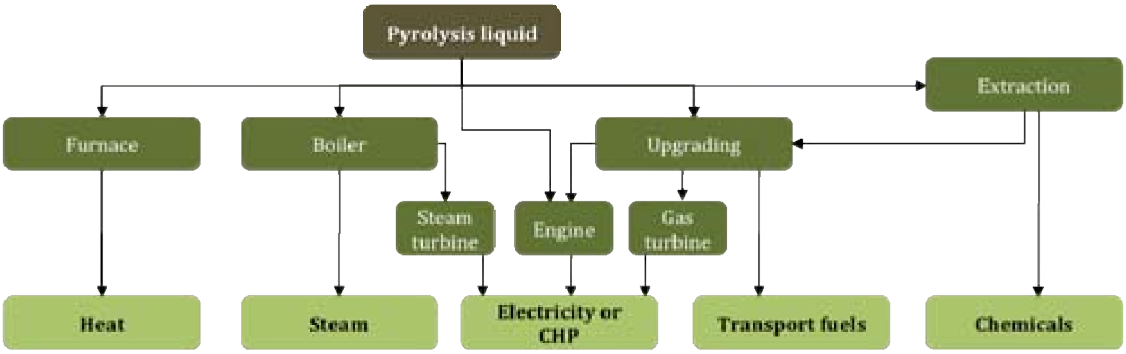
Table 2. Properties of wood pyrolysis bio-oil and heavy fuel oil.

Property	Bio-oil	Heavy fuel oil
Moisture content, wt %	15-30	0.1
pH	2.5	-
Specific gravity	1.2	0.94
Elemental composition, wt %		
C	54-58	85
H	5.5-7.0	11
O	35-40	1.0
N	0-0.2	0.3
ash	0-0.2	0.1
HHV, MJ/kg	16-19	40
Viscosity (at 50 °C), cP	40-100	180
Solids	0.2-1	1

Source: [14].

The objective of fast pyrolysis is to produce high liquid yields. Fast pyrolysis processes produces 60-75 wt% of liquid bio-oil, 15-25 wt% of solid char, and 10-20 wt% of non-condensable gases, depending on the feedstock used [12]. Moreover, the residence time of the gas is much lower than in conventional pyrolysis. Most fast pyrolysis processes demand feed pre-treatment since they need a finely divided and substantially dry feed [15].

There are several applications for bio-oil (see Figure 3). Bio-oil can be readily stored and transported and can be burned in engines, boilers and turbines or can be upgraded to high-quality hydrocarbon fuels, although their quality has still several technical and economic challenges [14,16]. It is also a potential source of chemicals with higher-added value than fuels; especially those produced from the whole bio-oil or its major fractions [16].



Source: [15].

Figure 3. Applications of pyrolysis liquid.

There are many pyrolysis reactors: bubbling fluidized beds, circulating and transported beds, cyclonic reactors, vortex reactors, auger reactors and ablative reactors, among others [13,14,17] (see Figure 5). Even though this reactor's diversity, there are four main technologies available for commercial fast pyrolysis plants are: (i) shallow fluidized beds; (ii) vacuum pyrolyzers; (iii) ablative pyrolyzers, both cyclonic and plate type; and (iv) circulating fluid beds [18]. Mohan et al. add a fifth technology in this classification, which is (v) auger reactors [12].

The bubbling fluidized bed reactor is usually referred to simply as fluidized beds, opposed to circulating fluidized bed reactors [12]. It has the advantages of a well-understood technology that is simple in construction and operation, good temperature control and very efficient heat transfer to biomass particles due to high solids density [19]. They need small biomass particle sizes of less than 2-3 mm to achieve high biomass heating rates. Sand is often used as the solid phase of the bed and these reactors produce good quality bio-oil with a high liquid product yield [12].

Circulating fluidized bed and transported bed reactors are similar to the bubbling fluidised bed, except for the fact that the residence time of the gas and the char are practically the same [12]. In circulating fluid bed reactor systems heat supply is usually from recirculation of heated sand from a secondary char combustor, which can be either a bubbling or circulating fluid bed.

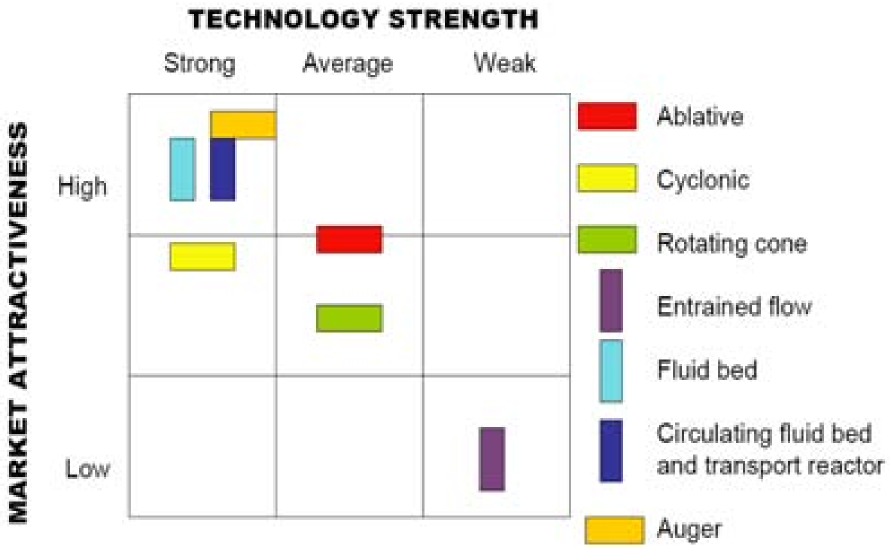
Vacuum pyrolysis reactors the heat transfer rate is much slower than other reactors, although the gas residence time is comparable to those in fast pyrolysis. It involves thermal biomass decomposition under reduced pressure, normally 15 kPa [12]. The major drawback of this technology is that requires larger-scale equipment.

In the rotating cone reactor, the sand and biomass transport is performed by centrifugal forces. It has negligible char formation, rapid heating and short residence time of the solids. After leaving the impeller the particles flow outwards over the conical surface and experience a high heat transfer rate due to their small distance from the heated surface [20].

In ablative pyrolysis a biomass particle impacts and slides over a solid hot source [12]. The characteristics of ablative pyrolysis are: high pressure of particle on hot reactor wall, achieved due to centrifugal force or mechanically; high relative motion between particle and reactor wall and the reactor wall temperature is less than 873 K [19]. In ablative pyrolysis the reaction is limited by the rate of heat transfer through the biomass particle and, thus, very small particles are required.

The auger reactor does not require carrier gas and can operate continuously at lower process temperatures (673 K) [12]. It moves the biomass through a cylindrical tube while it decomposes to a gaseous product and char. The condensed gases are condensed as bio-oil, while the gas can be stored as biogas.

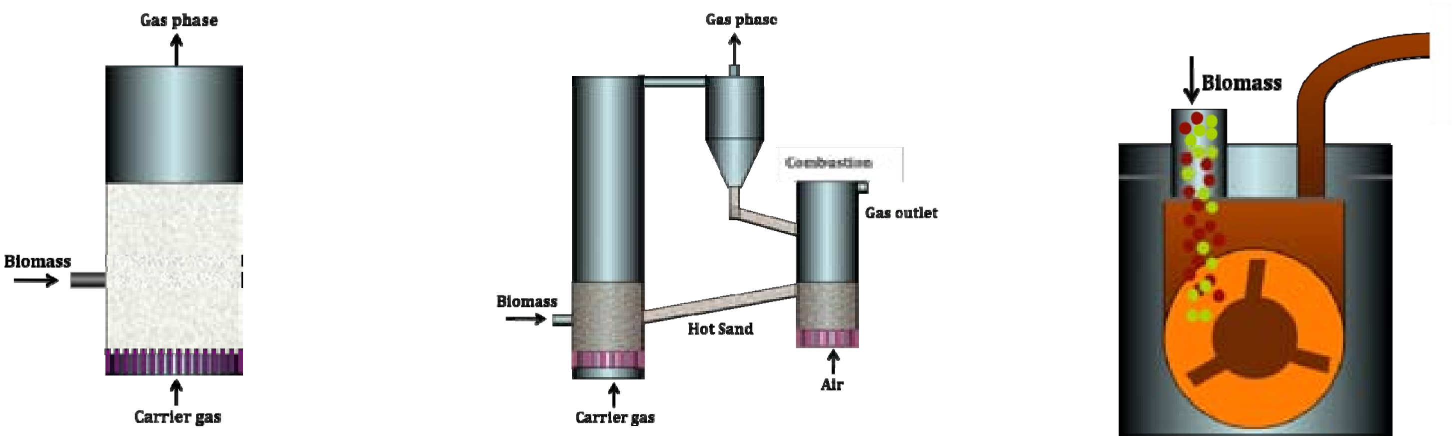
These technologies have been classified [21] according to strength and market attractiveness (see Figure 4). The technological strength and the market attractiveness show that the circulating and bubbling fluidised bed reactors have the highest commercial potential, along with the auger reactor.



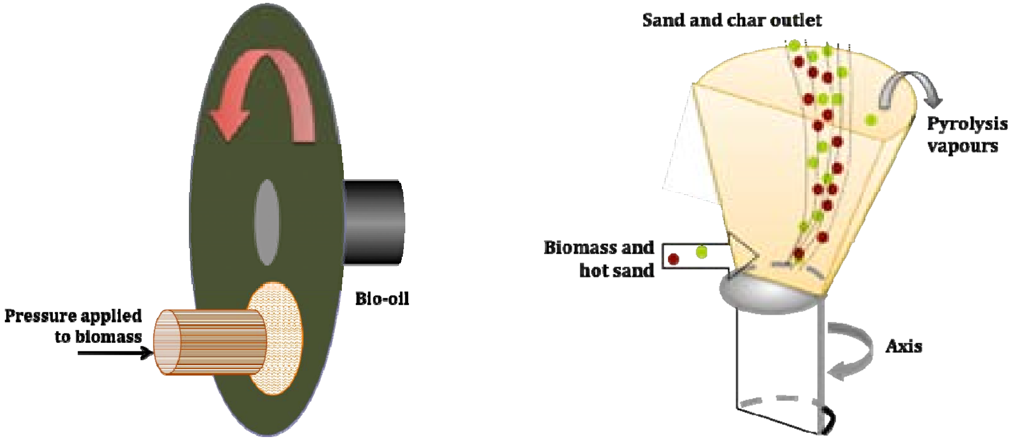
Source: [21] adapted from PYNE IEA Bioenergy [19].

Figure 4. Status of pyrolysis technologies according to market attractiveness.

In Table 3 it is presented a summary of the current pyrolysis reactors in existence, organisations, country, development, status, and heating methods and rates.



Bubbling fluidised bed reactor Circulating fluidised bed reactor Auger reactor



Ablative reactor Rotating cone reactor

Source: Adapted from [21] and [12].

Figure 5. Reactor configurations for biomass pyrolysis.

Table 3. Pyrolysis reactors, organizations, heating methods and heating rates.

Reactor type	Organisation	Country	Status	Method of heating	Heat transfer	Heating rate	Reference
Ablative tube	BBC	Canada	Commercial	Wall heating	Indirect	High	[13]
Ablative tube	University of Aston	UK	Pilot plant	Wall heating	Indirect	High	[22]
Ablative vortex	National Renewable Energy Laboratories (NREL)	USA	Pilot plant	Wall heating	Indirect	High	[23]
Auger	Renewable Oil International LLC (ROI)	Italy	Pilot plant	Wall heating	Indirect	Low	[12,24]
Auger	Mississipi State University	USA	Lab- scale	Wall heating	Indirect	Low	[12,25]
Auger	ETIA (Technolic Evaluation, Ingeneering & Application)	France	Commercial	Auger electrically heated	Direct	Low	[26]
Circulating transported bed	Ensyn	Canada	Commercial	Hot sand	Direct	High	[27]
Circulating transported bed	VTT	Finland	Pilot plant	Hot sand	Direct	High	[13,28]
Circulating fluidised bed	Chemical Process Engineering Research Institute (CPERI)/Centre of Renewable Energy Sources	Greece	Pilot plant	Partial gasification	Direct	High	[13,29]
Circulating fluidised bed	Pasquali/ENEL	Italy	Pilot plant	Hot sand	Direct	High	[13]
Entrained flow	Egemin	Belgium	Shut down	Combustion products	Direct	High	[13]
Entrained flow	Georgia Tech Research Institute (GTRI)	USA	Pilot plant	Combustion products	Direct	High	[13,30]
Fluidised bed	University of Aston	UK	Pilot plant	Heated recycle gas	Direct	Low	[22]
Fluidised bed	National Renewable Energy Laboratories	USA	Pilot plant	Heated recycle gas	Direct	Low	[23]
Fluidised bed	VTT	Finland	Pilot plant	Hot sand	Direct	High	[13,28]
Fluidised bed	Dynamotive	Canada	Commercial	Heated recycle gas	Indirect	High	[31]
Fluidised bed	Resource Transforms International (RTI)	Canada	Commercial	Heated recycle gas	Indirect	High	[13]
Fluidised bed	University of Waterloo	Canada	Pilot plant	Heated recycle gas	Indirect	High	[13]
Fluidised bed	Union Fenosa	Spain	Commercial	Heated recycle gas	Indirect	High	[13]
Fluidised bed	University of Santiago	Spain	Pilot plant	Heated recycle gas	Indirect	High	[13]
Rotating cone	Twente University	Netherlands	Pilot plant	Wall and sand heating	Indirect	High	[32]
Rotating cone	Biomass Technology Group BV (BTG)	Netherlands	Commercial	Wall and sand heating	Indirect	High	[33]
Vacuum moving bed	Pyrovac/University of Laval	Canada	Commercial	Molten salt	Indirect	High	[13]

1.2. Context of the dissertation - Forestry sector in Catalonia

This dissertation focuses on the case of Catalonia, a region located in the northeast of Spain (see Figure 6). Catalonia has a forested area of 1.930.481 ha, representing 60.1% of its total surface area, well over the Western European average of 36.8% and comparable with more forested European countries (Finland with 73.9% and Sweden with 66.9%) [34]. The effects of economy tertiarization, added to the rural depopulation in the second half of the twentieth century, have increased the forested area in Catalonia, especially the tree cover, which is currently more than 1.5 million hectares and represents the 38% of Catalonia and the 10% of the Spanish forestry area [34,35]. Of these, 40% have been incorporated since 1970s and consist of high-density masses gained mainly from neglected cultivated lands. Four main tree species occupy two third parts over the whole forestry territory: *Quercus ilex*, *Pinus sylvestris*, *Pinus halepensis* and *Pinus nigra* [35]. Such overgrown of the tree covers can lead to forest fires that affect periodically the Catalan forests and are characterized by their high temporal and spatial irregularity [36]. At present, the deployment of an important institutional and technological capacity to combat forest fires has also lead to a further growth of forests' extension and biomass accumulation in detriment of intermediate open spaces and buffer zones which are also crucial in performing a number of ecological and socio-economic functions such as biodiversity conservation. Also the orography of these forests, with steep slopes, hinders their accessibility with regard to forestry management and exploitation.

Another factor that characterizes forest management in Catalonia is the predominantly private structure of forest property, where the 76.9% corresponds to privately owned land [34]. The rest is divided between municipal bodies' forests (18.2%) and those of the Government of Catalonia (4.9%). Furthermore, it has been estimated that the number of forest owners in Catalonia is 264747, of whom over 220000 own properties of under 5 hectares and the rest, the 4.5%, have properties grouped into plots of over 25 hectares (corresponding to 1 million hectares) [34].

Despite the fact that Catalonia is a country of forests, it has a serious wood deficit due to the lack of profitability of biomass harvesting, which ends up with important imports of wood per year. This deficit is accounted as between 4 and 5 million cubic metres [34] and this situation has been enhanced by the recent crisis in 2009 in a context where the wood prices were already precarious in the last ten years. Moreover, the impact of the French timber market is remarkable due to the imports of more affordable and quality wood comparing to Catalan wood. For instance, the east wind and storms in late 2008 generated an extra amount of wood that could not be placed in the market partly because of the wood also generated by storms in France that could enter the market due to the French government subsidies [37].

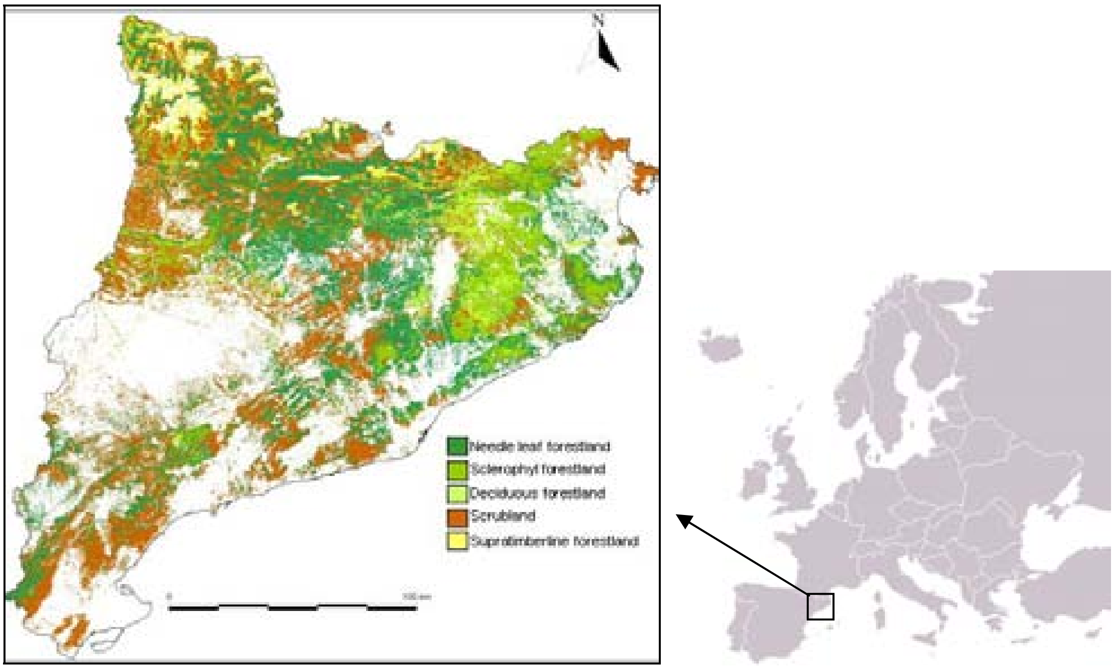


Figure 6. Forestland of Catalonia comprised of needle leaf forestland, sclerophyl forestland, deciduous forestland, scrubland and supratimberline forestland.

These facts make relevant the complex structure of the forestry sector in Catalonia, which has to be taken into account when discussing sustainable forest management, ecosystem services and novel uses in not only Catalan forests, but also in Mediterranean forests. It must be considered that forest management no longer needs to be driven by their economic function, but also for the social and environmental services they provide and that sometime may be valued as externalities, such as conservation of areas and species or leisure activities, services that move towards the multifunctionality that define forests nowadays.

1.3. Bioenergy in the European context

A brief introduction about the European, Spanish and Catalan policies and plans regarding renewable energy and bioenergy in particular are addressed below to be acquainted with their current situation.

(a) Bioenergy policies and plans in Europe

Bioenergy can be of great significance in mitigating climate change by reducing carbon dioxide emissions and by a progressive replacement of fossil fuels in the transition towards sustainable energy futures. According to the Kyoto protocol, the EU is to reduce green house gas emissions by 8% from the level of 1990 [38] by the period years of 2008-12.

The White Paper for a Community Strategy and Action Plan regarding the topic of energy set the objective of 12% share of renewables in the European energy sector in 2010 [39]. However, as it has been stated widely, this objective is far from being achieved. According to Eurobserver [40], the economic financial crisis has not brought solid biomass energy growth to a standstill since primary electricity production only increased a 2.3% from 2007. In 2008, the primary energy production from solid biomass in the European Union was 68.7 Mtoe and the electricity produced was 57.8 TWh. The trend for 2010 is at least achieving 73.7 Mtoe of primary energy production from solid biomass.

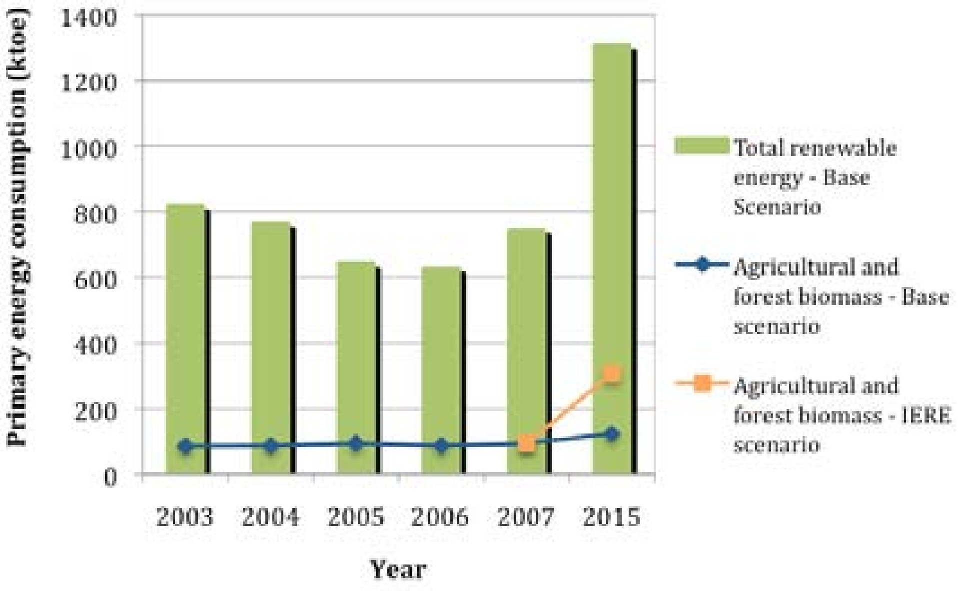
In 2005, the European Plan of action’s goals for biomass [41] aimed for 149 Mtoe of consumption (55 Mtoe fro electricity, 75 Mtoe for heat and 19 Mtoe for transport by the end of 2010) for all bioenergies (solid and liquid biomass, biogas and renewable municipal wastes), which have been unattainable for a long time.

(b) Bioenergy policies and plans in Spain

From the UE White Paper, the Spanish government set the same goal of achieving the 12% of gross consumption from renewable sources in the National Action Plan for Renewable Energy [42]. In this plan, the biomass development was fixed at 6 Mtoe, where 5.1 Mtoe was for electricity production and 0.9 Mtoe for thermal production. Biofuels were expected to provide an alternative for 5.8% of petrol and diesel consumed by transport sector. However, biomass development in Spain was below all expectations since at the end of 2004 only the 9% of the goal for 2010 was achieved. This fact led the Spanish Government to lower the goals for the biomass, which were set at 0.6 Mtoe and 4.5 Mtoe for thermal and electric production respectively. Despite the fact that this goals are lesser than the initial ones, it is hard to believe that these objectives can be accomplished, since, for example, in 2004 the primary electricity production in terms of installed electric power was 344 MW out of the 1695 MW set for the Renewable Energy Plan 2005-2010. Currently the Renewable Energy Plan 2011-2020 is under development, which surely will shed light on the real situation in Spain.

(c) Bioenergy policies and plans in Catalonia

In relation to the Catalan situation, the Catalan Energy Plan 2006-2015 sets very ambitious goals with regard to renewable energies [43]. Two main scenarios are defined in this plan: the Base Scenario, referred to the actual economic and technologic development tendencies; and the Intensive in Energy Efficiency and Renewable Energy (IERE) Scenario, where a most optimistic approach is foreseen including measures as energy efficiency and the use of renewable energies. In the IERE scenario, a goal of 11.5% of the primary energy production is expected to be accomplished with renewable energy in 2015. Relating to forest and agricultural biomass, the primary energy consumption expected in 2015 is 306.6 ktoe in the IERE Scenario, which would represent the 11% of the renewables and the 1% of the total energy consumption in 2015-IERE Scenario (2703 ktoe per year). In Figure 7 it is shown the current tendency of the primary energy consumption until 2007 and both forecasts until 2015.



Source: Own elaboration from [43].

Figure 7. Primary energy consumption for agricultural and forest planned for Catalonia in two scenarios: Base Scenario (current tendencies) and Intensive in Energy Efficiency and Renewable Energy (IERE).

1.4. Motivation of the dissertation

Finding and studying novel uses of biomass represents a challenge that should include a sustainability integrated analysis from an interdisciplinary perspective taking into account social, environmental, technological and economic aspects. Only a thorough and transversal understanding of the complex context in the development of biomass systems in Mediterranean countries can result in equally practical and applicable prospects in short and long term.

Thus, this dissertation is motivated by the following realities:

- The need for energy diversification and the incorporation of renewable energy requires an interdisciplinary assessment including social, environmental, technological and economic aspects. This global approach has been hardly addressed in Mediterranean regions, not to mention in Catalonia.
- Forest biomass has not contributed significantly to the development of renewable energies in Europe, being the resource that has contributed less to the deployment of renewable energy in Europe due to different grounds that should be addressed.
- Several factors linked to Mediterranean forests, such as the increase of forested areas due to abandoned cultivation zones and lack of profitability of forest products or fire risks converge to the need for sustainable forest management related to new uses of forests biomass, which has been explored to a small extent.
- The slow take-off of bioenergy systems in Mediterranean areas compared to northern European countries denotes the necessity of identifying what social, environmental, technological and economic barriers have prevented these systems to be further developed in a Mediterranean context such as Catalonia.
- The necessity to study, develop and adapt technology for biomass conversion, which may be successful in northern countries but not currently implementable in Mediterranean countries and that need to be studied.

1.5. Objectives of the dissertation

The main objective of this dissertation is to provide novel solutions to forest biomass use, which is not currently widespread in Mediterranean areas, according to a multidisciplinary perspective.

In order to achieve this main aim, several goals are outlined:

- To identify the political, social and environmental barriers that have prevented integrated forest bioenergy systems to be further developed in Mediterranean areas.
- To quantify the environmental and energy balance of a bioenergy system using Life Cycle Assessment methodology.
- To determine the most environmental-friendly biomass comparing post-consumer wood and forest residues as feedstock for a bioenergy system.
- To study experimentally a novel biomass use such as biomass pyrolysis for the production of bio-oil.
- To understand the biomass devolatilisation and to model it to know beforehand how a certain type of biomass is going to decompose when pyrolysis is carried out.
- To determine the technological opportunities of novel biomass uses, taking into account a local perspective to make use of regional forests.
- To approach to novel methods to process biomass by means of green chemistry.
- To assess the economic profitability of a novel bioenergy system as in biomass pyrolysis.

2. Methodology

This section describes the methodology followed in this dissertation. Several methods have been used in order to fulfil the objective of this study, which can be grouped in two main groups:

(i) Sustainability assessment tools, which consist of several methodologies to perform the social, environmental and economic assessment;

(ii) Experimental methods, which include not only the models and the experiments carried out, but also the simulated mass and energy balances carried out from the results obtained in the experiments.

In the following section all the methodologies used in this dissertation are described.

2.1. Sustainability assessment tools

The integration of various sustainability assessment tools is a technique being applied and developed increasingly. An example of the different sustainability assessment tools that can be used and integrated according to the Sustainability A-test [4] can be observed in Table 4.

The sustainability assessment tools used in this dissertation are: a social tool by means of Integrated Assessment methodology; an environmental tool using the Life Cycle Assessment methodology; and an economic assessment tools through the use of economic indicators, which are explained in the subsequent section.

Table 4. Assessment tools for sustainability according to the Sustainability A-test.

Physical assessment tools	**Multi-criteria analysis**
- Economy-wide Material Flow Analysis - Life cycle assessment - Ecological Footprint - Global Land Use Accounting/Total Resources Use Accounting emerges - National Accounting Matrix including Environmental Accounts - Characterising Lifestyles and Their Resource Consumption	- Multi Attribute Value Theory - Weighted Summation - Analytic Hierarchy Process - Regime - Preference Ranking Organisation Method for Enrichment Evaluations - Novel Approach to Imprecise Assessment and Decision Environments - Dominance method
Monetary assessment tools	**Sustainability appraisal tools**
- Cost-benefit Analysis - Cost-Effectiveness Analysis - Measures of Economic Welfare - Index of Sustainable Welfare - Genuine Savings - Sustainable National Income	- Sustainable Impact Assessment - Strategic Environmental Assessment - Vulnerability Assessment
Modelling tools	**Stakeholder analysis tools**
- Climate models - Hydrology models - Biogeochemistry models - General economy models - Partial economic sector models - Demography models - Public health models - Land use models - Integrated assessment models - Qualitative systems analysis - Scenario building and planning tools	- Consensus Conference - Focus group - Repertory Grid Technique - Backcasting - Electronic Focus Group - Tools to Inform debates, Dialogues & Deliberations
Scenario analysis	**Transition management**
- Scenario Analysis - Application - Scenario Analysis – Developing New Scenarios	- Transition Management

Source: Sustainability A-test [44].

2.1.1. Social tool: Integrated Assessment

In order to analyze the feasibility of using forest biomass as energy source, the integrated assessment methodology is applied by means of a public participation process. This process begins conducting two focus groups, where several people meet from different areas to discuss a topic and ends with the analysis of results and the output stage to help the decision-making process.

Integrated Assessment: definition

Integrated Assessment (IA) is an interdisciplinary and participatory process of combining, interpreting and communicating knowledge from diverse scientific disciplines to allow a better understanding of complex phenomena [45]. It aims to gather, structure, synthesize and present interdisciplinary knowledge in order to inform in a relevant manner policy decision on complex issues, with the aim of which will serve to support policy decisions. It is known as

Integrated Assessment because it tries to produce new knowledge by integrating various realms of knowledge, not only both experts and non-experts, both local and "universal" and social but also from natural science [46].

Integrated assessment should contain added value compared to insights derived from disciplinary research and it should provide decision-makers (and society) with useful information [45]. At the same time, the Integrated Assessment, through participatory processes that make search better equity (social distribution) and the feasibility of the proposals obtained, as well as encourage communication and transparency in policy making.

The final goal of the IA is explicitly influence political decisions through creating a process more rational, structured and representative as possible, which have to be placed in the intersection area among the expert evaluation, public communication and political action.

Within IA, there is the Integrated Environmental Assessment (IEA) that may be defined as “the interdisciplinary process of identification, analysis and appraisal of all the relevant natural and human processes, which affect the quality of the environment and environmental resources” [47]. The objective of IEA is to facilitate the framing and implementation of optimal policies and strategies, accounting for both environmental effects and other priorities.

IEA provides information to help decision makers to draw conclusions about the state of environmental resources and relate the findings to appropriate management issues [47]. It seeks to create a procedure to allow decision-makers to take the best decisions, both from the point of view of efficiency and equity of the various alternatives that can be identified. It is about building a more open and orderly process, which involves a more representative number of sectors that may function as a bridge of communication between multilateral and learning science, politics and citizenship (see Figure 8).

In integrated assessment, these three fields are closely intertwined, because appropriate communication is essential for decision-making and an adequate evaluation. And, at the same time, these three dimensions can only be built through the processing of public participation and mutual learning [46].

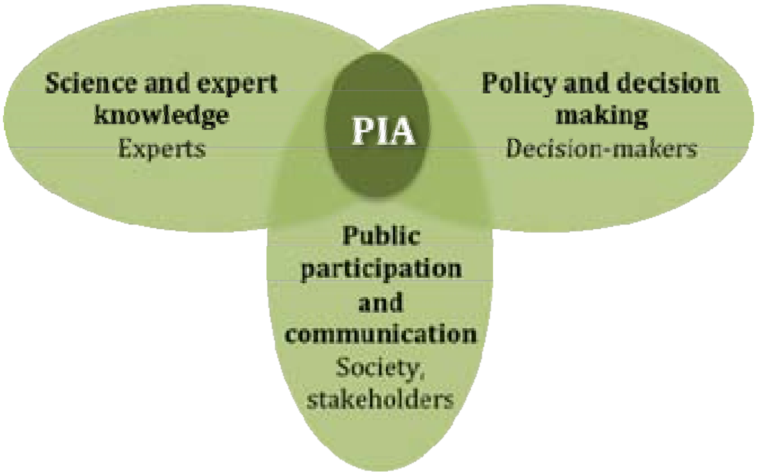


Figure 8. Participatory integrated assessment (PIA) as the intersection of the three domains of knowledge, decision-making and public participation and communication.

IEA consists of three main stages: (i) problem structuring; (ii) problem analysis; and (iii) communicating the results and assessment directly or indirectly to the users of the evaluations [48] (see Figure 9). The final stage of communication of results can be carried out to the stakeholders involved or directly to decision-makers in order to deal with the knowledge drawn from the overall process.

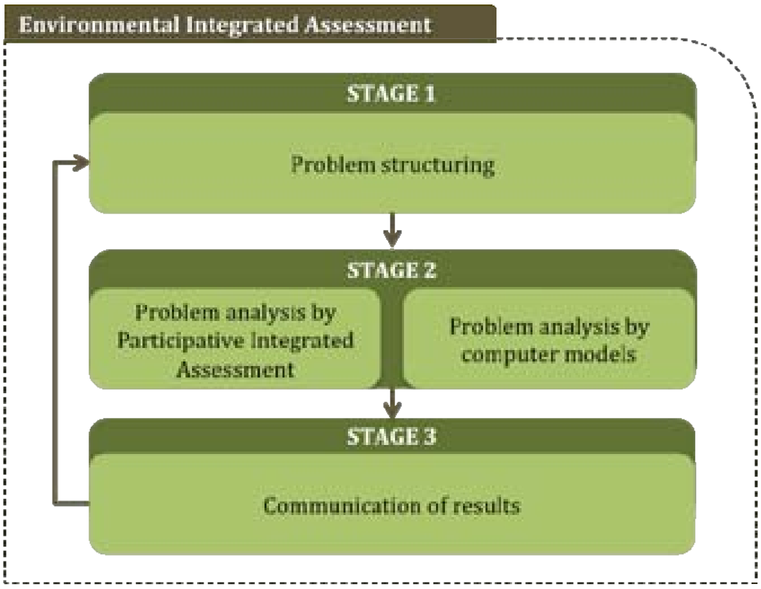


Figure 9. Stages of the Integrated Environmental Assessment.

Integrated assessment- focus groups (IA-FGs)

In IA-FGs, expert information from a variety of sources, such as computer models, are used to support group conversations among a diversity of stakeholders, including non-expert publics. An IA-FGs can be designed along the following lines: a group consists of approximately six to eight citizens, sampled according to a pre-established recruitment criteria yielding a broad heterogeneous mix of participants, including different attitudes towards the environment. These groups meet for several sessions of about 2.5 h each. A moderator facilitates the discussions of the participants on the issues at stake and both quantitative and qualitative statements are gathered to obtain narrative assessments on causes–effects of specific policy-related processes as well as the possible options and pathways to deal with their future evolution.

IA-focus groups also depart from the assumption that group discussions produce a different kind of results –richer, more reflective and collective, and potentially more policy relevant-than those obtained simply through the aggregation of individual preferences, such as it is the case with quantitative opinion polls. IA-FGs intend to increase the opportunities to obtain not only (superficial) 'opinions' but more distinctively in-depth *reflections* on collective matters. Participatory IA processes serve different purposes and functions, and very often most of them are carried out at the same time. Specifically they can help to [49]:

a) *Better framing*: by defining in more relevant ways the problems at stake, their possible causes, effects, and feasible courses of action or even futures on the basis of the stakeholders' views. By doing so, there is less likelihood for the wrong formulation of the problems and for adopting false underlying research and policy assumptions, out of which only wrong answers can emerge.

b) *Improve efficiency and equity*: By enhancing the efficiency of the available information, communication and participation channels both for the production of knowledge and for feeding the policy-making process with preferences and views which would rarely be taken into account otherwise. And by doing so, they can contribute to increase the potential to yield more effective and equitable assessments and decisions on complex issues, especially when large number of uncertainties are present.

c) *Enhance the integration*: of diverse knowledge and value domains, both from experts and non-experts sources, as well as from different scientific disciplines. In this way, participatory IA procedures, can improve the diversity and representativeness of the knowledge used in decision-making, being those criteria fundamental in the new emerging Sustainability Assessment.

d) *Contribute to social learning*: by optimising the existing processes of social and institutional learning, by rising awareness of complexities and uncertainties of the situation, as well as the limits or the gaps in the available knowledge and of the capacities to deal with them. And in doing so they can become central in all mutual and social learning processes occurring between policy makers, experts and the general public or relevant stakeholders.

The group discussion procedure that inspired the research performed in Chapter II is part of the growing research field of participatory Integrated Assessment (IA) [50] and also of the emerging field of Integrated Sustainability Assessment (ISA) [51,52]. In focus groups, stakeholders from different backgrounds are gathered together in order to discuss the topic under study. Also, it is assumed that scientists can learn from the society, which plays a crucial role in the co-production of relevant knowledge and, hence, integrating the public constitutes an important movement to the democratization of the science and its applications.

Participants have access to expert sources of information, including experts themselves and usually the group is complemented with a note taker and several audio or video means to record the conversations. Other visual forms and analytical tools can be used, such as participative scenarios, to enrich the IA process. In this case, the meeting only lasted one day and did not use computer models, although other expert knowledge was provided to the stakeholders beforehand. The focus of the participatory exercise was mostly to devise participatory scenarios on driving forces and hindrances, which condition the future of biomass forest energy systems development in Catalonia.

It is understood that group discussions such as those carried out in our research can help a better framing support of policy-making, since they can integrate the knowledge of all the society sectors and continuous process of social learning, rather than holding science as something external and above it [53].
The Integrated Assessment methodology can typically be structured in a cycle of three stages

(see Figure 10):

(i) Input Stage: consists of all the information that is required to be used as preparation for the meetings.

(ii) Integration and participation Stage: is when the focus group meeting is held.

(iii) Output Stage: corresponds to the information that results from the meetings

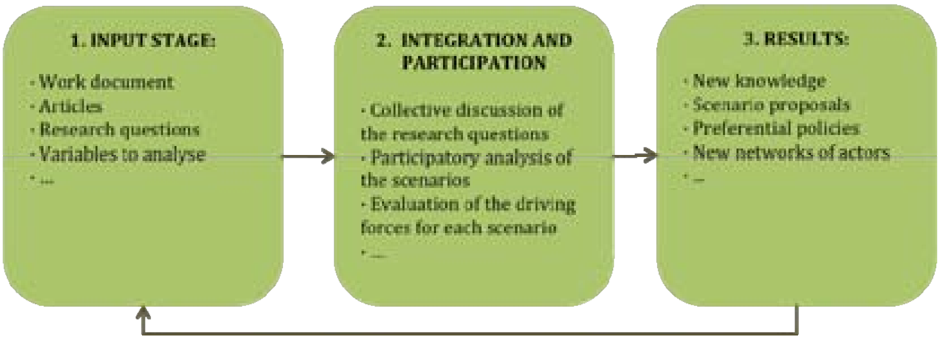


Figure 10. The three typical stages of the Integrated Assessment methodology.

2.1.2. Environmental tool: Life Cycle Assessment

The concept of Life Cycle concerns a more global understanding of the environmental implications of the ecosystem services required by society. For this reason, a cradle-to-grave perspective is applied, where the overall process is taken into account from the extraction of raw materials to the final disposal. Thus, the assessment of the life cycle of products, processes or activities moves towards a global approach that considers material and energy flows between the productive system and its environment.

Life Cycle Assessment: definition

Life Cycle Assessment (LCA) is an environmental assessment methodology that aims to assess the environmental load associated with a product, process or service, considering all stages of its life cycle.

The first consensus definition of LCA was made by the SETAC (Society of Environmental Toxicology and Chemistry), whereby the LCA is:

> *"Life Cycle Assessment is a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and materials used and releases to the environment; and to identify and evaluate opportunities to affect environmental improvements. The assessment includes the entire life cycle of the product, process or activity, encompassing, extracting and processing raw materials; manufacturing,*

> *transportation and distribution; use, re-use, maintenance; recycling, and final disposal".*

In 1997, the International Organization for Standardization (ISO) also developed a set of rules regarding the methodology of LCA (ISO 14040:1997), which has been updated by the technically revised ISO 14044:2006 [54]. This ISO defines the LCA as:

> *"LCA considers the entire life cycle of a product, from raw material extraction and acquisition, through energy and material production and manufacturing, to use and end of life treatment and final disposal. Through such a systematic overview and perspective, the shifting of a potential environmental burden between life cycle stages or individual processes can be identified and possibly avoided".*

Finally, the Spanish standard UNE-EN ISO 14040:1998, which is identical to European standards, describes the technique of LCA explaining in detail each of its stages: defining the purpose and scope, inventory analysis, environmental impact assessment and interpretation of results. It defines LCA as:

> *"The LCA is a compilation and evaluation, according to a systematic set of procedures, of inputs and outputs of materials and energy, and potential environmental impacts directly attributable to the functional system of the product throughout its life cycle".*

Life Cycle Assessment: methodology

LCA studies comprise four phases: (i) the goal and scope definition; (ii) the inventory analysis; (iii) the impact assessment; and (iv) interpretation. The relationship between the phases can be observed in Figure 11.

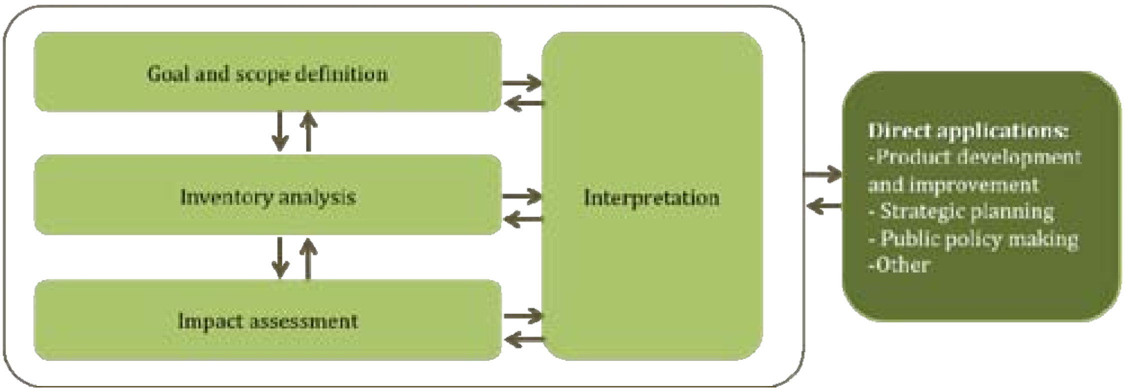


Figure 11. Stages of the Life Cycle Assessment (LCA).

The goal of a LCA states the intended application, the reasons for carrying out the study, the intended audience and whether the results are aimed to be used in comparative assertions with the intention to be disclosed to the public [54]. The scope includes the following items [54]:

- the product system to be studied;
- the functions of the product system or, in the case of comparative studies, the systems;
- the functional unit;
- the system boundary;
- allocation procedures;
- impact categories selected and methodology of impact assessment, and subsequent interpretation to be used;
- data requirements;
- assumptions;
- limitations;
- initial data quality requirements;
- type of critical review, if any;
- type and format of the report required for the study.

The Inventory Analysis, known as **Life Cycle Inventory (LCI)**, involves data collection and calculation procedures to quantify relevant inputs and outputs of a product system (see Figure 12). This stage includes the allocation of flows and releases, since industrial processes normally yield multiple products that can be recycled or discarded as raw materials.

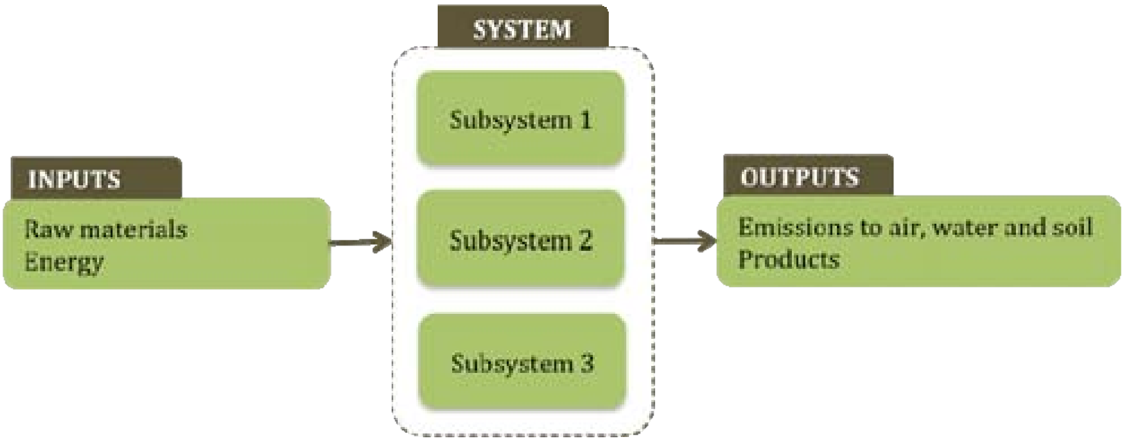


Figure 12. Flowchart of a general system considered in LCA.

The **Life Cycle Impact Assessment (LCIA)** is aimed at evaluating the significance of potential environmental impacts using the LCI results. In general, this process involves associating inventory data with specific environmental impact categories and category indicators, thereby attempting to understand these impacts [54]. This stage involves three mandatory elements [54]:

- Selection of impact categories, category indicators and characterization modes
- Classification (assignment of LCI results): the inventory data (inputs and outputs) are grouped into several categories depending on the environmental impact that can contribute.
- Characterisation (calculation of category indicator results): the inventory data is aggregated within each impact category, considering the amount in which each category contributes to increase the corresponding environmental impact. This is carried out using characterization factors (internationally accepted and scientifically justifiable) that reflect the relative contribution of a pollutant in a particular category of impact and in relation to a particular compound in a given reference value of 1 (eg CO_2 in the case of the greenhouse effect).

There are three additional elements, which are optional since there is no consensus about them in the scientific community. These elements are:

- Normalization (calculation of the magnitude of the category indicator results relative to reference information): in this stage the characterization data is evaluated, normalizing the data regarding certain reference amounts. That is, dividing them by the real or expected value for each impact category considered, for a defined area and time.
- Grouping: the environmental profile is reduced to a set of indicators, in order to facilitate understanding the results from the LCA.
- Weighting: consists of weighting the relative importance of each impact category comparing to the other categories. Thus, the results are converted to a numerical score of environmental impact.

Interpretation is the phase of LCA in which the findings from the inventory analysis and the impact assessment are considered together. The interpretation phase should deliver results that are consistent with the defined goal and scope and which reach conclusions, explain limitations and provide recommendations to decision-makers [54].

Once the above-mentioned stages are implemented, reporting the results effectively is needed, where the limitations of the study should be clear, not only those caused by data quality but also the methodology and assumptions used.

Finally, the last stage of the LCA is the critical review. It is a process to verify whether an LCA or LCI study has met the requirements for methodology, data, interpretation and reporting.

Even though it is a methodology well established, there are some limitations that must be taken into account. The core feature of LCA is its "holistic nature", which is its major strength and, at the same time, its major limitation [55]. For example, the LCIA only addresses the environmental issues that were previously defined in the goal and scope and cannot always demonstrate significant differences between impact categories and the related indicator results of alternative product systems. This can be explained mainly due to limitations of the LCI phases or limitations in the collection of inventory data appropriate and representative for each impact category [54].

Guinée et al. defined the limitations in the LCA process [55]:

- It cannot address localised and time impacts, since LCA does not provide the framework for a risk assessment to identify which impacts can be expected in a specific place related to a specific facility; and it is a steady-stage rather than a dynamic approach.
- Does not include market mechanisms or secondary effects on technological development, it only focused on the physical characteristics of processes.
- All the processes considered are linear, both in the economic and environmental approach.
- It focuses on environmental aspects, avoiding their economic, social and other characteristics.
- It involves a number of technical assumptions and value choices.
- The availability of data, since data is frequently obsolete, incomparable or of unknown quality.
- It cannot replace the process of decision-making, because it provides information for decision support.

In spite of these limitations, following the LCA-ISO procedure helps to avoid arbitrariness and overcome these drawbacks. On this respect, transparency is the major pillar to provide enough information and tools not only to help the critical review stage, but also performing a comprehensive LCA. The software employed in this dissertation, and more specifically in Chapter III, to carry out the LCA is SimaPro 7.0.1, developed by Pré-Consultants [56].

2.1.3. Economic tool: cost and benefit analysis

The economic assessment is carried out by means of two major investment indicators: Net Present Value (NPV) and Internal Rate of Return (IRR). These indicators will be used to carry out a cost assessment of mobile pyrolysis plants.

(a) Net Present Value

The **NPV** is defined as the difference between the present value of a stream of benefits and that of a stream of costs. A positive NPV occurs when the sum of the discounted benefits exceeds the sum of the discounted costs. A negative NPV is usually called a Net Present Cost (NPC). The decision rule is to select the option that offers to maximise NPV, or minimise NPC. NPV is a primary investment decision criterion.

$$NPV = \sum_{k=1}^{n} \frac{F_k}{(1+ir)^k} - I_o \qquad \text{(Eq. 1)}$$

where n is the plant life; k is the number of years; ir is the discount rate; I_0 is the investment cost; and F_k is the annual cash-flow at the kth year, which is:

$$F_k = RV - TFC - TVC - T - F + D \qquad \text{(Eq. 2)}$$

where RV are the revenues from the sale of products; TFC are the fixed costs calculated as the sum of amortization, insurance costs and repayments; TVC are variable costs that involve labour, maintenance and biomass costs; T are the taxes; F are the financial charges and D is the amortization or depreciation.

(b) Internal Rate of Return

The **IRR** of an investment is the interest rate that would give a project a net present value of zero (see Equation 8). That is, the interest rate at which the costs of the investment lead to the benefits of the investment. In other words, a project investment is acceptable when IRR is greater than an established cost of capital. This cost of capital can be defined as the cost of a project, which from the investor's point of view is the expected return of the investment. It can also be defined as yield on project.

$$NPV = \sum_{k=1}^{n} \frac{F_k}{(1+IRR)^k} - I_o = 0 \qquad \text{(Eq. 3)}$$

Therefore, a project could be accepted with a positive NPV and with a greater IRR than other investment with the same risk.

The total costs of a project are the sum of the fixed cost (TFC) and variable cost (TVC):

$$TC = TFC + TVC \qquad \text{(Eq. 4)}$$

The TFC consists of the amortization (D_H), Loan refunds (L) and Insurance and Taxes (IT).

The amortization or depreciation is calculated as the investment cost divided by the lifetime of the investment, normally in years.

To calculate the cost assessment of the different machinery involved in the use of biomass, the economic analysis is carried out as costs per hour. The subsequent equations are used to calculate the cost per hour of the equipment, following the cost assessment methodology from Arno et al. [57].

The amortization is calculated as:

$$D_H = \frac{P - RP}{H} \qquad \text{(Eq. 5)}$$

where P is the purchase price (in €); RP is the resale price (in €); and H is the lifetime (in hours).

The interest is calculated as:

$$I = \frac{P \cdot i_A}{h} \qquad \text{(Eq. 6)}$$

where i_A is the average interest (per unit); h the annual hours (h=H/N); ir is the annual interest rate (per unit). In turn, i_A is:

$$i_A = \frac{i \cdot (1+i)^N}{(1+i)^N - 1} - \frac{P - RP}{N \cdot P} - RP \cdot \frac{i}{P \cdot [(1+ir)^N - 1]} \qquad \text{(Eq. 7)}$$

where N is the the lifetime of the machinery in years.

The insurance and taxes costs (IT) is calculated as:

$$IT = \frac{I+T}{h} \quad \text{(Eq. 8)}$$

where I is the annual insurance cost (€) and T is the annual tax (€).

On the other hand, the VC includes the fuel (F_p or F_T), the lubricant oil (O), the spare pieces (S) and the maintenance (M). The costs associated to the fuel depend on the type of machinery. If it is a portable machine (F_p), it follows:

$$F_P = 0.37 \cdot N_e \cdot p \quad \text{(Eq. 9)}$$

where N_e is the effective maximum engine power (in CV) and p is the gasoline price (€/l). In the case it is a tractor or similar the cost of the fuel follows:

$$F_T = 0.12 \cdot Ne \cdot p^* \quad \text{(Eq. 10)}$$

where p^* is the gasoil price (€/l).

The lubricant oil (O) is calculated as:

$$O = K \cdot F \quad \text{(Eq. 11)}$$

where K is a factor between 0.10 and 0.30, in this case 0.30 is applied.

The Spare pieces (S) are estimated as:

$$S = \frac{(H - H^i) \cdot Pi}{H \cdot H^i} \quad \text{(Eq. 12)}$$

where H^i is the spare piece lifetime (in hours), P^i is the spare piece price (€).

Finally, the maintenance (M), which includes repairs, is calculated as:

$$M = \frac{\%M \cdot P}{100 \cdot F} \cdot f \quad \text{(Eq. 13)}$$

where %M is the percentage of maintenance applied; and f is the use factor (dimensionless) that is estimated as:

$$f = \frac{N^* \cdot f}{H} \quad \text{(Eq. 14)}$$

where N^* is the number of years that you intend to use the machine that in this case is $N^*=N$ and, for this reason, f=1.

The parameters chosen to carry out the economic assessment and the variables studied are described in more detail in Chapter IV.

2.2. Experimental methods

The following section describes the experimental methodology used in the study of biomass pyrolysis. It comprises: (a) the materials used; (b) the experimental setup consisting of the auger reactor pilot plant; (c) the analytical techniques to characterise both the feedstock and the pyrolysis products; and (d) the experimental modelling applied to study the pyrolysis process.

2.2.1. Materials

The materials used in the experiments are: (a) the forest biomass feedstock that consists of pine woodchips; (b) biomass compounds (cellulose, hemicellulose and lignin); (c) the ionic liquid used in the greener processing technology approach.

a) Forest biomass feedstock

The forest biomass feedstock used in all the experiments was pine woodchips from the northern area of Catalonia, provided by the Forest Technology Centre of Catalonia [58]. Pine woodchips of two different species were used as raw material: Scots pine (*Pinus sylvestrys*) and Aleppo pine (*Pinus halepensis*); which are representative from Mediterranean forests. In Spain, the coniferous specie with the largest territorial occupation is the Aleppo pine, followed by the Maritime Pine (*Pinus pinaster*), Scots pine and Black pine respectively [59]. In Catalonia, the forest distribution according to largest forest area is the following: Aleppo pine; Scots pine; Holm oak (*Quercus ilex*); followed by Black pine [60].

Samples of Scots pine, Aleppo pine and a mixture of both species named Wood blend were used in different experiments.

b) Biomass compounds (cellulose, hemicellulose and lignin)

Samples of cellulose (cellulose fibrous, long C6663 Sigma-Aldrich), lignin (Organosolve 37017 Sigma-Aldrich), and xylose (Xylan from breech wood, xylose residues >90 % 0502 Sigma-Aldrich) as hemicellulose model compound have also been used.

c) Ionic liquid

Ionic liquid 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) was purchased from Sigma-Aldrich (94128 Sigma-Aldrich).

Table 5 shows the proximate, ultimate analysis and calorific value of the woodchips and the samples of lignin, cellulose and hemicellulose used. A picture of the three different woodchips samples is shown in Figure 13.

Table 5. Proximate and ultimate analyses, and calorific value of the samples. All data, except moisture, are expressed in dry basis.

	Proximate Analysis (%wt)				Ultimate Analysis (%wt)					HHV
	Moist.	**Ash**	**VM**	**FC[1]**	**C**	**H**	**N**	**S**	**O[1]**	**(MJ/kg)**
Cellulose	-	-	-	-	65.02	5.78	0.19	0.00	29.01	-
Lignin	-	-	-	-	42.47	6.03	0.03	0.00	51.47	-
Hemicellulose	-	-	-	-	40.64	5.91	0.05	0.00	53.40	-
Pinus sylvestris 1	6.21	0.39	78.52	14.88	48.28	6.34	0.12	0.00	45.26	-
Pinus sylvestris 2	6.36	0.35	78.76	14.53	48.29	6.28	0.12	0.00	45.31	19.36
Pinus halepensis	8.96	1.72	73.82	15.50	46.05	6.08	0.12	0.00	47.75	18.50
Wood blend	9.43	0.94	73.50	16.13	46.47	6.17	0.12	0.00	47.24	17.95

[1] *Calculated by difference; Moist: Moisture; VM: Volatile Matter; FC: Fixed Carbon; HHV: High Heating Value*

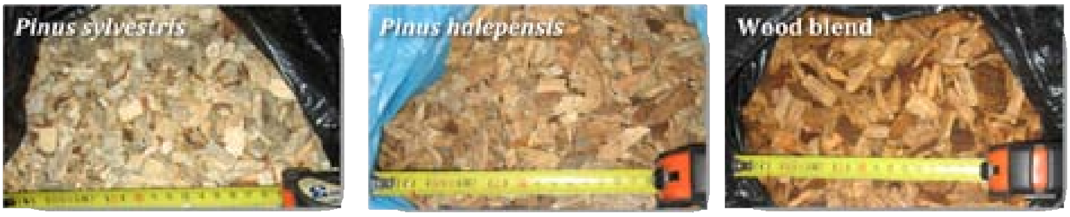


Figure 13. Pine woodchips used in the experiments.

2.2.2. Experimental setup: pyrolysis in an auger reactor

Pyrolysis of the pine woodchips was carried out in an auger reactor pilot plant capable to process up to 15 kg/h of feedstock, which had been used in previous studies to pyrolyse tyres [61,62] and was adapted to pyrolyse biomass. In this section the description of the auger reactor pilot plant, the reactor calibration and the experimental design are reported.

Description of the auger reactor pilot plant

The auger reactor pilot plant comprises nine main parts (see Figure 14): (1) Feeding hopper; (2) Feeding auger conveyer; (3) Auger reactor; (4) Furnaces; (5) Vessel for solids; (6)

Condensing system; (7) Liquid collecting system; (8) Gas expanders; and (9) Gas burner. In Figure 15 various pictures of different parts of the auger reactor pilot plant are showed.

This pilot plant is located in Instituto de Carboquímica, a public research centre belonging to the Spanish National Research Council (CSIC), in Zaragoza (Spain).

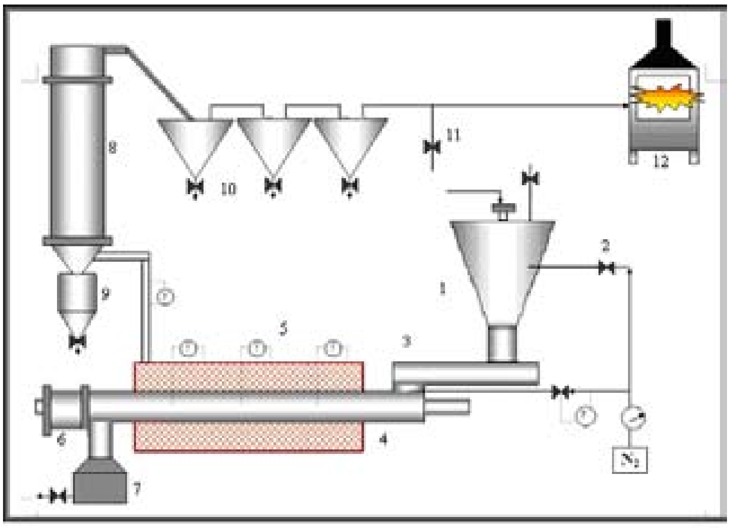


Figure 14. Continuous auger reactor used in this study. (1) Feeding hopper; (2) Nitrogen flow; (3) Feeding auger conveyer; (4) Auger reactor; (5) Furnaces; (6) Reactor closure system; (7) Vessel for solids; (8) Condensing system; (9) Liquid collecting system; (10) Gas expanders; (11) Gas sampling valve; (12) Gas burner.

Feeding hopper

A feeding hopper with a capacity of 15 kg was specifically designed in order to feed the biomass into the reactor. This hopper has a mechanical stirrer propelled by an electric engine to avoid biomass clogging up, which was a major drawback of the first feeding hopper designed to process waste tyres. The hopper is connected to a feed screw (60 cm long, 3.4 cm diameter and 2 cm pitch) that carries the biomass into the reactor. An engine controls the spin velocity of the feed screw.

Auger reactor and furnaces

The reactor consists of an auger reactor, which has a concentric screw (80 cm long, 8 cm diameter, 4 cm pitch) inside a cylindrical casing. The solid residence time can be controlled varying the screw spin frequency. Three ceramic electrical furnaces that can supply up to 13 kW heat the reactor (see Figure 15). Temperature profiles along the reactor are measured by three thermocouples. An expansion chamber was installed to improve the volumetric efficiency of the reactor and thus avoiding risks of overpressure and leakage. Consequently, the gas residence time decreased, reducing the cracking reactions and therefore increasing bio-oil production.

The reactor sealing mechanism includes a silicone seal, a bronze fitting and graphite cord to assure the pyrolysis requirement of inert atmosphere. Woodchips move through the reactor while decomposing into a solid residue and a gaseous product, which reaches the condensing system by natural convection with the help of the carrier gas (nitrogen, 5 LN/min). The advantages of the auger reactor are its robustness, flexibility and versatility, besides the fact that is widely used in industry. In addition, it is able to operate with significant amounts of biomass, from 5 to 15 kg/h.

Vessel for solids

The solid residue or char leaves the auger reactor falling into a closed vessel for solids.

Condensing system

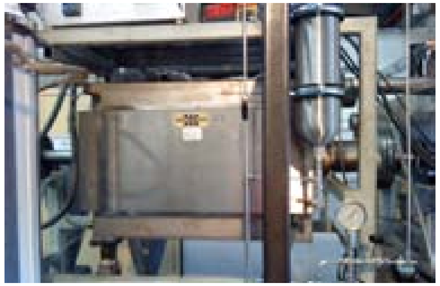
The condensable gases are condensed and recovered in a liquid collector after moving down by gravity. The condenser consists of 17 tubes of 1 m long, 1.27 cm diameter and 2 mm thickness, and the shell has a diameter of 12.5 cm. Water flows through the shell side and the gas moves inside the tubes in counter current. Three gas expanders with a volume of 10 L help to avoid head loss, since remaining liquid droplets carried by the gas are trapped in the expanders.

Gas burner

Finally, the non-condensable gas at ambient temperature is conducted to a burner, where it is combusted before reaching the atmosphere. A gas-sampling valve is located before the burner to enable gas sampling.

1. Feeding hopper

2. Auger reactor



3. Furnace

4. Condenser

5. Gas expander

6. Gas combustor

Figure 15. Pictures of the parts of the auger reactor pilot plant.

Calibration of the auger reactor

Several calibrations were carried out in order to know accurately the revolutions per minute of the biomass fed into the reactor: the calibration of the reactor and the calibration for the solid residence time.

Reactor calibration

The calibration of the feed screw is intended to relate the frequency of rotation with the amount of biomass fed per hour. The measurements were taken once the reactor had reached steady state, after 15 min from the beginning of the experiment. Several tests were performed within a frequency range between 18.5 and 50 rpm. The amount of biomass fed to each frequency was determined by weighting continuously the solid output from the feed screw for different time intervals.

Figure 16 shows the calibration curve obtained for the biomass particles fed into the reactor.

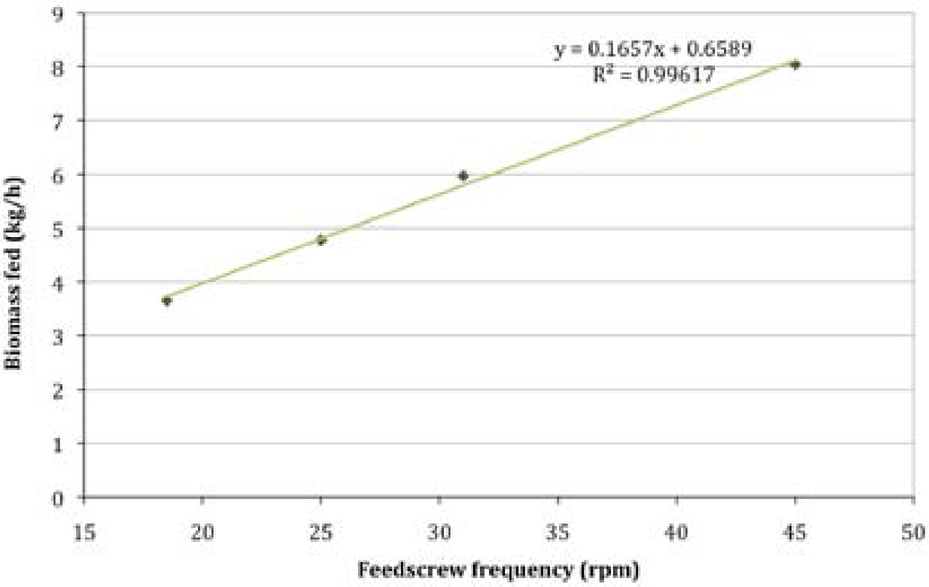


Figure 16. Calibration curve of the biomass fed into the reactor for different interval times.

Calibration for the solid residence time

The residence time is the average amount of time that a particle spends in a particular system. In the auger reactor (0.8 m long; 0.04 m pitch), the solid residence time of the woodchips can be explained by:

$$t_r = \frac{L \times 60}{rpm \times PL} \qquad \text{(Eq. 15)}$$

Where t_r is the solid residence time (s); L is the length of the auger reactor (m); PL is the pitch of the auger reactor (m) and rpm is revolutions per minute ($r \cdot min^{-1}$).

From which the following reduced expression is obtained:

$$t_r = 1200 \cdot rpm^{-1} \qquad \text{(Eq. 16)}$$

where t_r is the solid residence time (s) and rpm is revolutions per minute.

A recalibration curve was performed in order to compare the frequency displayed by the monitor and the real frequency of the screw (see Figure 17). Once the real frequency was obtained, the solid residence time was calculated using Equation 15. The calibration curve between the solid residence time and the real frequency is shown in Figure 18.

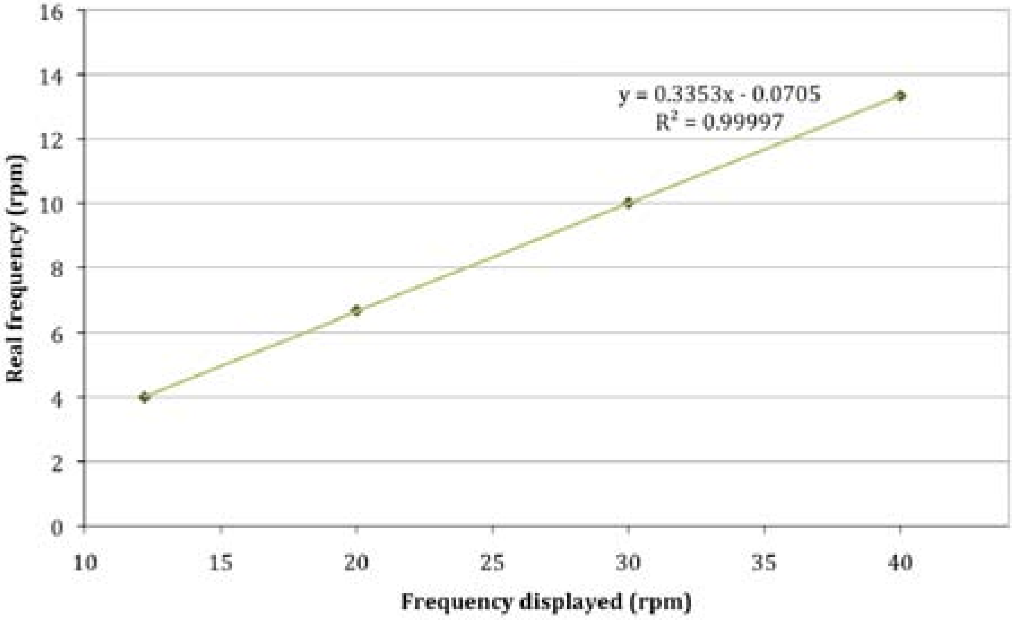


Figure 17. Calibration curve to compare the real frequency with the frequency displayed by the monitor.

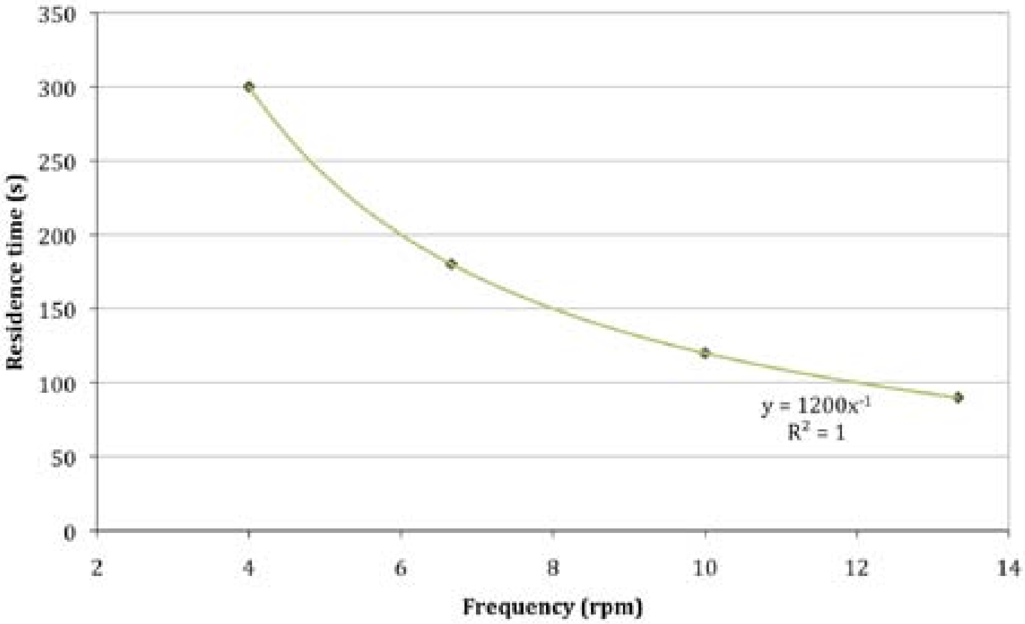


Figure 18. Calibration curve where solid residence time is function of the real frequency.

Experimental design

Three different operational variables were studied in the auger reactor:

- reaction temperature: 1073 K, 973 K, 873 K, 823 K and 773 K
- solid residence time: 5 min, 3 min, 2 min and 1.5 min
- mass flow rate: 3.9 kg/h, 4.8 kg/h and 6.9 kg/h

Liquid and solid yields of the experiments were directly obtained by weight, which are explained and discussed in Chapter IV. The gas yield was calculated by means of the nitrogen fraction sampled in the gas bag, except for the experiments performed at highest temperatures (823K, 873 K, 973 K and 1023 K) where the gas fraction was calculated through mass balance, owing to the inconsistency of the results obtained. Each experiment lasted approximately 3 hours, depending on the experimental conditions.

2.2.3. Analytical techniques

Several analytical techniques and analytical instruments were used to characterise the feedstock and the pyrolysis products (bio-oil, char and non-condensable gas) (see Figure 19). Samples of the three fractions (solid, liquid and gas) were taken at timed intervals throughout the experiments.

Basically, to characterise the feedstock the determination of collective properties was carried out, along with thermogravimetric analysis. Product characterisation was performed by means of determination of collective properties, simulated distillation, gas chromatography and gas chromatography coupled with mass spectrometry. Further details of product characterisation are provided in the following section.

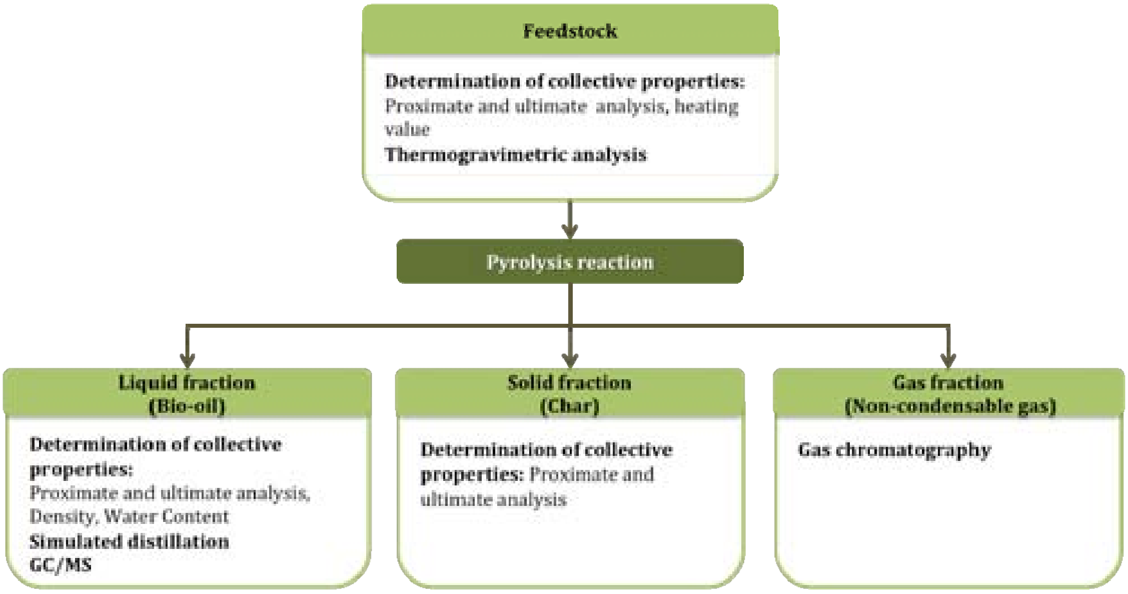


Figure 19. Feedstock characterisation and pyrolysis products characterisation diagram.

Determination of collective properties: Proximate and ultimate analysis, density, water content and heating value

Chemical composition is determined by means of the ultimate analysis (also known as elemental analysis) and the proximate analysis.

The ultimate analysis determines the carbon, hydrogen, nitrogen, sulphur and oxygen total content in a sample and was determined in a Carlo Erba EA1108 elemental analyser.

The proximate analysis gives the moisture, ash, volatile matter contents of a sample and they are determined by ISO standards. These analyses were carried out using ovens for the determination of moisture content and muffles for the determination of both volatile matter and ash following European standards. The moisture content was determined by ISO-589-1981 and using different ovens; the ash content by ISO-1171-1976 and the volatile matter by ISO-5263-1974 using muffles. The calorific value was measured experimentally with a bomb calorimeter IKA C-2000 and determined by UNE 164001 EX.

Water content of the pyrolysis liquids was determined by means of Karl-Fisher titration (Crison Titromatic) and the density of the liquids by the Antor-Paar portable density meter DMA35N.

Thermogravimetic analysis

Thermogravimetric analysis (TGA) is a technique based on continuous recording of mass changes of a sample of material, as a function of a combination of temperature with time, when temperature follows a programmed heating rate, at a given gas composition. The thermobalance used in this work is a SETARAM Setsys Evolution, where initial pyrolysis tests were performed.

The inert gas is introduced into the system through the bottom with a predefined composition and total flow. In this study all tests were run at constant flow of nitrogen of 0.05 LN/min in a reactor with 20 mm of internal diameter to produce a gas stream with a linear velocity of $2.51 \cdot 10^{-3}$ m/s. The sensitivity of this apparatus is $3 \cdot 10^{-11}$ kg. The thermobalance is provided with an electric oven that can operate up to 2023 K and it is controlled with a PID temperature controller. A thermocouple is located close to the platinum basket where the sample is located for temperature monitoring and control. The solid weight loss, together with other process variables like temperature, is recorded.

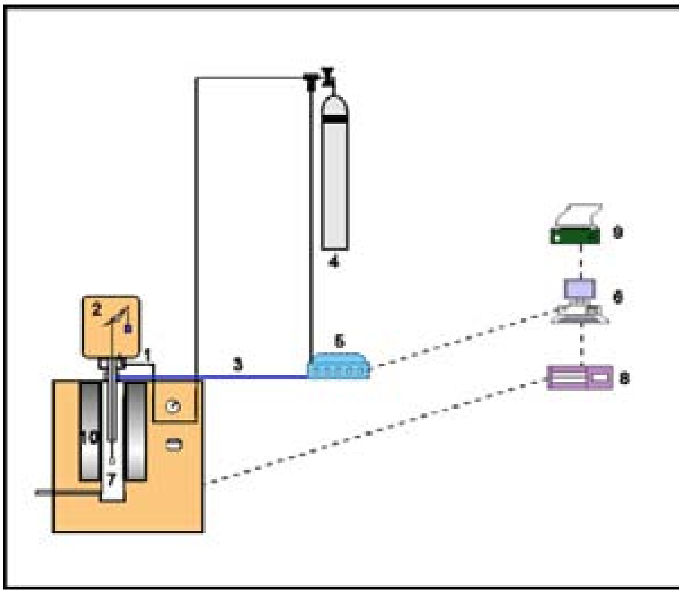


Figure 20. Diagram of the thermobalance used to perform thermogravimetric analysis. (1-Nitrogen upper-flow; 2-Microbalance; 3-Nitrogen lower-flow; 4-Nitrogen bottle; 5-Mass flow controllers; 6-Computer; 7-Platinum basket; 8-Data acquisition card; 9-Printer; 10-Oven)

Depending on the type of experiment carried out, different experimental conditions were applied. These are detailed in each experimental section in the following chapters.

Simulated distillation

The simulated distillation was performed according to ASTM D2887-04 to find the boiling point range in a Varian Star 3400 model GC. The capillary column was a VF-5ms (30 m x 0.25 mm ID x 0.25 µm film thickness) and Helium as carrier gas with a constant flow of 3.0 mL/min. The oven temperature was programmed from 313 K (2 min) to 613 K at a heating rate of 15 K/min and held at 613 K for 15 min. The injector was kept at a constant temperature of 613 K. Sample volumes of 0.6 and 1.0 µL (1:2 in MeOH) were injected applying 1:30 split mode.

Gas Chromatography/Mass spectrometry (GC/MS) analysis

Qualitative GC/MS analysis was performed in a Perkin Elmer Clarus 500MS System to identify the main compounds in the liquid samples. Previous to analysis, bio-oil samples were filtered and diluted with MeOH (1:5). The capillary column was a Petrocol DH (100 m x 0.25 mm ID x 0.50 µm film thickness) with Helium as carrier gas with a constant flow of 1.0 mL/min. The oven temperature was programmed from 313 K (4 min) to 473 K at a heating rate of 3 K/min and held at 473 K for 40 min. The injector was kept at a constant temperature of 523 K. A sample volume of 1 µL (1:5 in MeOH) was injected applying 1:15 split mode. After a solvent delay of 12 min, a full mass spectrum was acquired. The MS was operated in electron ionization mode and an m/z range from 16 to 500 was scanned. Standard mass spectra with 70 eV ionization energy were recorded. The voltage applied to the photomultiplier detector was 350 V in order to obtain the total ion chromatograms (TICs) in a full-scan acquisition method. The identification of peaks is based on computer matching of the mass spectra with the NIST library [63].

Gas chromatography (GC)

Pyrolysis gases were sampled using Teflon gas bags every 10 minutes during the first hour and when the steady state was reached, samples were taken every 20 min until the experiment finished. Gas compositions of the experiments were analysed in a Varian's 490-GC PRO using a Molseive 5Å column to analyse H_2, O_2, N_2 and CO; and a CP-PoraPLOT Q column to analyse CO_2 and hydrocarbons from C_1 to C_4. Both columns were coupled with a TCD detector.

2.2.4. Experimental modelling

Two modelling tools were used to study the pyrolysis process. First, the Distributed Activation Energy Model (DAEM) was applied to study biomass devolatisation and, second, the experimental process mass and energy balances were carried using Aspen HYSYS simulation software.

Distributed Activation Energy Model (DAEM) applied to biomass devolatilisation

Pyrolysis process modelling is performed applying the Distributed Activation Energy Model (DAEM). This model has been widely used to model coal pyrolysis [64-68] and lately it has been applied also to biomass [69-72]. DAEM assumes that the thermal decomposition of numerous components is described by a distribution of activation energies. Therefore, DAEM can explain biomass pyrolysis since biomass is comprised of multiple compounds that decompose according to their own activation energies.

The mathematical model that describes pyrolysis kinetics is:

$$\frac{dV_i}{dt} = k_i(V_i^* - V_i) \qquad \text{(Eq. 17)}$$

where V^*_i is the initial mass for reaction i; $V_i(t)$ is the mass fraction for the *i*th constituent; and k_i is the rate coefficient. The rate coefficient k_i is taken to be Arrhenius in form,

$$k_i(t) = k_{0i} \cdot e^{-E_i/RT(t)} \qquad \text{(Eq. 18)}$$

where k_{0i} is the pre-exponential or frequency factor (s^{-1}), E_i is the apparent activation energy for constituent i (J/mol), R is the ideal gas constant, and T(t) is the time-dependent temperature of the biomass.

If i=1, the model is known as a single first-order reaction model (SFOR). DAEM, in contrast, allows for a more complicated set of reactions by considering a continuous distribution of reactants [67]. In DAEM, the dependence on volatile number i is replaced by a continuous dependence on activation energy E, so that it follows:

$$dV = V^* f(E) dE \qquad \text{(Eq. 19)}$$

The solution then becomes:

$$\frac{V^* - V}{V^*} = \int_0^\infty \exp\left(-\int_0^t k_0(E) e^{-E/(RT(u))} du\right) f(E) dE \qquad \text{(Eq. 20)}$$

To study pyrolysis process on wood, the distributed activation energy model (DAEM) has been applied to the experimental results found in the TGA. The methodology to carry out the application of DAEM to biomass is further described in Chapter IV.

Process mass and energy balances: HYSYS simulation

Process mass and energy balances are carried out to compare the energy inputs and outputs from the pyrolysis process performed in the pilot plant. Process mass and energy balances were carried out using Aspen HYSYS® simulation software [73]. This software is a process-modelling tool for conceptual design and optimization of engineering processes, among other applications.

One of the simulation objectives is to determine the energy of non-condensable gases in order to recycle them into the reactor, since pyrolysis is an endothermic process that needs an extra input of energy. Therefore, it is intended to close the process energetically as much as possible.

Following this simulation, a novel mobile pyrolysis plant is designed to operate with 1500 kg/h of biomass with the intention of determining the energy and mass balances, as well as the efficiency of the overall process. In this respect, several sensitivity analyses are carried out in order to evaluate the process performance varying the moisture content of the biomass; the drying efficiency and changing the carrier gas from nitrogen to air.

To simulate biomass pyrolysis, it is necessary to calculate empirical formulas, molecular weights and enthalpies of combustion and formation for the biomass and the products obtained from the pyrolysis process (solid, liquid and gas fraction). The empirical formulas were calculated from the chemical composition (ultimate and proximate analysis) of the biomass, the solid fraction (char) and the bio-oil. In turn, molecular weights were determined by the empirical formula. Enthalpies of combustion were calculated from the molecular weight and the heating value of each fraction, which was determined experimentally. Finally, the enthalpy of formation was calculated from the enthalpy of combustion and the empirical formula.

Further details of the methodology used for the different assessments are specified in each chapter.

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II

Social assessment:
Integrated assessment of forest bioenergy systems

3. Integrated Assessment of forest bioenergy systems in Mediterranean basin areas. The case of Catalonia and the use of participatory IA-focus groups

The present chapter applies and adapts the methodology of Integrated Assessment focus groups in order to understand and analyse the enhancing factors, as well as the constraints which drive or limit the take off and development of sustainable forest biomass energy systems in a selected large forested area of the Mediterranean Basin. This study provides historical trends in forest expansion; an assessment of technological, socioeconomic, and ecological options of forest management; and plausible scenarios of its future evolution.

3.1. Introduction to Chapter II

As it has been stated in Chapter I, biomass has the potential to become one of the major renewable primary energy sources and forest biomass in particular has an important role to play in the landscape management and in the climate policy domain during the present century. However, the state of development of the wood energy sector is far from homogenous across the EU member states [1-5]. Drivers and barriers behind the development of the bioenergy market have been investigated, although they mainly focused on northern countries [6]. In northern European countries, energy production systems are well developed and studied. In contrast, they are not widely established in Mediterranean regions, where orographic characteristics limit particularly forest biomass harvesting. Despite the targets set by European Union and the national and regional governments cited in Chapter I [7-9], the developments in the sector are slower than had originally been anticipated. On the other hand, the risks of forest fires have increased due to a number of reasons, including the growth of biomass accumulation and the overgrown forest floor vegetation as a result of abandonment of some traditional activities and the lack of forest management [10-12]. The following chapter is focused on the case of Catalonia, which has been previously described in section *1.2. Context of the dissertation*.

Therefore, it is necessary to analyse specifically which factors impede or can enhance the take-off and development of sustainable and socially integrated energy systems based on the adequate management, exploitation, and conservation of forest management resources in the Mediterranean basin countries, such as our case study area of Catalonia.

While the opportunities for the sustainable use of such biomass potential and the prevention of risks are high, the constraints seem to be of multiple and complex nature. This study looks at the factors that could make forest biomass commercially viable as well as could enhance the biodiversity and social equity potentials of those areas. The interest is in identifying what political, social and environmental barriers have prevented integrated forest bioenergy systems to be further developed in a Mediterranean context such as Catalonia. The aim is meeting this goal by complementing the analysis of quantitative historical and update information on evolution of forest biomass in this area, analysing alternative technologies and options of exploitations and by the use of a participatory Integrated Assessment methodology.

3.2. IA-Focus Groups: Process and results

In order to analyse the viability of the implementation of forest bioenergy systems in Catalonia, the integrated assessment methodology by means of public participation process was applied. Specifically, it is presented the use and adaptation to the case study of the Integrated Assessment focus groups (IA-FGs) methods reported in Chapter I.

This participation process consisted of the organization of two focus groups where different actors from different fields were brought together. The participatory techniques used in this research adapted and shortened the procedure discussed by Kasemir et al. [13]. These two meetings were carried out in March and April of 2005 and allowed identifying the major gaps for which forest bioenergy systems have not been implemented in Catalonia. The participants came from different fields, and they should be eager to explore the topics explained and introduced [14], which must be appropriated for the participants, in order to generate a free-flowing and productive conversation on the topic [15]. That setting was also complemented with a series of previous interviews with relevant stakeholders to identify the key issues at stake as well as the main agents were invited.

A total of twenty-three people participated in the focus groups and they were from the: Policy Field (local and catalan government); Science and Expert Knowledge (researchers from different universities and institutes; technicians from local governments and businessmen of forestry business); and Non – Academic knowledge (forestry owners, non-governmental organizations and ecologists; interested businessmen, that were interested in the implementation of these systems in their sectors (i.e. a factory interested in the reduction of CO_2 emissions)) (see Figure 21).

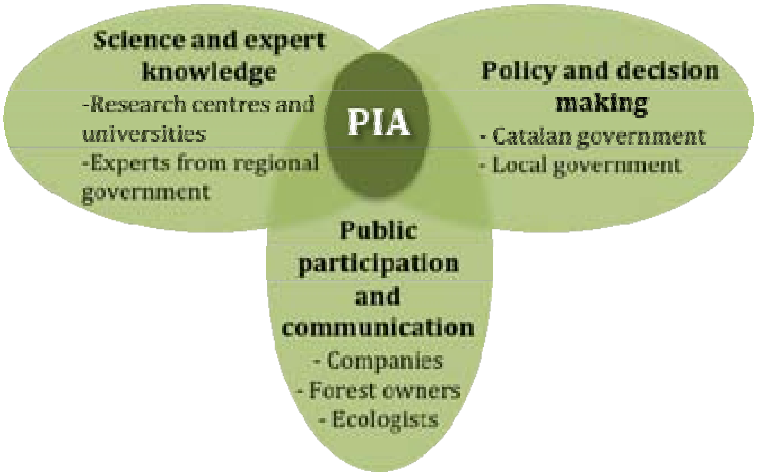

Figure 21. Participatory Integrated Assessment (PIA) as the intersection of the three domains of knowledge, decision making and public participation and communication, and the participants of the focus groups.

3.2.1. Development of the IA-FGs

A fortnight prior to the focus group sessions, a working document was sent to the different participants to introduce the topic and facilitate the discussion. This document presented the session structure and the questions to be discussed. Three main parts were differentiated in the document: presentation and objectives of the meeting; problem characterization; and a preliminary proposal of the scenarios to discuss, which are explained subsequently.

1) Presentation and objectives of the meeting

The presentation and objectives of the meeting consist mainly of the definition of the questions and topics that will be addressed. Problem definition requires a clear statement of what kinds of information are desirable and from whom this information should be obtained. A clear understanding of the problem, or general research question, is critical because it gives rise to the specific questions that should be raised by the moderator, and identifies the population of interest [16]. Hence, six key questions were depicted to start the discussion (see Table 6).

Table 6. Key questions introduced to the focus group.

Key questions
1) Is the characterization of the forestry biomass problem appropriated?
2) Which are the most probable environmental and social consequences of not taking part in the current dynamic?
3) Which is the role of the security of the biomass supplier in the evolution of the present scenario? Which practices are needed in terms of the different agents in order to assure the forestry biomass supply?
4) Which are the possible impacts of the forestry biomass used in the present wood market?
5) How should the new wood market be planned?
6) Which should the role of the government, as a forestry owner, be?

2) Characterization of the problem

The characterization of the problem was introduced with a review of the current context of forest bioenergy implementation in Catalonia. The text described the economic infeasibility of the forest exploitation, which results in an extra-accumulation of biomass during the last decades. There are two principal motivations in order to influence this tendency: at a local level, the forest fire risk and, at a global level, the Kyoto protocol coming into effect to decrease the greenhouse gases, and the creation of an emission market.

In order to give appropriate information to group participants, the Catalan background presented was mainly related to two fields: state of bioenergy in Catalonia and biomass potential in Catalonia. How these were presented and approached is described below.

Bioenergy in Catalonia

Many policies are settled in Catalonia referring to bioenergy, as the Catalan Energy Plan 2006-2015, which estimates an increasing forest and agricultural biomass consumption of 197% within this period of time (279 ktoe). This biomass consumption is mainly dedicated to heating options for household use and industrial use, such as sawmill industries. There are few bioenergy plants working, all with a maximum power of 5 MW, which operate with agricultural residues mostly.

Biomass potential in Catalonia

In order to know the availability of the bioenergy systems implantation in Catalonia, the biomass potential in Catalonia was estimated. Moreover, not only the potential of forest residues was calculated but also the potential of agricultural, sawmill industries and bulky wastes. Considering all these types of biomass, the Catalan biomass potential is about 2,6 millions of dry matter tones, which represents approximately 1 Mtoe (see Table 7). It is important to note the different seasonality and availability of the resources, which is more apparent in relation to forest and agricultural residues.

Table 7. Biomass potential estimated in Catalonia per year (2001).

	QUANTITY (kton)	LHV (toe/ton)	ENERGY (ktoe)	Percentage (%)
FOREST				**23.8**
Tree cover	323	0.42	136	12.3
Shrub area and dead trees	300	0.42	126	11.4
INDUSTRY				**3.8**
Industry and manufacturing	100	0.42	42	3.8
AGRICULTURE				**68.1**
Herbaceous crops	1500	0.40	603	57.2
Woody crops	285	0.43	510	10.9
BULKY WASTES				**4.4**
Furniture	71	0.42	30	2.7
Pruning and gardening	44	0.37	16	1.7
TOTAL	2623		1076	

Source: [17,18,19].

3) Proposal of scenarios

Finally, the working document presented the description of the scenarios to discuss. Three scenarios were defined to discuss during the session; and many variables were defined to analyse the scenarios, all of which are detailed in Table 8.

Table 8. Scenarios and variables defined to discuss during the focus group session.

Scenarios
Scenario 1: Small plant (from 1 ton 500 KW of power), to install into houses and public equipments such as schools, sports centre, etc. to produce heat;
Scenario 2: Medium plant (from 0,5 to 2 MW of power), to produce heat for district heating;
Scenario 3: Cogeneration plant (from 5MW of power), to produce heat and electricity.
Variables
1) Environmental variables: difficulty in the wastes management, impact of the emissions of the plant and the transport, infrastructure impact and global warming impact.
2) Economic and technological variables: economic profitability, synergic possibility of other economic activities, energy efficiency, plan requirements in the fuel shape, and the effect of the forestry fires in the supplier guarantee.
3) Social and policy variables: benefits for the local economy, creation of employment, possibility to use synergies in the urban planning, impact of the forestry owner’s fragmentation and the supplier business, and importance to communicate and inform society about the implementation process and exploitation of the plants.

The first few moments during the focus group consisted of welcoming the assistants. Afterwards, a general overview of the topic was given, explaining the objectives of the sessions. Guidelines and ground rules of the interaction between stakeholders were also explained in order to set strategies and encourage good discussions. Finally, an opening question was introduced to get each participant to talk.

Every focus group session (see Figure 22) longed approximately three hours, and was organized in the following parts:

(1) Presentation and discussion of the key questions. After the focus group presentations and the participant presentations, and open discussion was realized about the bioenergetics forestry use in Catalonia. Each participant had five minutes, at maximum to express his/her point of view in a general fashion. This part lasted one hour.

(2) Scenarios group discussion. During the work session, comparative analysis of the technological, economic, political, social and environmental variables was performed for the three scenarios. The assessment of these variables for each scenario followed a punctuation of quite positive, not so positive, neutral, very negative, quite negative and not so negative. This session also lasted an hour.

(3) Conclusions and process evaluation. After a small break, the conclusions of the session and evaluation of the process were carried out. In this part, the participants not only could express their feelings about the bioenergy systems implementation, but their opinions about the focus group organization and performance.

Figure 22. Pictures of the development of the focus groups.

3.2.2. Focus Groups results

After interpreting the qualitative data obtained during the focus group sessions, the results fell into four categories: (i) biomass situation analysis in Catalonia; (ii) policy recommendations to the Catalan forestry sector; (iii) aspects to consider in a bioenergy system implementation in Catalonia; and (iv) scenario analysis.

(i) Biomass situation analysis in Catalonia

Some cause-effect relations were devised that helped to explain the existing situation of the forestry biomass in Catalonia. The interrelationship between the several factors that fall on the lack of implementation of bioenergy systems in Catalonia is revealed in Figure 23.

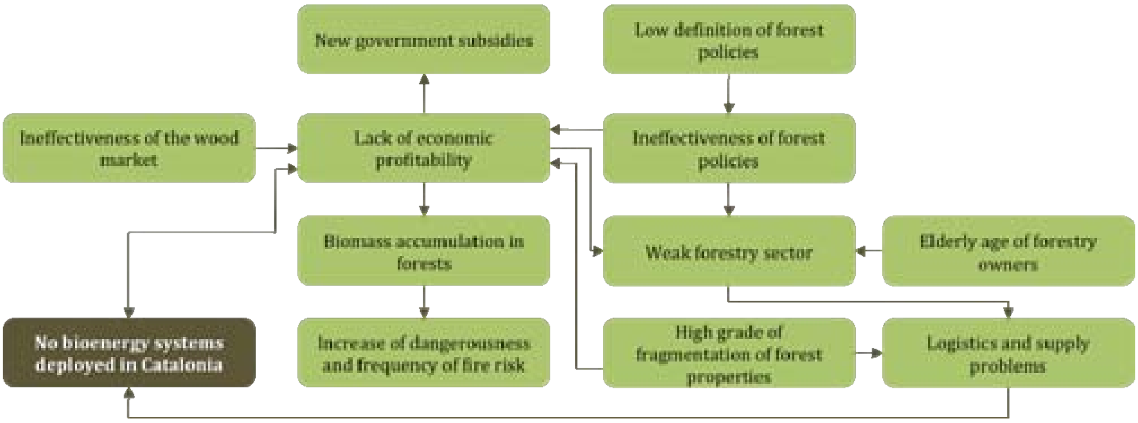

Figure 23. Cause-effect diagram of the relationship of the forestry biomass sector in Catalonia devised in the focus groups.

(ii) Policy recommendations to the Catalan forestry sector

The main actions to take in order to solve the present problems of the Catalan forestry sector according to the focus groups were:

1) Consensus and effective forestry planning between all people involved (forestry owners, businessmen, researchers, users, etc).
2) Fire preventive action by means of forestry cleaning and a related forestry policy.
3) Creation of a real wood market capable to incorporate all real needs and expectations of the forestry products developed in Catalonia.

(iii) Aspects to consider in a bioenergy system implementation in Catalonia

According to the focus group, many general aspects have to be considered in a bioenergy system implementation. The first thing that has to be regarded is its complementariness with other renewable energies, since forestry biomass can not only easily interact and complement them but the forest biomass contribution to produce neutral CO_2 emissions depend on this interaction. However, harvesting, transportation and waste management emissions should be taken into account, as the carbon fixation.

An adaptation of forest management strategies is necessary and binding them to the territory, since the forestry area in Catalonia is characterized by its heterogeneity, both in an environmental and social way. Its diversity means that for a determinate area there are capabilities that are possible to be developed, but they may completely differ from other areas. The social actors and the natural territory characteristics are those that determine which is the model and the option more adequate. It is also important to adapt the type of the energy production (heat, electricity) to the particular demand of that territory.

The results of this analysis are divided in environmental; economic and technological; social and policy aspects and are detailed in Table 9.

Table 9. Key aspects to be considered in the economic, technological and environmental fields, according to the focus group.

FIELDS	KEY ASPECTS
Economic	- To allow forest bioenergy systems with the present wood market - To define and regulate which biomass is viable to use - To generate a forestry market for bioenergy systems - The market regulation has to be intervened by the administration - To limit transportation distance up to 50 km.
Technological	- Projects should be possible at short term (combustion processes) - To adapt harvesting machinery to Mediterranean forests - To standardize and normalize the fuel shape before its commercialization - To assure the electricity evacuation in the electric grids
Environmental	- To define sustainable forest harvesting - To control combustion emissions - To maintain the landscape mosaic and biodiversity - To consider other possibilities as energy crops
Social	- Logistic and supply problems - To manage adequately possible bad social perception of bioenergy systems in the beginning

(iv) Scenario analysis

The three scenarios were analysed on a basis of their complementarity and relevance. The results of this analysis are also divided in environmental, economic, technological, social and policy aspects, as can bee seen in Table 10.

Table 10. Key aspects to be considered for the scenarios analysis, according to the focus group.

SCENARIOS	KEY ASPECTS
Environmental	- Difficulty of the waste management - Transport and combustion emissions - Infrastructure impacts (electricity connection, etc.) - Contribution to global warming
Economic and technological	- Economic profitability in short term in small and medium plants - Competence in the wood market - Plant requirements about biofuel standards (size, humidity and LHV*) - Forest fires affect more the small and medium plants, for the biomass supplying and dependence
Social and policy	- Positive indirect impacts, as territory development. - Direct benefits are bigger in a big plant. - Employment creation depends on the size plant - Difficulty to find qualified workers for working in forest areas. - Positive synergies with the urban planning. - Importance to communicate and inform the citizenship.

* LHV - Lower Heating Value (also known as *net calorific value*)

3.3. Conclusions for Chapter II

This chapter presents the results of a participatory experience to understand the driving forces that guide the implementation of forest bioenergy systems, which are not widely introduced in the Mediterranean basin, although the need of incorporating renewable sources in the energy sector and a sustainable forest and landscape management. Generally it is considered that the implementation of the forest bioenergy systems in Catalonia is a process soon to be developed and put into practise, not only for the global necessities of energy diversification, foster new sources of renewable energies and the decrease of forest fires risk, but also for the high interest aroused in a great part of the society. Besides, forestry biomass plays a fundamental role as energy source in climate change, due to its capacity to fix carbon dioxide, which helps to mitigate the global warming effect. The main research findings drawn from focus groups are that the bioenergy sector in Catalonia is characterised mainly by a lack of economic profitability of forestry products; logistics and supply problems; and biomass accumulation in forests which derivate to a dangerousness and fire risk. There is also a lack of a real forestry market; a high fragmentation of forestry properties along with the conservative owners' character; and a lack of a well defined forestry policy. The scenarios analysis also demonstrated that the scenarios definition was insufficient, since it was mainly based on technology aspects; and that the positive and negative impacts seemed to be quite dependent on the government regulation and control.

On the whole, Integrated Assessment methodology, such as the one developed in this chapter, is regarded as a good approach to face up to sustainability problems, which involve a large number of issues intimately interrelated, associated to social structure, culture, political and economic aspects. Furthermore, it facilitates to implement and continue different processes of public participation and decision-making, helping to meet all the actors involved in the process, and thus create a discussion forum which gathers the relevant views that needed to be considered in the implantation of these new energy sources. With this methodology, it is possible to make a step forward to a global and integral knowledge of sustainability.

Above and beyond these findings, further assessments should be carried out to evaluate the feasibility and sustainability of different alternatives of bioenergy systems, which will be addressed in the following chapters.

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III

Environmental assessment of a gasification bioenergy system

4. Environmental assessment of post-consumer wood and forest residues gasification: the case study of Barcelona metropolitan area

From the integrated assessment using focus-group methodology (see Chapter II), some relevant aspects and conclusions were highlighted that should be taken into consideration in a bioenergy system implementation. In the environmental scope there was the difficulty of the waste management, transport and combustion emissions, infrastructure impacts in the landscaping and the potential contribution of these systems in global warming. In the economic and technological level, among others, the requirements about biofuels, which were different depending on the biomass conversion technology used, were mentioned. And, in the social and policy level, it was pointed out that logistic and supply problems could arise and that positive synergies with urban planning could be an asset when considering the implementation of bioenergy systems.

In such a context, the objective of this chapter is to study these aspects and for this reason, an integrated environmental assessment of a bioenergy system is performed using Life Cycle Assessment methodology. As mentioned in Chapter I, the commercially available biomass conversion technologies are combustion and gasification, where combustion is the most extended process and gasification is under important research and development [1]. Additionally, gasification technologies with respect to energetic performance are more efficient than CHP and power generation combustion technologies [2]. Therefore, a life cycle assessment of a bioenergy system based on gasification of two different biomass sources is performed in order to compare different biomass supply chains and logistics: forest biomass and post-consumer wood, which is presented in the following chapter.

4.1. Introduction to Chapter III

In the context explained and discussed in Chapter I and II, it has been apparent that biomass as an energy source provides an array of diverse sustainable development services [3,4] in the commitment to increasing the share of renewables by means of bioenergy systems at different global, regional and local levels [5-9].

This chapter assesses the life cycle of post-consumer wood and forest residues for energy conversion in a gasification plant located in Cerdanyola del Vallès (Barcelona), a city located in the outskirts of Barcelona (see Figure 24) in Catalonia (see Chapter I for further description). This analysis was performed within the framework of the POLICITY project, in which large urban areas in different countries are developed, particularly in the fields of energy optimization and the use of renewable energies. In this study, the case of the metropolitan area of Barcelona is presented, where a development area planned for 50.000 inhabitants consisting of eco-buildings for residential, industrial and service purposes will be established on a common basis of innovative sustainable construction. It also promotes the use of renewable energies, represented by a 1 MWe gasification plant fuelled by different types of biomass [10].

Source: Adapted from [11].

Figure 24. Location map of Cerdanyola del Vallès (Barcelona).

Therefore, this study applies Life Cycle Assessment (LCA) methodology, which is described in Chapter I, in order to compare the environmental and energy impacts of post-consumer wood and forest residues, as well as analyzing and identifying the most critical stages of the system. As specified by ISO 14040-14044 [12,13], the obligatory elements (classification and characterisation) of impact assessment methods are applied. The software employed is SimaPro 7.0.1, developed by Pré-Consultants [14].

In order to achieve this goal, fieldwork was performed to obtain local data for both the fuel consumption of the machinery involved and the gasification emissions of a pilot study carried out with different kinds of biomass. The biomass analysed in this study is differentiated as: (i) post-consumer wood generated in the metropolitan area of Barcelona; and (ii) forest residues coming from a metropolitan radius of 50 km from Cerdanyola del Vallès. Post-consumer wood is defined as non-dangerous wastes (code 030105 from the European Waste Catalogue – Waste bark and wood). They come from both collection at recycling points and the collection of bulky wastes. Forest residues are obtained from the waste generated by forest exploitation (brushes; woodchips; etc.) as a result of conventional forestry (thinning; final cuts; etc.). The gasification technology entails three main specific requirements which will make the most suitable type of biomass conditional on: (1) moisture content lower than 15%; (2) a maximum chip section of 2 cm; and (3) high biomass homogeneity.

The Life Cycle Assessment of post-consumer wood and forest residues gasification was executed on the basis of three different scenarios: (1) Post-consumer wood from the recycling points; (2) Post-consumer wood from bulky wastes; and (3) Forest residues. The results provided the project architects, engineers, businessmen and politicians with information about which stages were the most critical in relation to environmental loads and which scenario and, therefore, which type of biomass, was the most appropriate for the case study defined, results that can be thoroughly extended to metropolitan and urban areas.

4.2. Life Cycle Assessment of Post-consumer wood and Forest residues Gasification

4.2.1. Goal and scope definition

The goal of this study is to evaluate and compare the resulting environmental loads associated to the life cycle of post-consumer wood and forest residues gasification, in order to compare different scenarios and to identify the most critical stages of the process. Two principal targets are defined to achieve this goal: (1) calculate the energy balance and (2) evaluate the environmental impacts, of all the stages involved in the system.

4.2.2. Functional unit

The functional unit of this study is defined as: 'the production of 1000 MJ of primary energy (thermal and electric) generated in a gasification plant with an efficiency of 0.588, in which the electrical efficiency is 0.284 while the thermal efficiency is 0.304.

The reference flows, known as the input of biomass needed to produce 1000 MJ of primary energy, are calculated as 0.103 ton for post-consumer wood and 0.113 ton for forest residues. These flows are calculated by means of the biomass' Low Heating Value, described below in the Data Inventory, and the cogeneration efficiency of the gasification plant. The efficiency is obtained from the Policity technical project [10], which was carried out using data from technology suppliers for the gasification plant.

4.2.3. Scenarios

Three scenarios are considered: (1) Post-consumer wood from the recycling points; (2) Post-consumer wood from bulky wastes; and (3) Forest residues. These scenarios were defined under the generic consideration of collection in the city centre and transport to the pre-treatment and gasification plant in the metropolitan area.

Scenario 1: Post-consumer wood from the recycling points

This scenario comprises the user who carries the wooden waste to the nearest recycling point in Barcelona (average distance of 2.0 km). At the recycling point, this by-product is separated and classified. The resulting by-products are transported to the Waste and Packing Plant in Gavà (distance of 24,0 km), where the by-products are separated and chipped. Finally, they are taken to the gasification plant in Cerdanyola del Vallès (distance of 36.4 km).

Scenario 2: Post-consumer wood from bulky wastes

This scenario consists of the bulky collection that is performed by the Barcelona City Council. Once collected, this waste is transported to the Waste and Packing Plant in Gavà (distance of 24.0 km), where it is classified and chipped according to its characteristics. The separated post-consumer wood has two destinations depending on the quality of the wood: (a) board industries if it's high quality wood; and (b) energy conversion systems if it's low quality wood. Finally, chipped by-products are taken to the gasification plant in Cerdanyola del Vallès (distance of 36.4 km).

Scenario 3: Forest residues

In this scenario, forest residues are harvested in different radius of action, 30 km at the most, from the gasification plant located in Cerdanyola del Vallès. These distances are delimited from a previous study of availability of supply carried out by the Forest Technology Centre of Catalonia [15]. The maximum distance considered for forest residues transportation is 50 km, since the transport route using the road network is longer than the 30 km supply radius.

4.2.4. System boundaries

The system boundaries of this study are:

- Geographical boundary, as the LCA refers to the metropolitan area of Barcelona (Mediterranean region). However, this limitation does not mean that the stages of the life cycle are limited to this geographical area (eg. fuel production).
- Time-based boundary, regarded as the year when the study was carried out, as the best technology presently available is considered for all the stages involved in the process.

Figure 25 shows the flowchart of the three scenarios (1 – Post-consumer wood from recycling points; 2 – Post-consumer wood from bulky wastes and 3 – Forest residues).

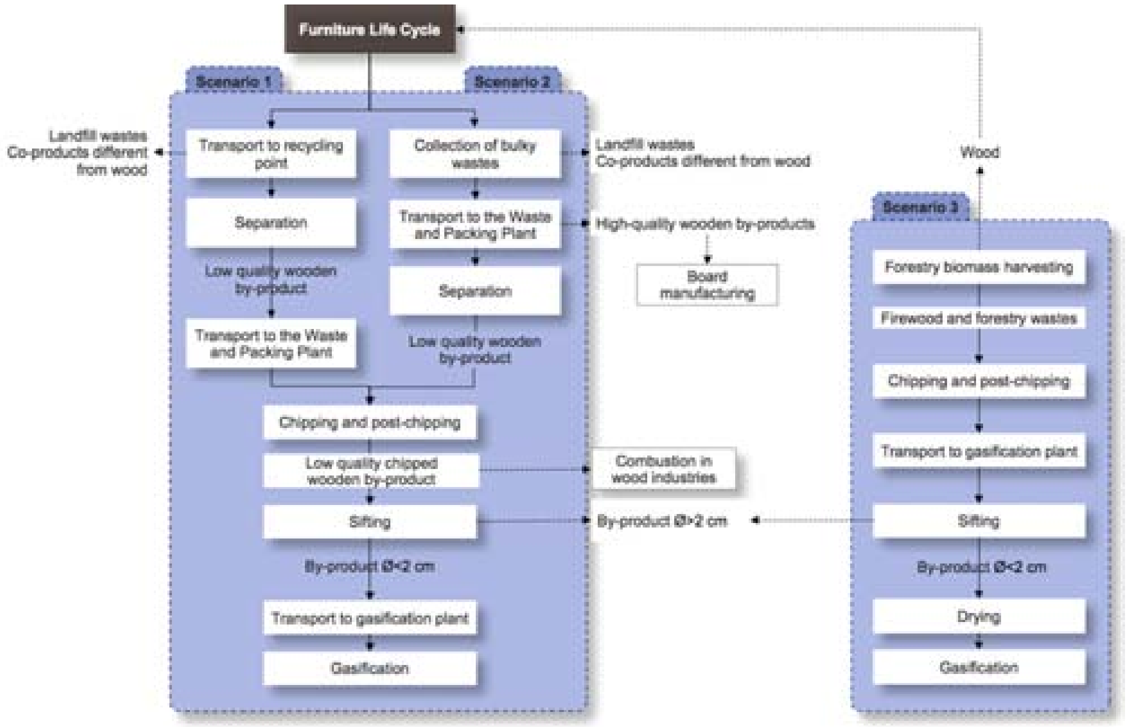

Figure 25. Flowchart of the three scenarios. Scenarios: 1– Post-consumer wood from recycling points; 2 – Post-consumer wood from bulky wastes; 3 – Forest residues.

Stages and processes considered

In relation to biomass pre-treatment and transport, inventories of these stages refer to the consumption of one ton of biomass.

Regarding fuel production, gas oil production includes the following stages: fuel extraction, petrol refinement processes and its transport from the refinery to the final user. The process used to model this stage was Diesel at regional storage /RER/U from Ecoinvent database [16].

The emissions considered are air emissions produced by the fuel combustion of machinery engines, which are modelled using the Ecoinvent database [16].

Finally, emissions of biomass gasification are related to the best available technology complying with an Order in Council from the Spanish Government (RD 653/2003 on the incineration of wastes), which implements Directive 2000/76/EC of the European Parliament and Council on the incineration of waste. This stage includes the construction, maintenance and operation, and waste disposal of both the plant and gasification wastes. Also included are substances needed for operation: lubricating oil, urea, organic chemicals, sodium chloride, chlorine and decarbonized water.

Cut-off rules

The aspects beyond the system boundaries are those included in the production of goods and maintenance of the machinery in the biomass pre-treatment and transport stages, since these stages represent less than 5% of the overall impact [17,18].

The construction of infrastructures and maintenance of machinery are not considered. Neither is the transport of personnel to carry out the different stages included.

4.2.5. Data sources and quality

The data used in this LCA corresponds to local data obtained by means of experimental work and interviews with experts in the sector carried out in 2006. The interviews were conducted with experts from the Waste and Packing Plant and with technicians from the Forest Technology Centre of Catalonia who were performing the biomass supply assessment for the Policity project. The technology of each Life Cycle Stage is the up-to-date technology used in these fields. When local data was not available, ecoinvent database is applied [16]. In Table 11 the data sources are summarized for the different stages analysed.

Table 11. Summary of quality of data sources

Life Cycle Stage	Geographical area	Age (year)	Technology	Origin
Pre-treatment and transport	Local	2005/2006	High	Fieldwork (interviews with experts and technicians of the Policity project)
	European	1999	High	Ecoinvent data v1.2
Gasification	European	2000	High	Ecoinvent data v1.2
Fuels	European	2000	High	Ecoinvent data v1.2

4.2.6. Life cycle impact assessment

The method to analyse the environmental impacts is based on the model developed by the Centre of Environmental Science (CML 2 baseline 2000) of Leiden [19]. LCIA is applied using the midpoint approach, where the variables are included in the environmental mechanism of the impact category between the environmental intervention and the category endpoint [20]. Hence, classification and characterisation impact assessment is carried out in order to analyse the system described. The midpoint impact categories considered in this LCA are: Abiotic depletion (AD); Global Warming (GW); Ozone Layer Depletion (ODP); Human Toxicity (HT); Acidification (A) and Eutrophication (E). As flux indicator, energy consumption is calculated.

4.3. Data Inventory

4.3.1. Biomass properties

Physical properties and heating values of post-consumer wood and forest residues are shown in Table 12.

Table 12. Density and heating value of the transported material: bulky wastes, post-consumer wood and forest residues.

Material	Lower heating value (MJ t^{-1})	Density (kg m^{-3})
Bulky wastes	--	62.5
Post-consumer wood	15604	176
Post-chipped post-consumer wood	16567	268
Post-chipped forest residues[a]	15000	215

[a] Average Lower Heating Value of the predominant forestry species at 30 km from Cerdanyola del Vallès.

4.3.2. Biomass transport

Three vehicles are considered to carry the biomass along the different routes depending on the scenario analysed: van, local truck, and regional truck. The transport model applied to this study associates the fuel consumption of the vehicle to the transported load. To calculate the fuel consumption of the different vehicles implied in transport a mathematical equation was used:

$$C_{xt} = C_0 + \left(C_p - C_0\right) \cdot \frac{Q_x}{Q_t} \qquad \text{(Eq. 21)}$$

where C_{xt} (litres km^{-1}) is the total fuel consumption of the vehicle when a load Qx is being transported; C_0 (litres km^{-1}) is the minimum fuel consumption equivalent to an empty load; C_p (litres km^{-1}) is the fuel consumption of the vehicle when it carries the maximum load (Qt); Q_t (ton) is the maximum load which a vehicle can carry; and Q_x (ton) is the load transported by the vehicle.

In order to consider the fuel consumption of the comings and goings of the vehicle, the following equation was established:

$$C_{xta} = C_0 \cdot K_0 + C_{xt} \cdot K_x \qquad \text{(Eq. 22)}$$

where C_{xta} (litres) is the total fuel consumption of the vehicle when travelling the outgoing (empty load) and the incoming (full load) routes; C_{xt} (litres km^{-1}) is the total fuel consumption of the vehicle when it carries a Q_x load; C_0 (litres km^{-1}) is the minimum fuel consumption equivalent to an empty load; K_0 (km) is the distance traveled when the vehicle is empty; and K_x (km) is the distance traveled when the vehicle is loaded.

4.3.3. Biomass pre-treatment

Due to the strict requirements in reference to the type of biomass in the gasification plant, certain steps are required to prepare the post-consumer wood and the forest residues, which are explained in further detail in the following sections.

Biomass pre-treatment in Scenario 1 – Post-consumer wood from recycling points and 2 – Post-consumer wood from bulky wastes

The following three main steps are required: (1) Separation; (2) Chipping; and (3) Sifting and post-chipping. The fuel consumption of the standard machinery involved in the biomass pre-treatment of Scenario 1 is shown in Table 13. The fuel consumption is related to one ton of biomass depending on the type of biomass separated, chipped or sifted (bulky wastes; post-consumer wood, and forest residues).

Table 13. Fuel consumption (in MJ t^{-1}) of the different machinery involved in the biomass pre-treatment

Scenario	Pre-treatment	Data source	Energy consumption (MJ t^{-1})
1– Post-consumer wood from recycling points Scenario 2 – Post-consumer wood from bulky wastes	Crane	[21,22]	94.40
	Bulldozer	[21,22]	27.14
	Chipping	[23,24]	153.41
	Post-chipping	[23,24]	46.02
	Sifting	[25]	11.94
3 – Forest residues	Power saw	[26,27]	39.37
	Tractor with chipper	[26,27]	201.19
	Sifting	[25]	11.94
	Drying	[28]	792.00

Biomass pre-treatment in Scenario 3 – Forest residues

The fuel consumption of the different machinery involved in the biomass pre-treatment of Scenario 3 is related to the biomass harvesting and pre-treatment shown in Table 13. In order to achieve 15% moisture content, a forced drying stage is needed since the wood contains 30% moisture when it is collected from forest tracks [27]. The fuel consumption is related to one ton of biomass depending on the type of biomass harvested, chipped, sifted or dried.

4.3.4. Biomass gasification

The efficiency of the biomass cogeneration unit is 0.588, where electrical efficiency is 0.284 and thermal efficiency is 0.304.

Referring to the emissions of the biomass gasification plant, the results are obtained from an experimental trial carried out in the facilities of Energia Natural de Móra S.A. in Móra d'Ebre (Tarragona) as part of the Policity project in 2006 [29]. The process took place in a fluidized gasifier applying air as oxidising agent. The electricity was produced by the combustion of the clean gas in two 250 kW engines, which needed a 5-8% of diesel injection regarding the overall engine energy consumption.

Hypothesis

The following hypotheses are adopted regarding the emissions of the biomass gasification plant:

- The maximum emission limits correspond to the limits set up by the Order in Council from the Spanish Government for the incineration of wastes (RD

653/2003), which implements Directive 2000/76/EC of the European Parliament and of the Council for the incineration of waste.

- The emissions from the trial are equivalent to the gasification of post-consumer wood, since the complementary fuel was composed of organic solid biomass, which does not entail high emission levels.
- When the trial emissions were lower than those established by the Order in Council from the Spanish Government for the incineration of wastes, the resulting emissions of the trial were applied.
- If any contaminant was not detected in the trial, the maximum limits established by the Order in Council from the Spanish Government for the incineration of wastes were used.
- The CO_2 emissions from the gasification of the post-consumer wood and forest residues are considered to be zero due to the fixation of carbon dioxide during the process of growing the forest [30-34].

The emission results of this trial and the limits established by the Order in Council from the Spanish Government for the incineration of wastes (RD 653/2003), as a result of Directive 2000/76/EC of the European Parliament and Council on the incineration of waste, are shown in Table 14.

Table 14. Emission results and data of the experimental trial and the limits established by the Order in Council from the Spanish Government on the incineration of waste (RD 653/2003) in the facilities of Energia Natural de Mora SA in Móra d'Ebre (Tarragona) in 2006.

Parameter/Contaminant	Result (*/ Nm^{-3})	Limit set by RD 653/2003
Solid particles	1.0 ng	10mg
Heavy metals		
Cd + Tl	37.6µg	50 µg
Hg	16.0 µg	50 µg
Others	340.0 µg	500 µg
O2	4.36%vol	--
CO	579.0 mg	--
NO3	2455.3 mg	--
SO2	ND[a]	50 mg
HCl	ND[a]	10 mg
HF	7.4 mg	1 mg
TOC, as total organic carbon	81.1 mg	--
PCDD/F	0.017 ngITEQ	0.1 ng

[a] ND: Not Detected; -- no limit is established by RD 653/2003.

4.4. Results and discussion of the environmental assessment

The evaluation and interpretation of the results for the three scenarios proposed (1 – Post-consumer wood from recycling points; 2 – Post-consumer wood from bulky wastes; 3 – Forest residues) consist of two assessments: Energy balance of the scenarios studied and Global environmental impacts.

4.4.1. Energy balance

The total primary energy balance of the three scenarios studied is numerically specified in Table 15. In Scenario 1 the pre-treatment stage involves the 58% of the energy consumption (27.27 MJ fu^{-1}), while the transport requires the remaining 42% (19.41 MJ fu^{-1}). In Scenario 2, these percentages are substantially similar and correspond to the 53% for the pre-treatment and the 47% for the transport and in terms of energy are 39.75 MJ fu^{-1} and 35.10 MJ fu^{-1} respectively. However, the energy consumption in Scenario 3 is up to the 89% of the energy required in this scenario (118.41 MJ fu^{-1}), whereas the transport the 11% (14.55 MJ fu^{-1}). This difference can be explained by the drying stage, which is the highest energy consumption step of the overall scenarios. It involves the 76% of the energy consumption of the pre-treatment, and the 68% of the scenario. In Scenario 1 the stage with higher energy consumption is the chipping and post-chipping, which is the 44% of the energy consumption. Regarding Scenario 2, transport is the stage with the most energy consumption, which requires the 47% of the total input. The transport stage in this scenario entails the higher energy consumption of all scenarios, due to the longer transport required and the low bulk density of the material transported. Thus, the pre-treatment stage is the one with higher energy contribution of the overall scenarios.

Table 15. Energy balance (in MJ fu^{-1}) per functional unit detailed for the three scenarios analysed.

Scenario 1– Post-consumer wood from recycling points
Scenario 2 – Post-consumer wood from bulky wastes

			Scenario 1	Scenario 2
OUTPUTS (MJ fu^{-1})	TOTAL OUTPUTS (Gasification)		1000.00	1000,00
INPUTS (MJ fu^{-1})	Transport	Van	1.56	-
		Local truck	10.02	27.26
		Regional truck	7.84	7.84
		Total transport	*19.41*	*35.10*
	Pre-treatment	Chipping and post-chipping	20.47	20.47
		Crane	-	9.69
		Bulldozer	5.57	8.36
		Sifting	1.23	1.23
		Total pre-treatment	*27.27*	*39.75*
	TOTAL INPUTS		46.68	74.85
ENERGY BALANCE (MJ fu^{-1})			953.32	925.15

Scenario 3 – Forest residues

OUTPUTS (MJ fu^{-1})	TOTAL OUTPUTS (Gasification)		1000.00
INPUTS (MJ fu^{-1})	Transport depending on the distance (km)	10	2.91
		20	5.82
		30	8.74
		40	11.64
		50	14.55
	Pre-treatment	Harvesting. chipping and post-chipping	27.26
		Sifting	1.35
		Drying	89.80
		Total pre-treatment	*118.41*
	TOTAL INPUTS IN 50 KM		132.96
ENERGY BALANCE in 50 km (MJ fu^{-1})			867.04

The global energy balance is illustrated in Figure 26. It can be observed that the energy input for the pre-treatment comprise between 3% and 12% of the total energy involved in the process, while the transport stage entails a range from 1 to 4%. This fact shows that not only the energy balance is positive, but also the small amount of energy required both in the pre-treatment and transport stages (from 5 to 13%) comparing to the energy obtained from the gasification process.

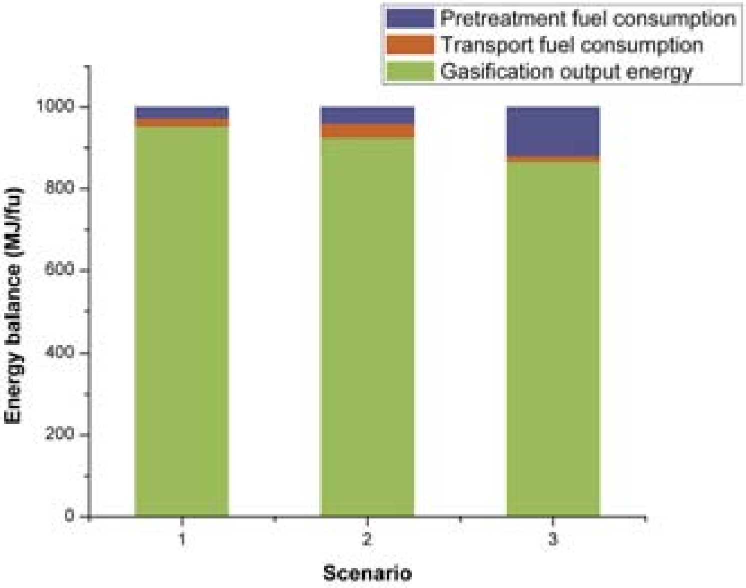

Figure 26. Energy balance of the biomass pre-treatment, transport and gasification output energy of the three scenarios. ***Scenarios: 1– Post-consumer wood from recycling points; 2 – Post-consumer wood from bulky wastes; 3 – Forest residues.***

4.4.2. Environmental assessment

The environmental impact load of the system is showed in Table 16 for the three scenarios studied. The contribution of the life cycle stages to the total environmental impacts is illustrated in Figure 27, where the environmental impacts are scaled to 1. As it can be observed, Scenario 3 has a greater impact in the majority of the impact categories, except for Eutrophication (E) in which Scenario 2 has the most substantial influence, although Scenario 3 is significally close to this highest impact contribution. The fact that Scenario 3 is the one with the highest impact on the environment can be explained by the energy consumption of the overall stages, mainly due to the drying stage which is the most energy intense. Comparing the two wooden by-product scenarios (Scenarios 1 and 2),

Table 16. Environmental impact of the system for each impact category per functional unit (AD: Abiotic Depletion; GW: Global Warming; ODP: Ozone Layer Depletion; HT: Human Toxicity; A: Acidification; E: Eutrophication).

Impact category	Unit	Scenario 1– Post-consumer wood from recycling points	Scenario 2 – Post-consumer wood from bulky wastes	Scenario 3 – Forest residues
AD	kg Sb eq	4.38E-01	5.59E-01	1.38E+00
GW	kg CO_2 eq	1.34E+02	1.58E+02	2.42E+02
ODP	kg CFC-11 eq	1.99E-05	2.22E-05	7.22E-05
HT	kg 1,4-DB eq	1.53E+02	1.62E+02	2.09E+02
A	kg SO_2 eq	1.43E+00	1.58E+00	2.89E+00
E	kg PO_4^{3-} eq	3.42E-01	3.75E-01	3.72E-01

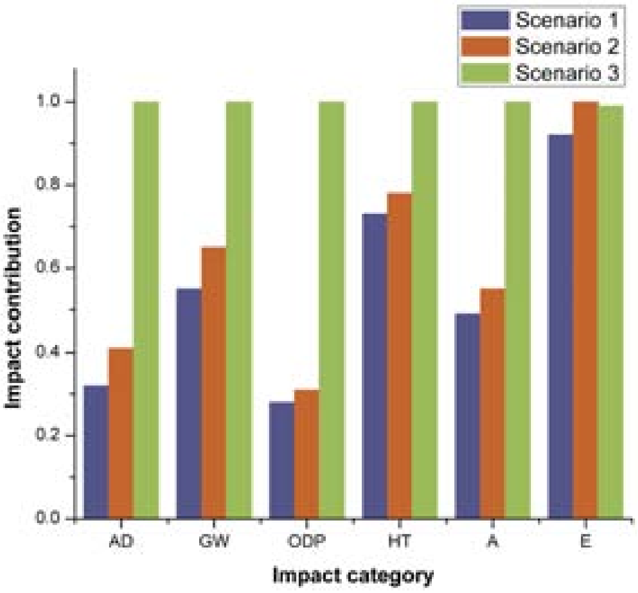

Figure 27. Contribution of the system stages to the different environmental impact categories for the three scenarios ***Scenarios: 1– Post-consumer wood from recycling points; 2 – Post-consumer wood from bulky wastes; 3 – Forest residues. Impact categories: AD: Abiotic Depletion; GW: Global Warming; ODP: Ozone Layer Depletion; HT: Human Toxicity; A: Acidification; E: Eutrophication.***

Scenario 2 is associated to a greater impact in the overall analysis owing to the higher energy demand of the involved processes. Hence, the Scenario 1 is the one with the smaller impact contribution.

In relation to the most critical stages of the system according to the relative impact associated to each stage (see Figure 28), for scenarios 1 and 2 the most critical stage is gasification, whereas for Scenario 3 it is biomass pre-treatment. Referring to impact categories, gasification stages entail the highest environmental impact in human toxicity and eutrophication and it can be explained by the emissions from the gasification process. On the other hand, abiotic depletion and ozone layer depletion have the greatest impact associated to the pre-treatment stage and both impact categories are associated to the fuels and electricity used in the machinery. Global warming and acidification do not show a clear tendency, since they contribute almost fairly to pre-treatment and gasification. In the global warming category, the transport stage implies between the 8 and the 24% of the overall impact, which is associated to the fuel used in the process.

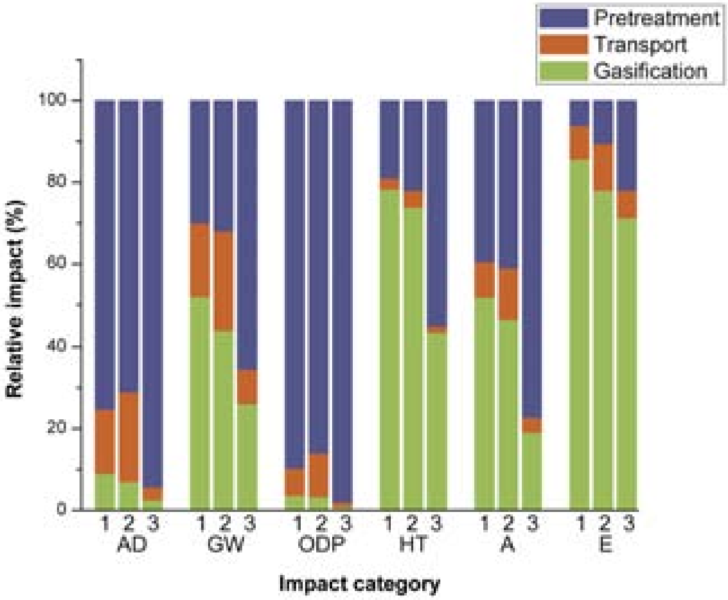

Figure 28. Critical Stage of the environmental impact associated to the scenarios. ***Scenarios: 1– Post-consumer wood from recycling points; 2 – Post-consumer wood from bulky wastes; 3 – Forest residues. Impact categories: AD: Abiotic Depletion; GW: Global Warming; ODP: Ozone Layer Depletion; HT: Human Toxicity; A: Acidification; E: Eutrophication.***

4.5. Conclusions for Chapter III

In this chapter a Life Cycle Impact Assessment has been carried out in order to determine the most critical stages in three scenarios studied. The energy consumption (%) used in both urban wastes and forest residues pre-treatment and transport stages is low in comparison to the energy obtained from gasification in all three scenarios. Post-consumer wood from the collection from recycling points requires the 5% of the energy involved in the process, followed by the post-consumer wood from the collection of bulky wastes (7%), and, finally, forest residues that entail the 13% of the overall energy.

The most appropriate biomass for the gasification plant is the biomass of Scenario 1 and 2 (Post-consumer wood from recycling points and bulky wastes), considering the high physical requirements (15% moisture content; homogeneity; chip section of 2 cm; etc.) of the gasification plant.

Referring to the environmental analysis and from the scenarios analysed, Scenario 3 – Forest residues is associated to a greater impact in five of the six impact categories analysed (within an increase of 22% and 72% in comparison to the other scenarios). Scenario 1 – Post-consumer wood from recycling points is associated to a lower contribution in all the impact categories (within 27% and 64% of the maximum impact), whereas Scenario 2- Post-consumer wood from bulky wastes has 30% to 93% of the maximum impact.

In relation to the stages, biomass pre-treatment is associated to a significant impact in two impact categories: Abiotic Depletion (AD) and Ozone Layer Depletion (ODP), calculated as 71% and 98% of the overall impact. The transport stage is of no significant influence either in the scenarios or in the impact categories (< 24% of the overall impact). This fact contradicts the statement reached by the focus group regarding the high transport emissions (see Chapter II), at least in the scenarios studied. Gasification represents an overall impact up to 78% of the different impact categories. In reference to Global Warming (GW), the impact percentage is between 26 and 52%, although the CO_2 balance is considered neutral, a finding that corresponds to the focus group conclusions.

These results point to the advantage of using post-consumer wood instead of forest biomass, since all the supply chains are already connected. Forest biomass pre-treatment is a critical stage that must be addressed. In addition, it is necessary to find other biomass conversion technologies to exploit the forest biomass.

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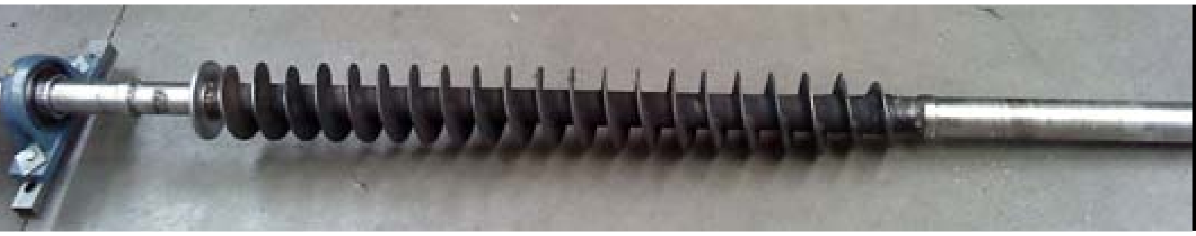


IV

Technological assessment: experimental, simulation and economic study on biomass pyrolysis; along with a green chemistry approach in the biorefinery context for processing biomass

5. Introduction to Chapter IV

The previous assessment carried out in Chapter III showed that forest biomass pre-treatment is a crucial stage of a bioenergy system due to its high-energy demands. In addition, the environmental assessment resulted in the fact that the post-consumer wood was a better alternative compared to forest biomass. From the integrated assessment by focus groups detailed in Chapter II it was highlighted the drawback of using forest biomass owing to logistic and supply problems. These outcomes point out the need to research on biomass conversion technologies to provide a solution to the disadvantages of using forest biomass in bioenergy systems. Regarding this aspect, biomass pyrolysis offers significant advantages due to the multiple products obtainable, which can be easily stored and transported. Moreover, it is becoming apparent that biomass pyrolysis permits the implementation of a local and regional strategy, which would overcome the drawbacks of supply and critical high demands regarding pre-treatment of the feedstock larger scale plants, such as gasification plants.

For this reason, this chapter deals with the technological aspect of using forest biomass. The first two sections examine pyrolysis of biomass, while the final section consists of a novel approach for greener processing technologies. Pyrolysis of biomass is approached by experiments run at pilot plant and, prior to them, the application of the Distributed Activation Energy Model to biomass devolatilisation. Additionally, simulation processes are performed to assess the mass and energy balances of the pyrolysis process in an auger reactor pilot plant. The aim of this simulation is to assess the mass and energy balances of the overall process and to design an energy self-sufficient auger reactor with a mass flow rate of 1500 kg/h. Following to this, an economic assessment is performed to assess the economic feasibility of this pyrolysis plant. Finally, the last section in this chapter focuses on microwave dissolution of wood using ionic liquids, a green chemistry approach to process forest biomass.

6. Application of the Distributed Activation Energy Model to Biomass and Biomass Constituents Devolatilisation

In this section, an investigation about the thermal behaviour of four different woods is carried out in order to deal with biomass devolatilisation. This assessment will help to understand and undergo devolatilisation process, which have a key role in biomass pyrolysis. Therefore, the distributed activation energy model (DAEM) is applied to study the effect of heating rate on the reaction of single solids. The possible calculation of biomass samples behaviour in pyrolysis conditions as the summation of their constituents, lignin, cellulose and hemi-cellulose is also explored.

6.1. Introduction to DAEM application to biomass devolatilisation

Many kinds of biomass species have been subjected to pyrolysis conditions to produce fuels, solvents, chemicals and others [1]. The study of biomass pyrolysis is advisable since it is the first step of biomass conversion processes such as gasification, liquefaction, carbonization and combustion [2].

Lignocellulosic biomass comprises three main components: cellulose, hemicellulose and lignin, as it has been pointed out in section *1.1.1. Lignocellulosic biomass.* Previous studies indicated that it is important to distinguish the behaviour of the three components for a better understanding of the biomass pyrolysis process. At low heating rates (<100 K/min), biomass materials decompose in well-described stages of moisture evolution, hemicellulose decomposition and cellulose decomposition, while lignin is decomposed very slowly and at minor level [3]. Moreover, it has been observed that there is no significant interaction among the three components in biomass pyrolysis [4].

Flexibility in the supply of biomass to the energy conversion facility, in terms of seasonal availability, is considered as one of the keys to guarantee their continuous operation and the yield investments [5]. Therefore, it is important to find a reliable kinetic model based on simply technical data analysis for different biomass feedstock. Moreover, this model can help optimize pyrolysis performance of the different biomass components (cellulose, hemicellulose and lignin), which can play an important role not only to scale up this process, but also in future integrated biomass systems such as biorefineries.

There are numerous works devoted to study the kinetics of different biomass pyrolysis as one-component mechanisms of primary pyrolysis but a more general approach to allow co-pyrolysis of biomass is to study the effect of the three different components in the biomass pyrolysis kinetics [1,6]. In this way, numerous works have also been devoted to use mechanisms comprised of several reactions, generally three reactions coinciding with hemicellulose, cellulose and lignin. These mechanisms are usually parallel reactions, although consecutive reactions can also be applied [7] due to significant reaction time overlap, all of them acting as if there were no interactions.

Therefore, Distributed Activation Energy Models (DAEM) are proposed as models for biomass pyrolysis strarting from treatments already used for coal. In Chapter I the basis of this model is addressed. This approach avoids the low values of activation energies which result when a single-step reaction is applied to fit a temperature dependence that arises from the occurrence of different temperature intervals [8]. Several approaches have been used, all combining the activity of both primary and secondary reactions in the estimated parameters using specific mathematical forms to describe the frequency factors and activation energies distributions like Gaussian, Weibull and Gamma distributions [9]. For instance, M. Becidan et al. [10] used a simple DAEM with the distribution of activation energy approached by a Gaussian distribution to describe the pyrolysis behaviour of wastes from breweries, industrial coffee roasting and fibreboard furniture.

The distribution can also be a finite discrete distribution of arbitrary form. The key to the widespread usage of this last routine is its flexibility to fit almost any reactivity distribution. Miura and Maki [11-13] also developed a model to obtain the distribution curve of activation energies and activation energy dependent frequency factors from three sets of data obtained under different heating profiles and applied it to 19 different coals in order to study the influence of coal rank on the model parameters. This model was applied by other authors in order to analyse kinetics pyrolysis of coal [14] and biomass samples like rice, rice straw and corncob [2] or sawdust and biomass constituents [2,15]. With a different approach of the model J. Cai et al. [16,17] used the DAEM describing the global reaction following a distribution of reactions of n^{th}-order. Finally, Burnham et al. [18] used an efficient nested nonlinear-constrained linear regression routine to develop a model based in only two sets of data at different heating rates.

This work aims to find the characteristics of wood pyrolysis process from four different samples in order to obtain operative parameters to further perform biomass pyrolysis in an auger reactor pilot plant. Their components hemicellulose, cellulose, and lignin are also studied. These parameters will be used to calculate wood behaviour at real conditions as single feedstock and from its contituents as a generic feedstock in plants for energy production.

6.2. Experimental for the DAEM application to biomass devolatilisation

Four wood samples used in the experiments were from different biomass species and correspond to the biomass characterised in section *2.2.1. Materials*. In addition, samples of lignin, cellulose and xylose as hemicellulose model compound were used, which are also characterised in the abovementioned section.

The samples were pyrolysed in a thermobalance SETARAM Setsys Evolution (see section *2.2.3. Analytical techniques*). The sample was placed in a platinum basket forming a small fixed bed with initial mass of 6 mg approximately for biomass, lignin, cellulose and hemicellulose. The particle size of the samples was in all cases lower than 0.250 mm. Sets of experiments at different heating rates of 5, 10 and 20 K/min were performed with every sample.

6.3. Results and discussion for the DAEM application to biomass devolatilisation

The following section provides the results of the application of the DAEM to biomass devolatilisation. First, experimental results from pyrolysis of all the samples studied are presented. Second, the DAEM is applied in order to compare the theoretical results with the experimental results. Third, the model is adapted to predict devolatilisation of wood from its constituents. Finally, the model is compared with different biomass samples, applying different heating rates and in different equipments to verify its applicability.

6.3.1. Sample pyrolysis comparison

Wood is mainly comprised of cellulose, hemicellulose and lignin, as it has been mentioned before. Cellulose is only composed of anhydrous glucose. Hemicellulose is a bunch of xylose, mannose, galactose, rhamnose and arabinose ordered by the usual percentage present in biomass. While Cellulose and hemicellulose are composed of sugar monomers, lignin from biomass is composed of three different monolignol monomers methoxylated to different degrees. Figure 29 shows the behaviour under pyrolysis conditions of 4 different wood samples and their main constituents (cellulose, lignin and xylose as hemicellulose). The results obtained at three different heating rates 5, 10 and 20 K/min are also compiled. It is observed that cellulose, lignin and hemicellulose present a different behaviour. Cellulose starts to decompose at higher temperatures, around 600 K, with a very steep decrease of fraction of mass remaining to a high extent of around 4 %. Lignin and hemicellulose start to decompose at the same temperature, around 450 K, but with a different behaviour, while lignin decomposes slowly mainly in a range between 450 to 700 K and to a high final weight (aprox. 40 %), hemicellulose decomposes only in 150 degrees, until 600 K to a final weight of approximately 20 % of the initial weight. The different behaviour of lignin could be due to a more heterogeneous composition than the one of cellulose or hemicellulose that are composed by anhydrous glucose and xylose respectively.

Regarding to the four biomass samples, all of them show a very similar behaviour in pyrolysis. It is observed that for the different heating rates, the fraction of mass remaining of all samples is very close. Wood decomposition takes place between 450 K and 650 K with a slight shift to higher temperatures with higher heating rates. All samples also reach a similar final weight between 15 % and 18 % of the initial one. They produce three steps, initially wood decomposition takes place like the one of lignin, at 550 K shows a steep decrease like hemicellulose and, at 600 K there is a second decrease like in the case of cellulose. Comparing the results of wood pyrolysis with pyrolysis of their constituents, biomass pyrolysis starts with lignin pyrolysis, secondly wood reaches temperature for hemicellulose to pyrolyse and lately it is the cellulose the one decomposing with a fast decrease of mass remaining. Finally, the remaining part of the lignin present in wood, which was reacting throughout the devolatilisation process, undergoes its pyrolysis.

6.3.2. DAEM application

Usually, mathematical models to describe overall decomposition of complex solids consider independent parallel reactions. Wood is a complex solid with a large volatile content which is mainly released during first steps of pyrolysis, flash pyrolysis, carbonisation or gasification. Products of these processes are obtained in three fractions, char, biooil and gas which proportions depend on the process conditions. Parameters like temperature or residence time influence the products through the kinetics of the reaction, therefore a thorough knowledge of the kinetics is a key factor to predict product fractions. To study this complex process on wood, the distributed activation energy model (DAEM) has been applied to the experimental results found in the TGA. This model assumes that a complex fuel as wood is a mixture of components, each of which decomposes following a first-order reaction. The complex composition produces a wide variety of chemical groups and a continuous distribution of reactions during pyrolysis with characteristic activation energy [19].

There are several approximations to the DAEM for pyrolysis of coal [20]. In this work the algorithm recently developed by Scott et al. [19] has been implemented in a Fortran subroutine to solve this model with equations described elsewhere [21] adapted to take into account the inert part of the samples. This algorithm was developed to solve the problem of determining the kinetics of reactions for a material decomposing subject to many, parallel first-order reactions described by the following equation:

$$\frac{M(t)}{M} = w + \sum_i f_{i,0} \exp\left[-A_i \int_0^t \exp\left(\frac{-E_i}{RT(t)} \right) dt \right] \qquad \text{(Eq. 23)}$$

where $M(t)$ is the mass of the sample, which contains a fraction w of inert material; M_0 is the initial value of M; $f_{i,0}$ is the fraction of M_0 which decomposes with an activation energy E_i and a pre-exponential factor A_i. Using experimentally measurements $M(t)$ at two different heating rates, the problem is to find $f_{i,0}$, A_i and E_i. This algorithm was applied to the results of thermogravimetric experiments of the pyrolysis of the four different kinds of wood, cellulose, lignin and hemicellulose. To introduce the thermogravimetric experiments data into the model, equation 24 was used, where X is the fraction of mass remaining; M_0 is the initial sample weight and $M(t)$ is the sample weight at any time:

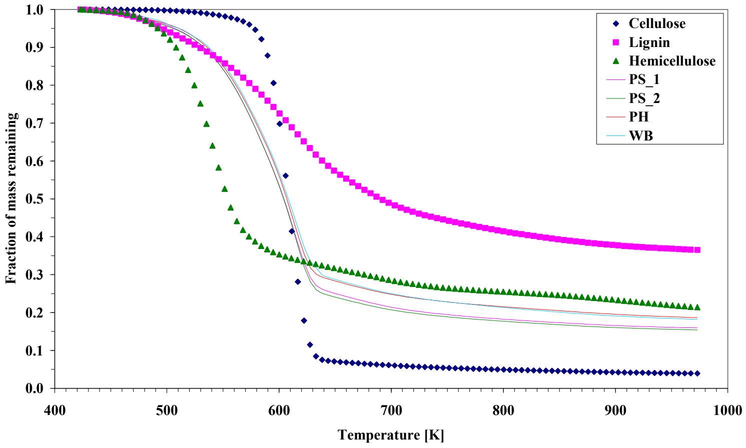
$$X = \frac{M(t)}{M_0} \qquad \text{(Eq. 24)}$$

Two experimental sets of data obtained at low heating rates (5 and 10 K/min) were used to calculate the distribution of activation energies and pre-exponential factors for every material. Subsequently three theoretical curves were generated at 5, 10 and 20 K/min and compared with experimental data in order to produce a robust test of how well the kinetics extracted by the algorithm reproduces the original data and extrapolate to different heating rates. For this last purpose, one more theoretical curve was produced for a heating rate of 10000 K/min close to the conditions of flash pyrolysis processes. This application has been previously tested [19] theoretically with model curves generated at different heating rates, 20, 40 and 10000 K/min and different number of parallel reactions. In this study the inversion algorithm evaluated E_i and A_i at 100 equally spaced intervals of conversion, corresponding to an unreacted fraction in the range 0.99 - 0.01.

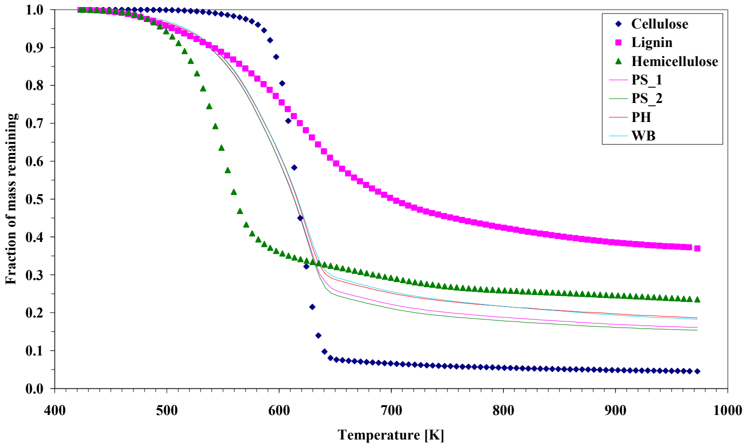
Results of evolution of the remaining mass fraction and rate of mass loss versus temperature for seven samples are compiled in Figure 30 and Figure 31. For all samples, experimental and calculated results generated by the program are compared. It is observed that the experiments performed at heating rates of 5 and 10 K/min were successfully fitted by the model.

Regarding to the evolution of the fraction of mass loss with temperature and heating rate, the model is able to describe properly the experimental data and, therefore, the shift in the rate of mass loss to higher temperatures as well as the general increase of rate of mass loss with the heating rate shown in the experiments. This behaviour can be explained on the basis of heat transfer and medium diffusion. The perfect fit of the pyrolysis path is not only carried out depending on the temperature, but the model also produces a perfect fit with the inert fraction of mass remaining for all the samples, for homogeneous constituents cellulose, lignin and hemicellulose and for heterogeneous wood samples in less than 5 % error.

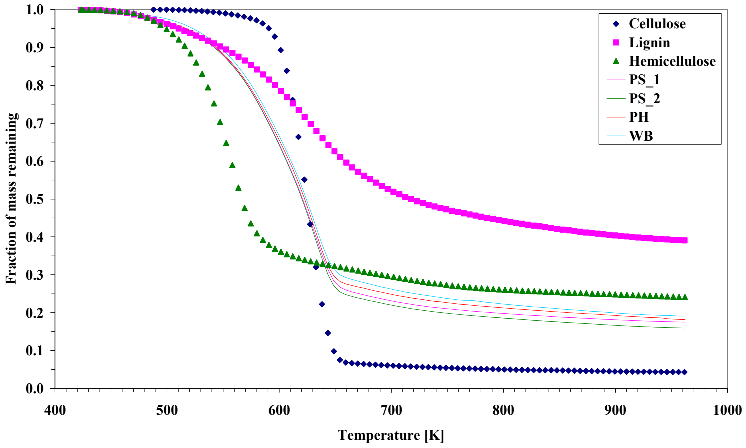
In the case of cellulose, when comparing experimental and predicted data there is a loss of accuracy for conversion higher than 0.96. This fact can be due to the sharp change in the slope of the curve for conversions above 0.96, that is, for small conversions the reaction turns from a very slow reaction into a very fast one. However, in spite of this inaccuracy, the fitting achieved by the model, not only for data obtained at 5 K/min and 10 K/min, but also for data obtained at 20 K/min is extremely good from this point to the end of the devolatilisation (see Figure 30). Generally speaking, the model gives a very good approximation of the temperature range where the reaction will take place at the high heating rates of gasification, combustion or flash pyrolysis processes.



5 K/min



10 K/min



20 K/min

Figure 29. Fraction of mass remaining vs. temperature for three different heating rates. Samples: PS_1 is Pinus sylvestris 1, PS_2 is Pinus sylvestris 2, PH is Pinus halepensis and WB is Woods blend.

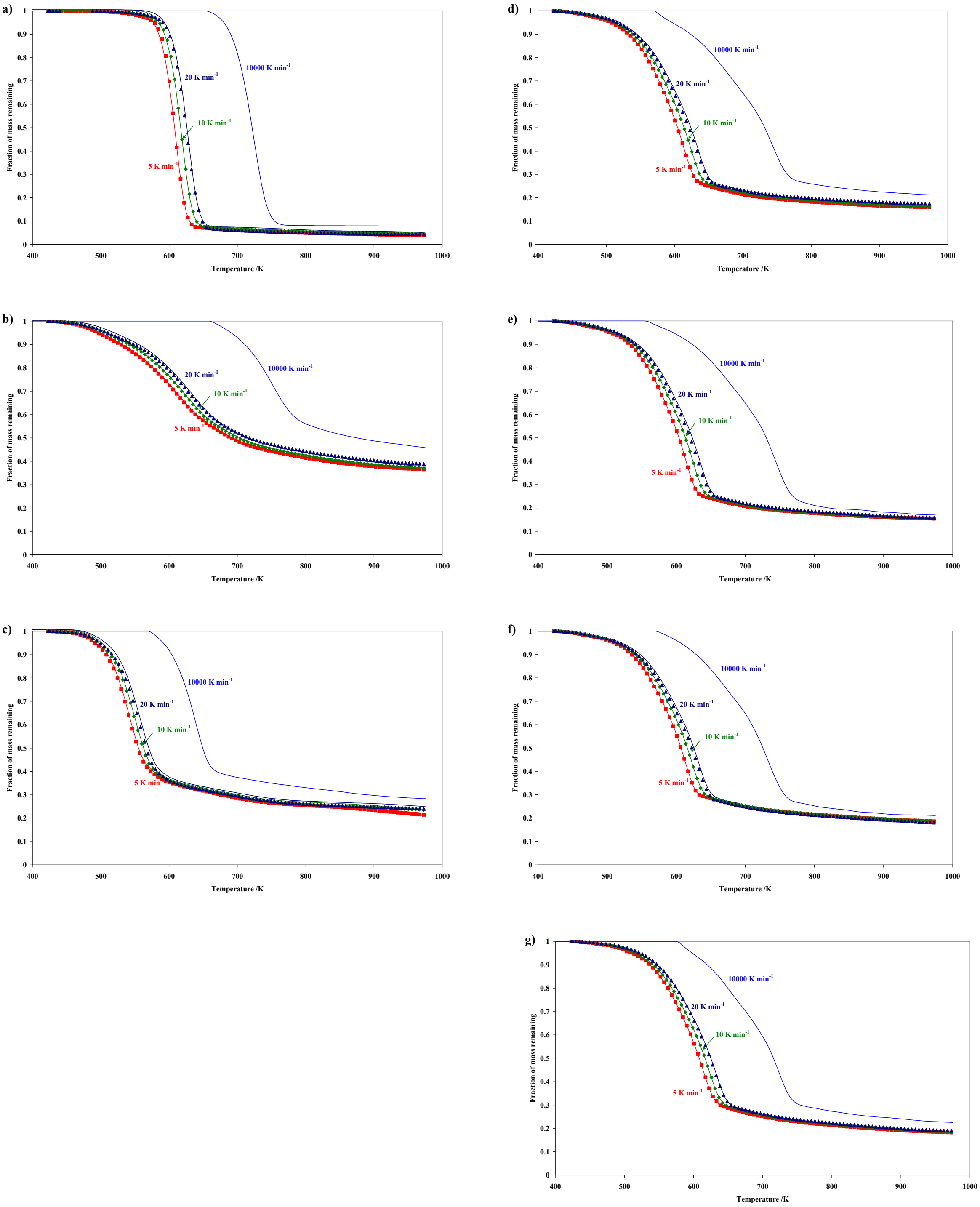


Figure 30. Fraction of mass remaining vs. temperature. Comparison of experimental data (points) and curves (thick lines) generated using parameters recovered by the algorithm using kinetic parameters deduced from experimental results at 5 and 10 K/min. Samples are a) Cellulose, b) Lignin, c) Hemicellulose, d) Pinus sylvestris 1, e) Pinus silvestris 2, f) Pinus halepensis and g) Woods Blend.

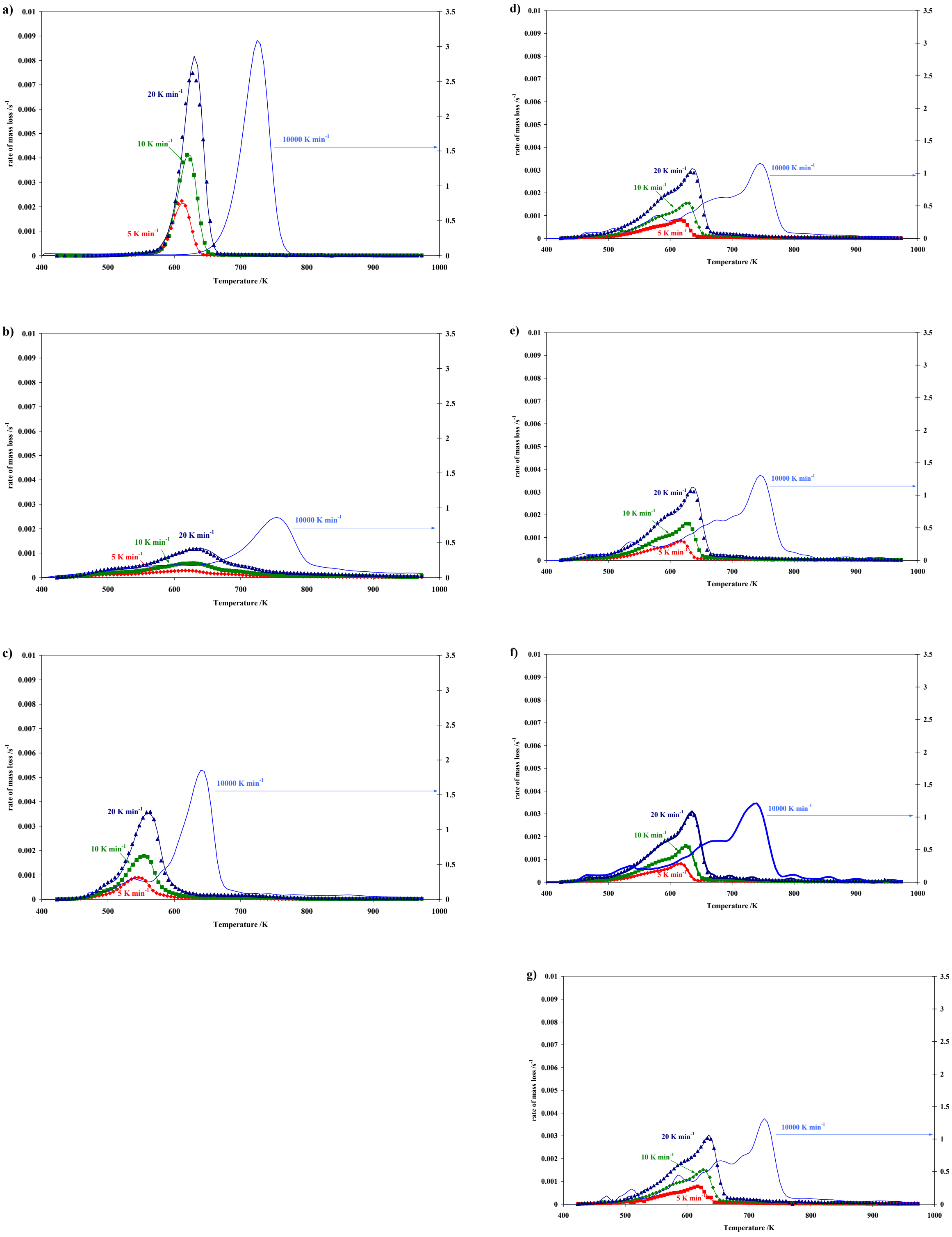


Figure 31. Rate of mass loss vs. temperature. Comparison of experimental data (points) and curves (thick lines) generated using the parameters recovered by the algorithm using kinetic parameters deduced from the experimental results at 5 and 10 K/min. Samples are a) Cellulose, b) Lignin, c) Hemicellulose, d) Pinus sylvestris 1, e) Pinus sylvestris 2, f) Pinus halepensis and g) Woods Blend.

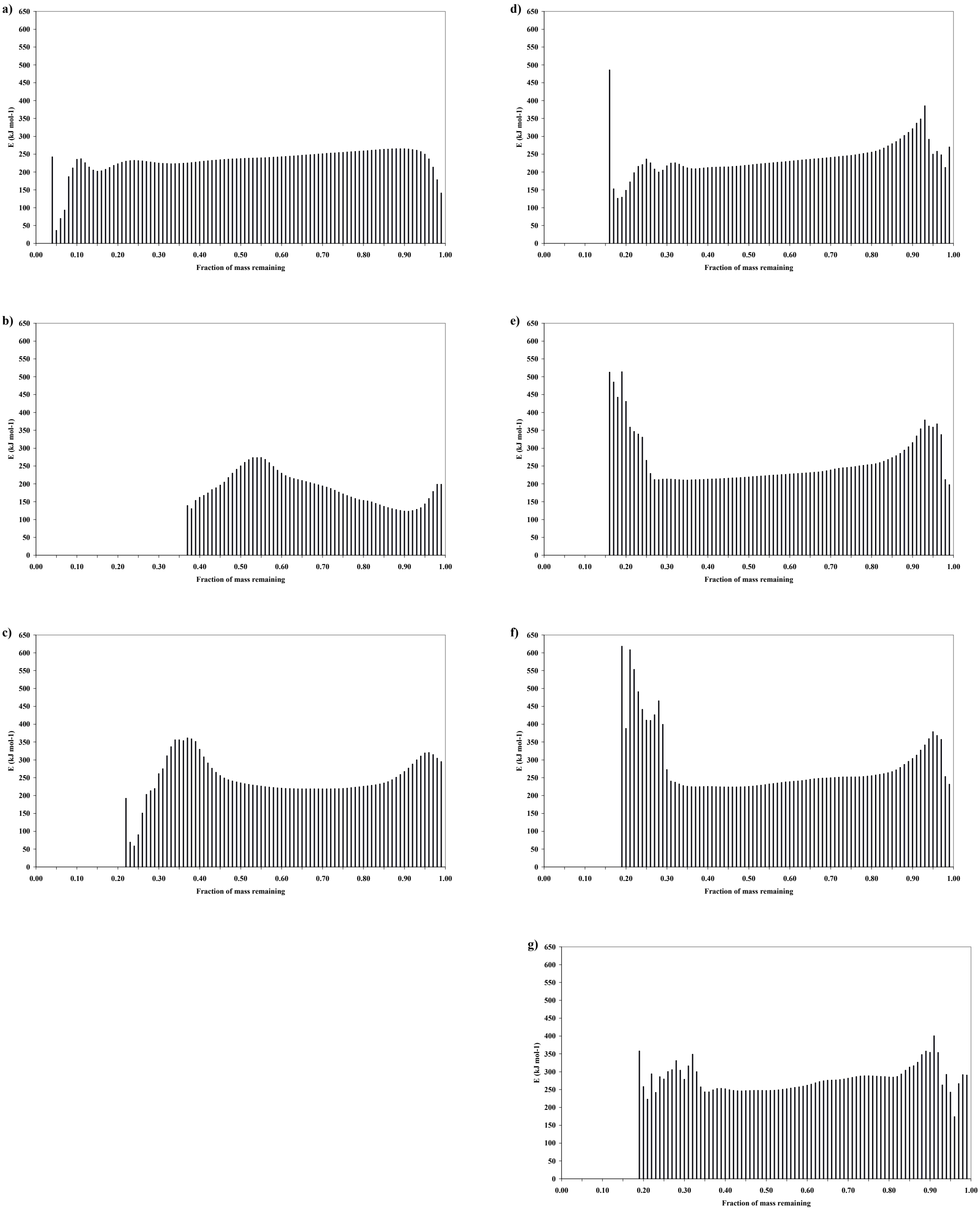


Figure 32. Activation energy vs. fraction of mass remaining calculated from the experimental results at 5 and 10 K/min. Samples are a) Cellulose, b) Lignin, c) Hemicellulose, d) Pinus sylvestris 1, e) Pinus sylvestris 2, f) Pinus halepensis and g) Woods Blend.

In Figure 31 the results obtained by the model for rate of mass loss versus temperature compared to experimental results are compiled. The axes are kept constant to facilitate the comparison. In the seven cases studied the model not only fits perfectly the data used at 5 and 10 K/min in both rate change with temperature and location of maximum devolatilisation rate with temperature, but also predicts the pyrolysis behaviour of samples when the heating rate is increased up to 20 K/min. Comparing the different samples, the model is able to deal with a wide range of reaction rate values, from the one of cellulose with a maximum of 0.004 s^{-1} to the maximum of lignin 0.0006 s^{-1} (heating rate 10 K/min), one order of magnitude lower. In addition, the model also placed correctly the peaks of reaction rate no matter the temperature. For example, hemicellulose has the maximum placed at 555 K and lignin at 625 K almost 100 degrees difference.

The most relevant point of the DAEM is the capacity of analysing the devolatilisation process in a distribution of reactions with characteristic activation energies and pre-exponential factors described by Equation 23. In Figure 32 the distributions of activation energies for seven samples are shown related to the fraction of sample remaining. Regarding to the distribution of activation energies, different trends can be observed depending on the sample. Components: for cellulose the most part of the reactions are favoured the same with a mean activation energy of 250 kJ/mol; for lignin there are two maxima of activation energy at the very beginning of the reaction (198 kJ/mol) and at 0.55 fraction of mass remaining (273 kJ/mol); hemicellulose has a similar behaviour with two maxima at the beginning (320 kJ/mol) and at 0.35 fraction of mass remaining (361 kJ/mol). Depending on the values of activation energies, apart from the maximum, lignin has the lowest values followed by cellulose and finally hemicellulose. Therefore, reactions of lignin will be more favoured than cellulose and than hemicellulose. Regarding to the wood samples, they also have two maxima, the first one at the beginning of the pyrolysis and the second one around the end of the reaction. According to the distributions of pre-exponential factors, the results obtained are in the same range of the results obtained previously by Scott et al. [21] for dried sewage sludge. Like in that case, the distribution of pre-exponential factors of each sample has a closely related behaviour to its distribution of activation energies; therefore, the comparison of samples follow the same pattern for that parameter and this discussion has been omitted.

Comparing the fraction of mass allocated for every reaction ($f_{i,0}$ in Equation 23) for the seven samples (Figure 33), one interesting point is that cellulose pyrolysis is described in more than a 75 % by only two reactions placed around 0.45 of fraction of mass remaining. This fact explains the steep decrease of fraction of mass remaining around 615 K (figure 2.a, heating rate 5 K/min). Other samples, lignin, hemicellulose and the wood samples, have an important fraction of mass allocated in the last fraction of mass related to the fraction of inert mass. Apart from that inert mass, while lignin has a homogeneous distribution of mass throughout the reactions defined, hemicellulose decomposes in an extent of 22 % by the reaction placed at 0.55 of fraction of mass remaining. The distribution of fraction of mass allocated for samples of wood is more focused in a couple of reactions placed at 0.4 in the case of *Pinus sylvestris* 1 and 2, at 0.42 for Pinus Halepensis and at 0.45 in the case of woods blend. These fractions of mass would be related to the influence of cellulose in the sample and the shift of the maxima to the hemicellulose influence.

Figure 34 compiles the description of the cumulative fraction of mass with activation energy. Regarding to the three main components of biomass, different behaviours can be observed again. For cellulose a steep increase is observed at 230 kJ/mol, lignin has a homogeneous distribution of activation energies depending on the mass fractions and hemicellulose shows again an increase, not as steep as in the case of cellulose, around activation energies of 220 to 230 kJ/mol. Studying the results obtained for wood samples, they have most of the mass allocated in reactions with activation energy around 225 kJ/mol (related to cellulose), from 0.4 for *Pinus sylvestris* 2 which would have a higher influence of cellulose, to 0.3 of wood blend, with a lower influence of cellulose.

To sum up, the model describes different properties of the devolatilisation of wood and its constituents that can be used to know the influence of these compounds in the final behaviour of the wood sample.

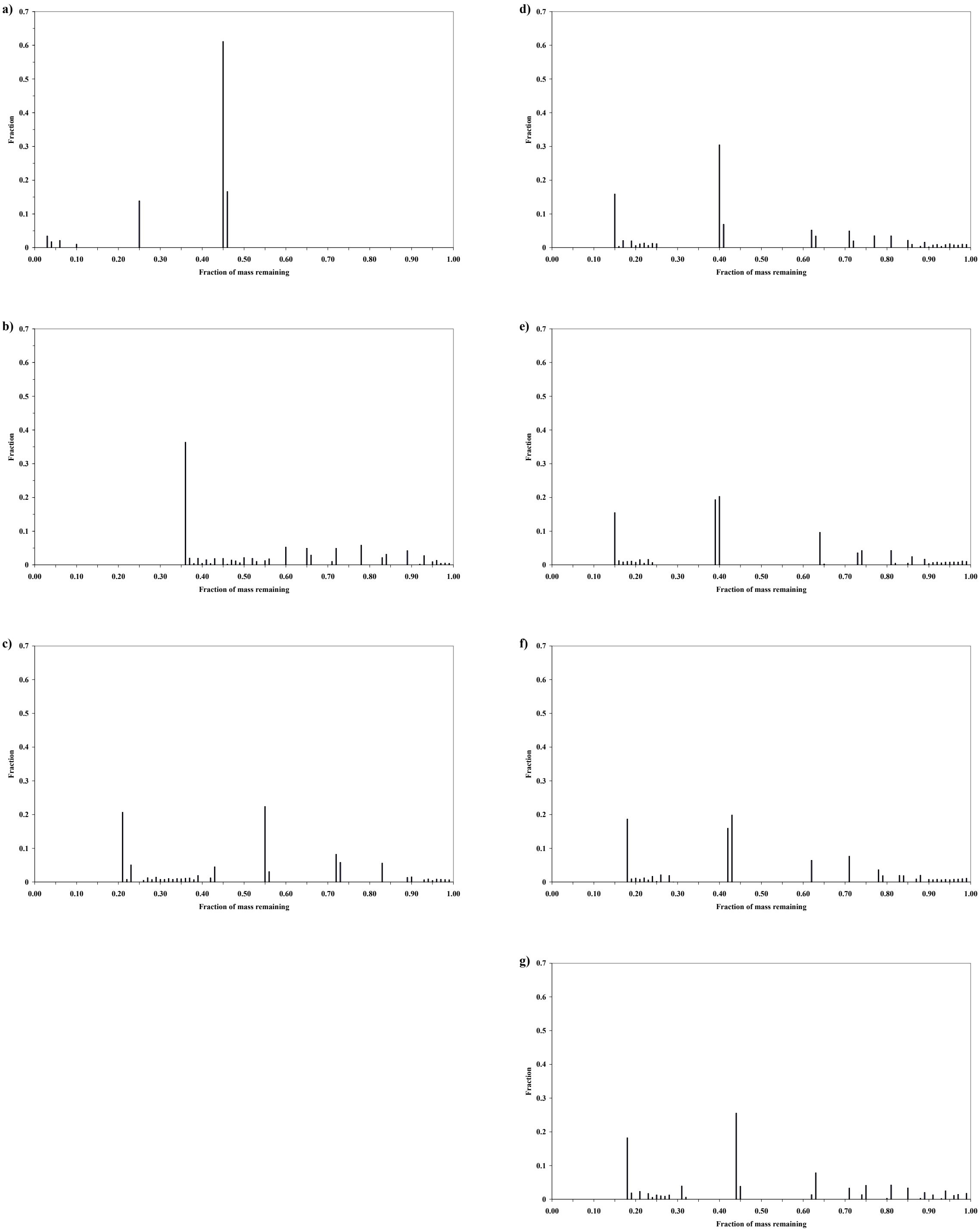


Figure 33. Fraction of sample vs. fraction of mass remaining calculated from the experimental results at 5 and 10 K/min. Samples are a) Cellulose, b) Lignin, c) Hemicellulose, d) Pinus sylvestris 1, e) Pinus sylvestris 2, f) Pinus halepensis and g) Woods Blend.

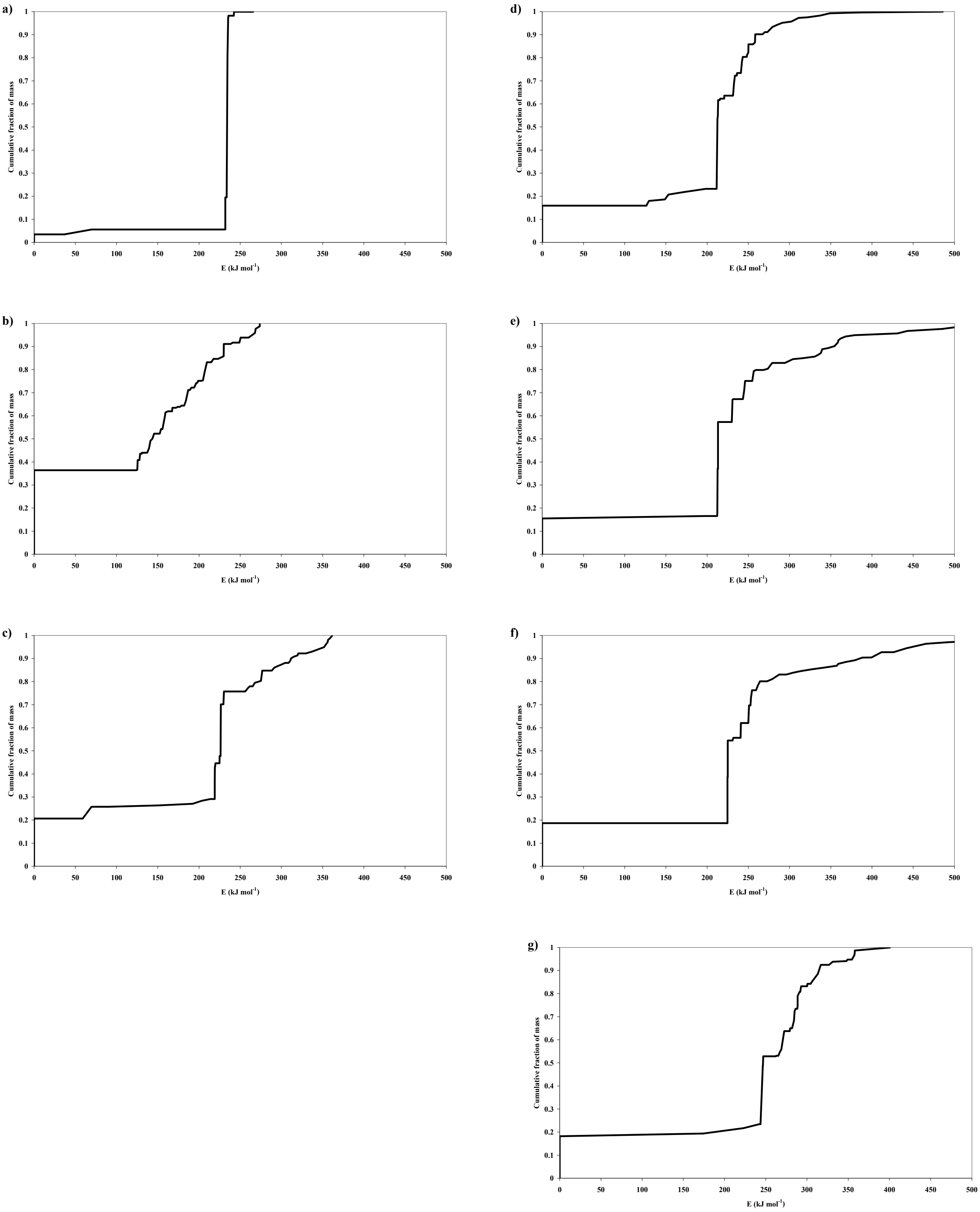


Figure 34. Cumulative fraction of mass vs. activation energy calculated from the experimental results at 5 and 10 K/min. Samples are a) Cellulose, b) Lignin, c) Hemicellulose, d) Pinus sylvestris 1, e) Pinus sylvestris 2, f) Pinus halepensis and g) Woods Blend.

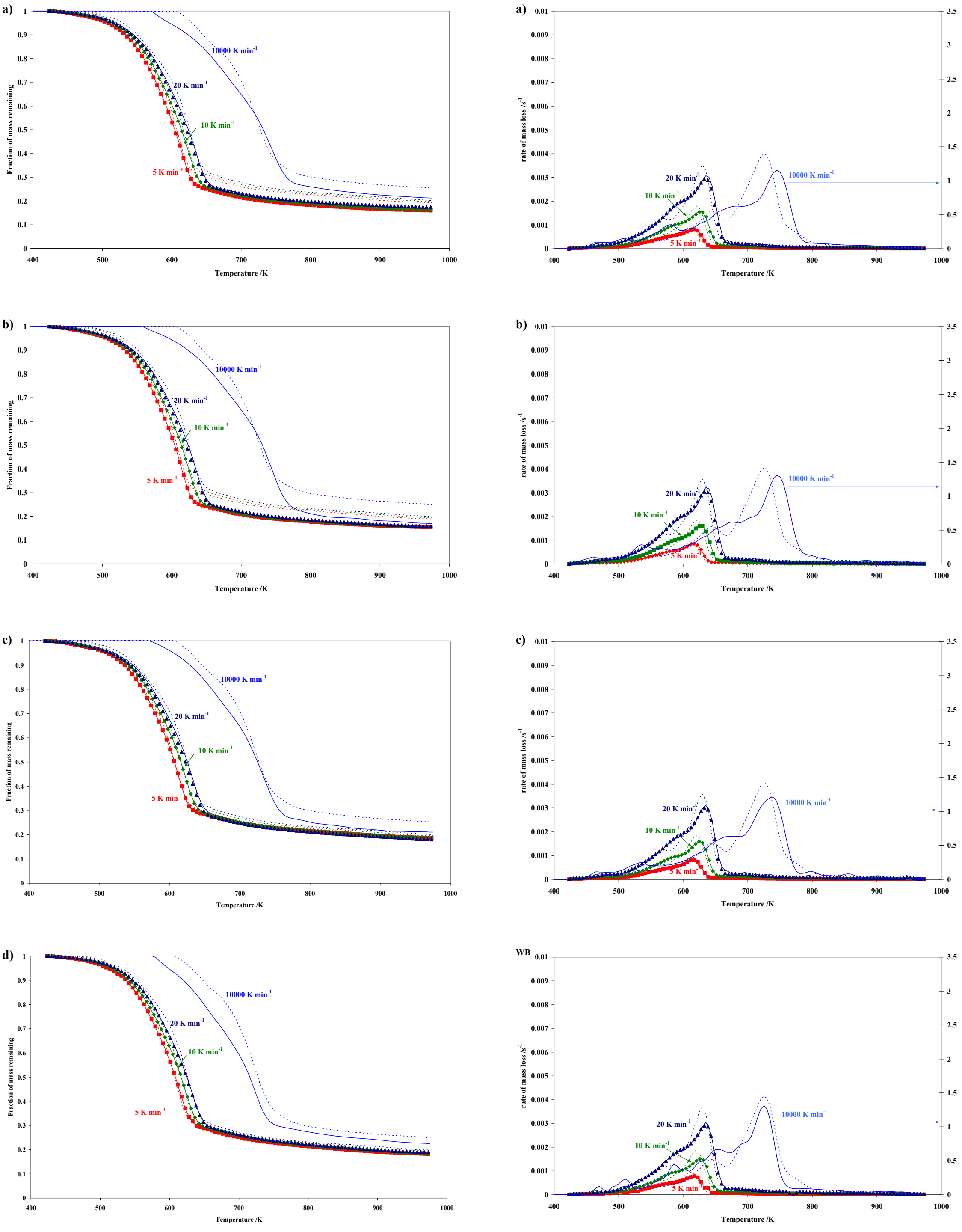


Figure 35. Comparison of the progression of experimental (points) fraction of mass remaining and rate of mass loss with curves calculated from data of the samples (thick lines) and from data of the constituents (dashed lines). Samples are a) Pinus sylvestris 1, b) Pinus sylvestris 2, c) Pinus halepensis and d) Woods Blend.

6.3.3. Model to predict biomass devolatilisation from its constituents

In order to put into production a process based on a biomass treatment, a wide range of biomass feedstock should be taken into account. This biomass would have in cellulose, lignin and hemicellulose its main components but in different proportions. To be able of predicting the behaviour of biomass from the behaviour of its main components will reduce to a minimum the needs of study of different samples and will increase process sustainability.

In this work, the equation proposed previously by this group [22] to deal with feed mixtures has been developed to take into account the inert part of the different components and increase the number of components in the blend.

$$\frac{M(t)}{M} = \sum_n CF_n \left(w_n + \sum_i f_{n,i,0} \exp\left[-A_{n,i} \int_0^t \exp\left(\frac{-E_{n,i}}{RT(t)} \right) dt \right] \right) \qquad \text{(Eq. 25)}$$

where CF_n are the fractions of n components of the feed. To use the model with biomass n will be 3 for cellulose, lignin and hemicellulose.

In Figure 35 there is a comparison of the experimental, fitted, and calculated data from constituents for the devolatilisation of four wood samples. The data calculated have been obtained using values of fractions of cellulose, lignin and hemicellulose provided by an external laboratory CIEMAT and normalised to 100. The analytical procedure for the determination of structural carbohydrates and lignin in biomass was carried out following the standards of the National Renewable Energy Laboratory (NREL). Therefore, carbohydrates were analysed by acid hydrolysis to determine the monomeric sugars in the solution, while lignin was determined as the insoluble solid after the acid attack. These values are compiled in Table 17.

Table 17. Relations of cellulose, lignin and hemicellulose in percentage.

Sample	Cellulose	Lignin	Hemicellulose
Pinus sylvestris 1	0.43	0.34	0.23
Pinus sylvestris 2	0.44	0.33	0.23
Pinus halepensis	0.44	0.34	0.22
Woods blend	0.45	0.34	0.21

In Figure 35 there is a very good fit between experiments and theoretically calculated data at three heating rates focused into two points: the relation of fraction of mass remaining with temperature and the prediction of the fraction of inert mass. These results allow thinking that the interactions between constituents during pyrolysis are very scarce [4], so an additive model as the one proposed is very useful to predict the behaviour of these samples from the composition analysis.

Regarding to the evolution of mass loss rate with temperature compared to the experimental results (see Figure 35), the model produces very good data. The results calculated by the model clearly distinguish the influence of cellulose and hemicellulose with a first knee at lower temperatures (related to hemicellulose) than the main peak (related to cellulose) in all cases. This fact could be explained by the weak interaction between constituents in the biomass samples described above. In spite of this weak interaction, the model predicts a reaction rate maximum 20 % higher than the experimental one. However, the error in the temperature prediction is lower than 1% which gives to this model a conservative characteristic. Therefore, this additive model of principal constituents is successfully describing wood pyrolysis both fraction of mass remaining and reaction rate versus temperature.

The predicted results for four wood samples (from its components assuming no interaction between them) has been analysed with the DAEM and the parameters obtained have been plotted in Figure 36 and Figure 37. From the comparison between these results and the results obtained from the DAEM applied to experimental results (Figures 30, 31, 32), the theoretical behaviour of the sample results in a homogenisation of the activation energies to lower values. Regarding to the fraction of mass allocated in the 100 different reactions studied, in addition to the fraction of inert mass (initial bar), the model distinguishes one main reaction for all the samples placed in a fraction slightly higher. Finally, the cumulative fraction of mass depending on activation energy is sharper and at lower activation energies in this theoretical case due to the more homogeneous activation energies with lower values.

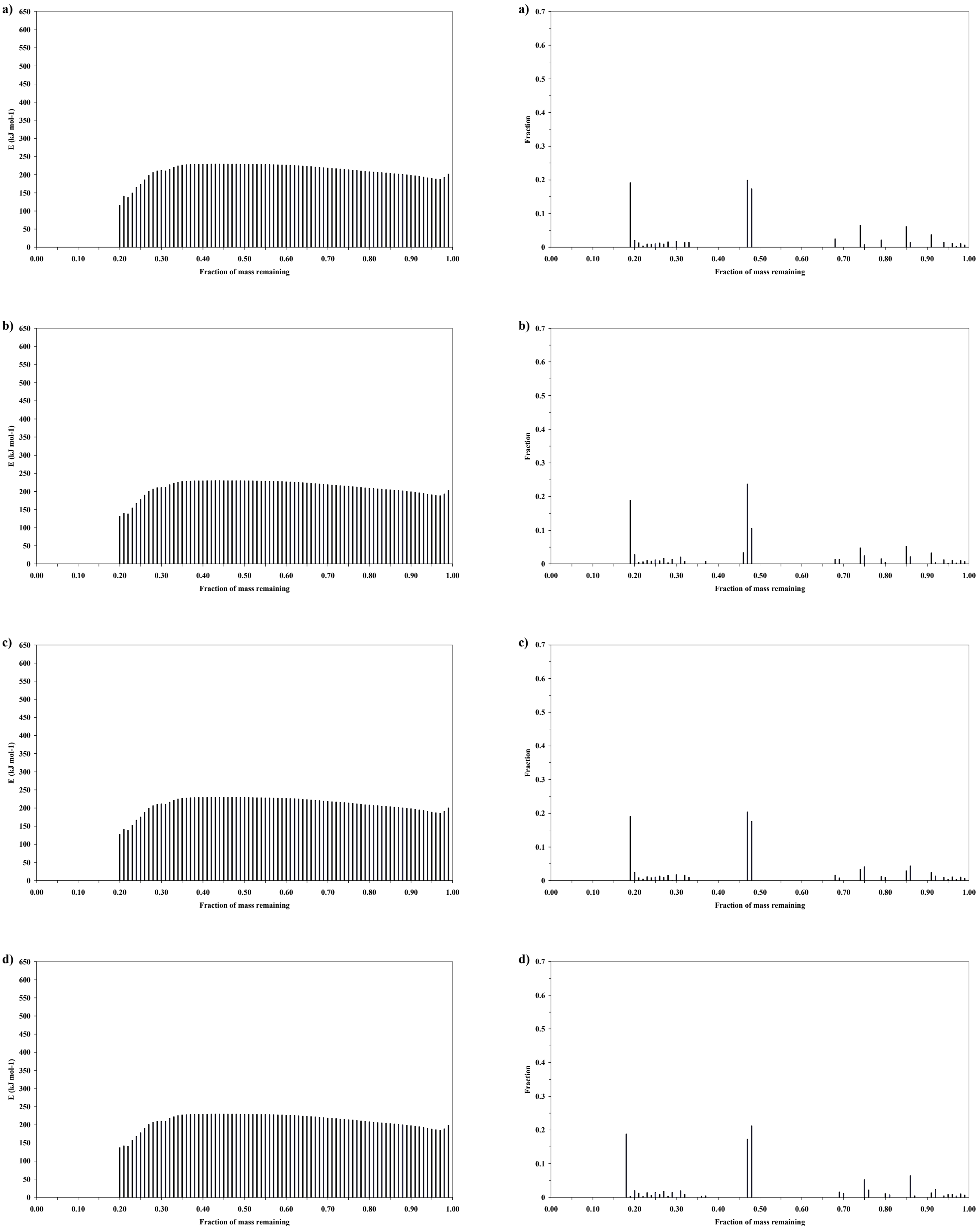


Figure 36. Activation energy and fraction of mass vs. fraction of mass remaining calculated from data of the constituents. Samples are a) Pinus sylvestris 1, b) Pinus sylvestris 2, c) Pinus halepensis and d) Woods Blend.

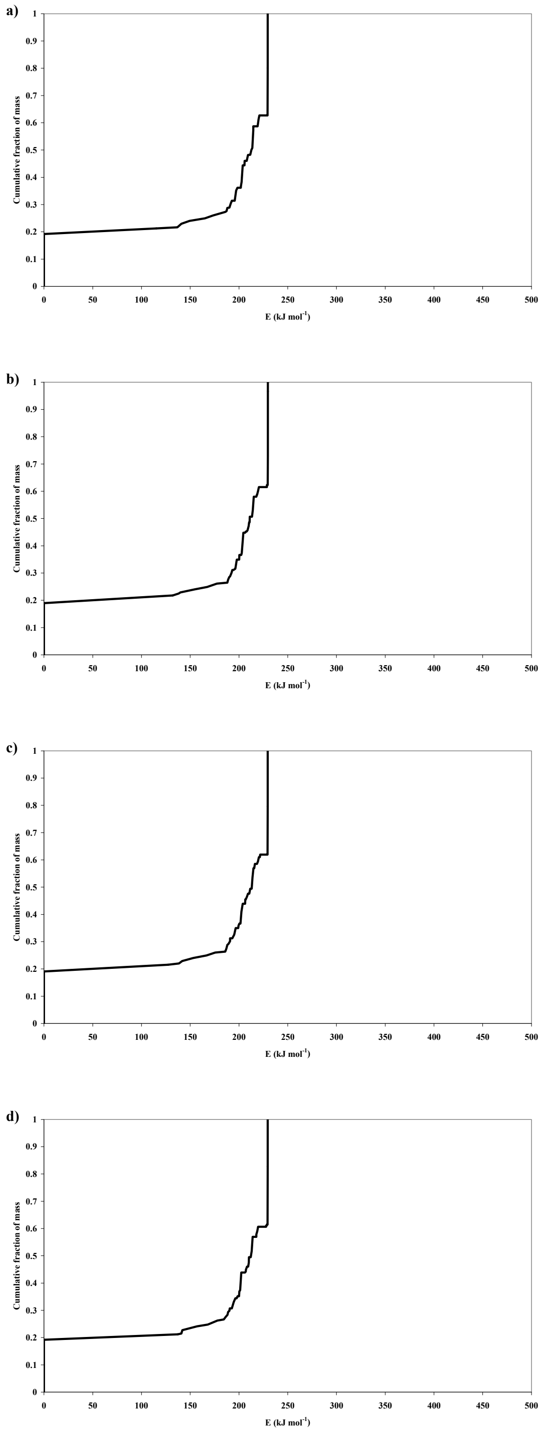


Figure 37. Cumulative fraction of mass vs. activation energy calculated from data of the constituents. Samples are a) Pinus sylvestris 1, b) Pinus sylvestris 2, c) Pinus halepensis and d) Woods Blend.

6.3.4. Validation of the model with different conditions

In order to complete the viability of applying this model to biomass, there are some points to take into account, i) different kinds of biomass samples, ii) calculation of pyrolysis behaviour at different heating rates, iii) use of data obtained in different equipments. To fulfil these points we used data published by N. Worasuwannarak et al. [2,23] for rice straw, rice husk and corncob. In these studies they used data from other researchers to get the composition of these samples related to cellulose, lignin and hemicellulose collected in Table 18. Comparing Table 17 and Table 18 we can observe the different nature of the samples studied. Wood samples are much more lignocellulosic than rice straw which has an increase in hemicellulose or corncob with a lower content of lignin.

Table 18. Relations of cellulose, lignin and hemicellulose for rice straw, rice husk and corncob.

Sample	Cellulose	Lignin	Hemicellulose
Rice straw	0.36	0.25	0.39
Rice Husk	0.35	0.30	0.35
Corncob	0.52	0.16	0.32

In Figure 38 the fitting results for these three samples at heating rates, 2 K/min, 5 K/min and 10 K/min are shown. Conversion is calculated excluding the inert part of the samples hence the model will be checked in other input conditions, from 1 to 0 fraction of mass remaining. Regarding to the evolution of this fraction of mass depending on the temperature, for rice husk and corncob samples the difference between experimental and calculated data is lower than 2 % for the whole range of conversion studied. Only for rice straw at the very beginning and at the end of the pyrolysis (more than 0.75 and less than 0.1 of fraction of mass remaining) the difference between experimental and calculated data is higher than this value of 2 % but lower than 10 %. It is worthy pointing out the fact that for all samples the model is able to keep the relation between data at 2, 5 and 10 K/min. In this case the data predicted are at a heating rate of 2 K/min compared to the 20 K/min used for wood samples. According to the evolution of rate of mass loss with temperature, the number of experimental points is scarce in this study but it still shows the first knee related to hemicellulose content and the maximum related to cellulose. For the calculated data, the model clearly distinguishes these two points and places them in the range of temperatures limited by the experimental data. The values of the maxima are lower than the experimental ones but, the lack of points could amplify mathematically this effect.

The DAEM study of the properties activation energy, fraction of mass allocated and cumulative fraction of mass (Figure 39 and Figure 40), show on one hand an increase in the values of activation energy at the beginning of the reaction to keep an almost constant value of around 220 kJ/mol. On the other hand there is only one main fraction of mass allocated close to 0.40 of fraction of mass remaining related to cellulose like in the case of wood samples. Finally, the previous properties are reflected in a distribution of cumulative fraction of mass centred in activation energy of 220 kJ/mol.

Data for pyrolysis of three biomass samples from literature have also been studied with DAEM. From the comparison of the results, it can be concluded that the model can perfectly explain biomass behaviour in pyrolysis from the behaviour of its components cellulose, lignin and hemicellulose. It can also be concluded that a slight interaction exists between constituents that not allow differentiate the influence of constituents as clear as for an additive behaviour. However, the model places a higher maximum for reaction rate in a very close temperature to the experimental one, so this model based on the three main constituents of biomass produces a conservative approximation to the biomass samples pyrolysis.

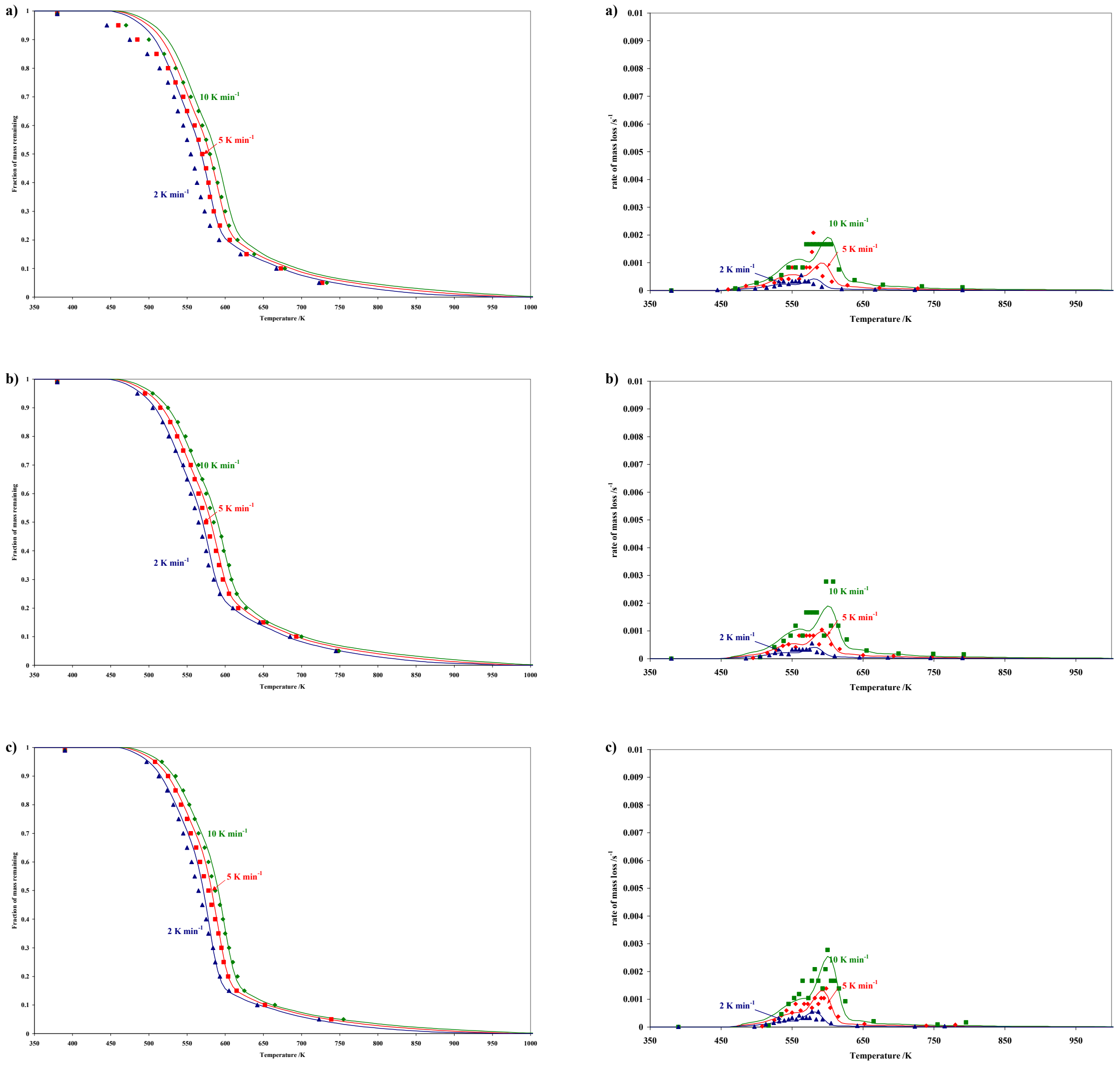


Figure 38. Comparison of the progression of experimental (points) fraction of mass remaining and rate of mass loss from literature with curves calculated from data of constituents (dashed lines). Samples are a) rice straw, b) rice husk, c) corncob.

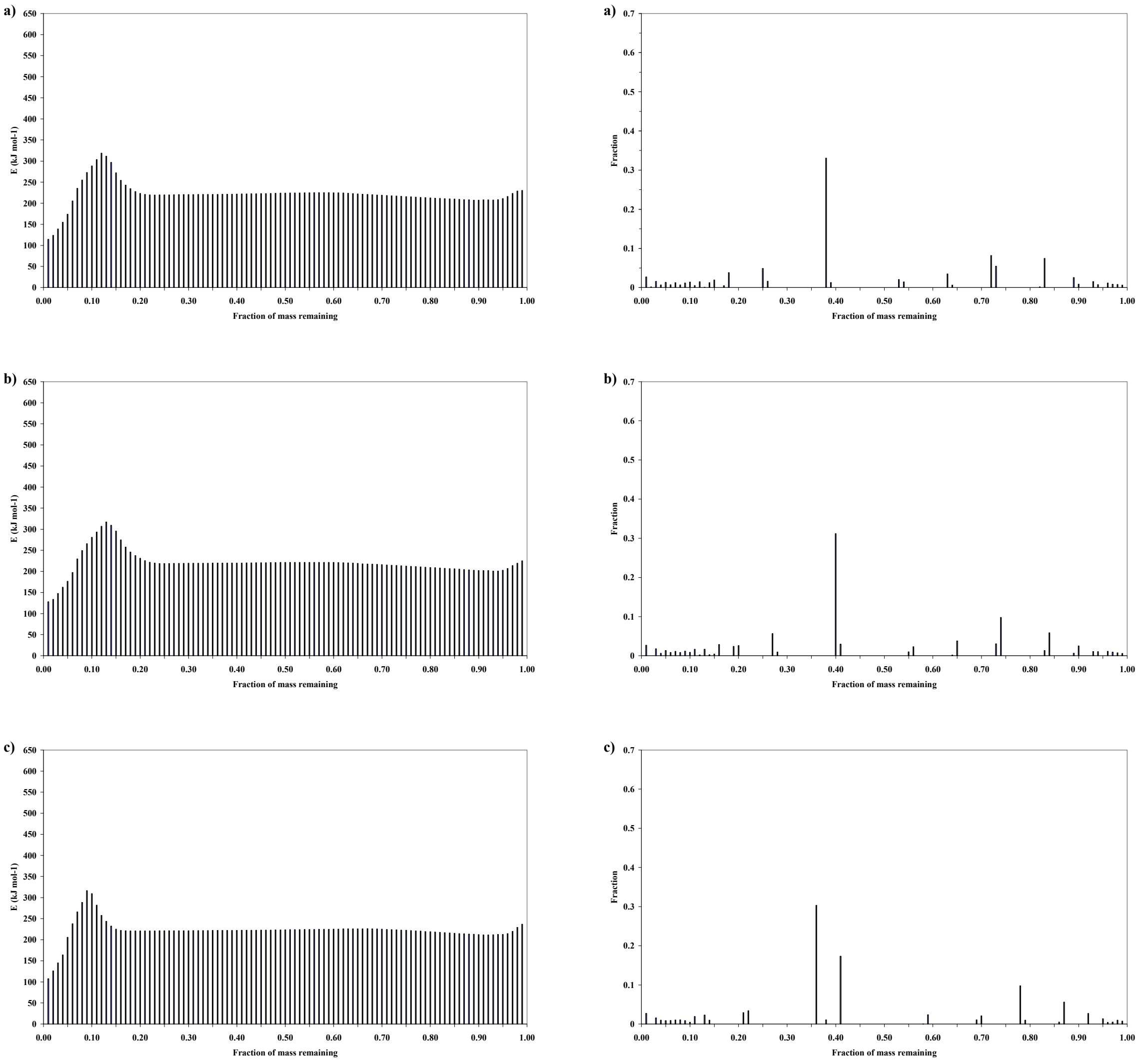


Figure 39. Activation energy and fraction of mass vs. fraction of mass remaining calculated from data of the constituents. Samples are a) rice straw, b) rice husk, c) corncob.

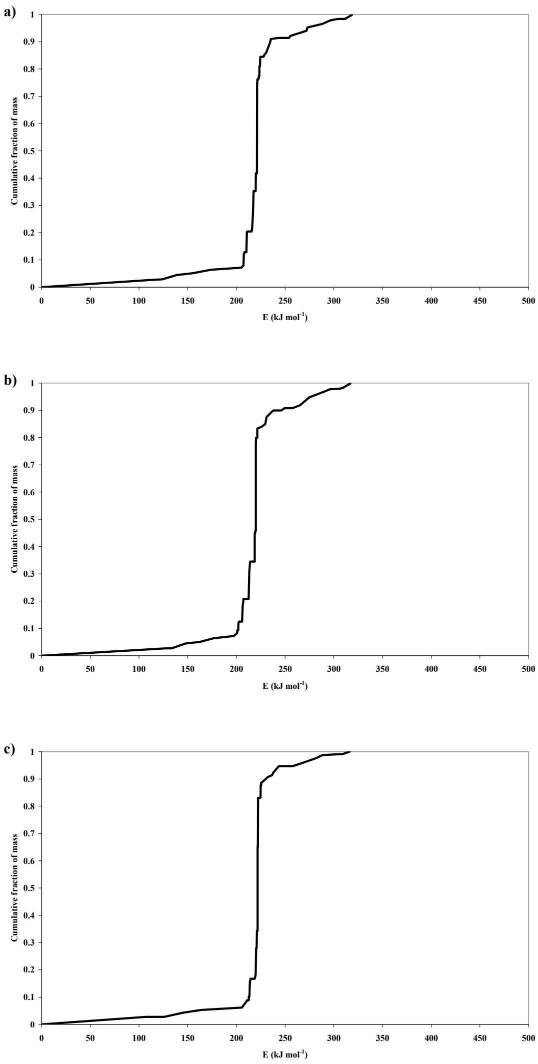


Figure 40. Cumulative fraction of mass vs. activation energy calculated from data of the constituents. Samples are a) rice straw, b) rice husk, c) corncob.

6.4. Conclusions for the DAEM application to biomass devolatilisation

An algorithm of DAEM developed by Scott et al. [19] has been applied to study biomass devolatilisation. By fitting two sets of data obtained in TGA with different heating rates the main parameters are calculated and will be used to calculate a new set of data in a different heating rate.

The good comparison of experimental and calculated data allows the use of this model to generate also good approximations of the temperature ranges where the reaction will take place at the high heating rates of flash pyrolysis, gasification or combustion processes. The model describes as well the influence of the activation energies and fraction of mass allocated to every reaction.

In addition, the model implemented previously by Navarro et al. [22] to predict the behaviour of coal and petcoke blends, has been developed to include the influence of the inert part of solids and work with wood samples and their three main constituents cellulose, lignin and hemicellulose. As a result of the comparison of predictions and experimental data, the DAEM can be used to produce a very good approximation to the wood sample pyrolysis from its main constituents with a good prediction both in fraction of mass and reaction rate variation with temperature.

Finally, the model has been tested against data from literature for rice straw, rice husk and corncob in order to check its applicability to different kind of biomass, heating rates, conditions of input data and different equipment. In order to put into production a process based on a biomass treatment, a wide range of biomass origins should be taken into account. To be able of predicting the behaviour of biomass from the behaviour of its main components will reduce to a minimum the needs of study of different samples and will increase process sustainability. In this sense, further experiments in pilot plant will be restricted to the results obtained from the model, as the following chapter will show. As introduced before, this model will help optimizing pyrolysis performance of the different biomass components (cellulose, hemicellulose and lignin) and can be used as a tool to control working conditions in future integrated biomass systems. From the very good results obtained both for fraction of mass remaining and rate of mass loss, the model has been proved to be a very good choice in order to study flexibility of biomass feed to operational systems. This is the previous step to perform biomass pyrolysis in an auger reactor, which is described in the following section.

7. Biomass pyrolysis in an auger reactor: influence of operational variables and properties of the products; energy, mass and economic balances of a scaled-up pilot plant

Pyrolysis of forest biomass has been carried out in an auger reactor in order to study the influence of operational variables on the reactor performance and the properties of the related products, which is explained in the following section. Moreover, simulation processes to assess the mass and energy balances of the pyrolysis process, as well as a cost-benefit analysis of a scaled-up plant are presented.

7.1. Introduction to biomass pyrolysis in an auger reactor

Research on biomass pyrolysis has gained relevance over the past years since it can be the opportunity of obtaining fuel from a renewable source. As stated in Chapter I, numerous pyrolysis processes have been studied with the aim of obtaining bio-oil for later upgrading it and producing improved marketable products [24,25] to achieve a progressive replacement of fossil fuels in the transition towards a sustainable energy future [26]. Biomass pyrolysis processes have been widely studied [25] and large-scale commercial processes have been developed during the last years, which are mainly based on bubbling and circulating fluidised bed reactors [24,27].

Moreover, in recent years interest has increased with the possibility of performing pyrolysis processes in remote locations as an alternative way to reduce the high transport costs of biomass. In fact, transport costs from forest were one of the main concerns from the IA-focus groups analysed in Chapter II. Therefore, this represents a major opportunity to process diverse biomass feedstock from forests or agricultural land, due to its dispersion and its seasonal production. In such a context, pyrolysis is an alternative to direct combustion of biomass due to the recovery of solid and liquid material, which is beneficial when biomass resources are remote from where the energy is required since the liquid can be readily stored and transported [24]. It is also clear that liquid products offer significant advantages in storage and transport over gas and heat [24]. In 2006 a preliminary assessment demonstrated the feasibility of modular and transportable bio-oil plants on auger reactors [28]. In 2007, Ingram and coworkers suggested that portable auger reactors might be used to produce bio-oil at locations in forests [29]. At TCBiomass2009, Briens and coworkers presented a mobile pyrolysis system for the conversion of biomass into bio-oil based on a fluidised bed reactor [30].

One of the major issues in mobile pyrolysis plants is not only achieving high bio-oil yields, but also producing a bio-oil that meets the standards to be processed in a future biorefinery [31,32]. In general, the liquid phase is a complex hydrocarbon mixture, highly oxygenated, which can be used as a fuel and as raw material to obtain chemicals. Bio-oils have been successfully tested in engines, turbines, and boilers, and have been upgraded to high-quality hydrocarbon fuels, although at a presently unacceptable energetic and financial cost [33]. In this sense, bio-oil characterisation is one of the most important steps to future upgrading and its properties depend on variables such as biomass feedstock or the conditions in which the pyrolysis process is carried out [34,35].

Auger reactors offer numerous advantages such as their compact design and the lower process temperature [25]. Several auger configurations have been studied in literature [25,29,36,37], although the influence of the operating conditions on the product yields and product composition has not yet been addressed before. Moreover, these studies pyrolyse biomass of small particle size (up to 4 mm) or pellets, which require grinding, sieving and pelletizing as pre-treatment stages that are, in turn, more energy intensive.

Therefore, this study aims to evaluate the process performance and chemical properties and composition of pyrolysis products obtained in an auger reactor using biomass woodchips (up to 20 mm of nominal size) as feedstock under different operational parameters: temperature, solid residence time and mass flow rate. In addition, bio-oil properties obtained in the auger reactor are compared with existing commercial processes such as a fluidized bed reactor and with other auger reactors. Finally, scaling up issues are addressed with a view to the further objective of converting the auger reactor, which has a compact design and operates continuously with low maintenance operations, to a mobile plant. This plant should be able to process large particle size biomass such as woodchips, which would represent lesser pre-treatment and less energy consumption of the overall process.

7.2. Experimental section for the biomass pyrolysis in an auger reactor

In the following section, the details of the materials and the experimental used in this section are described.

7.2.1. Feedstock

Pine woodchips of Scots pine (Pinus sylvestris) were used as raw material for the experiments. The proximate and ultimate analysis of the feedstock is detailed in Table 5 from section *2.2.1. Materials*. Woodchips were sieved to a nominal size of 20 mm and were seasoned up to 7% of moisture content.

7.2.2. Thermogravimetric analysis

Initial pyrolysis tests were conducted in a thermobalance SETARAM Setsys Evolution under the conditions described in section *2.2.3. Analytical techniques*. In this study, three experiments at different heating rates of 5 K/min; 10 K/min and 20 K/min were performed from room temperature up to 973 K placing 9.5 mg of biomass (particle size less than 0.2 mm) in the basket.

7.2.3. Pyrolysis reactor

Pyrolysis of the pine woodchips was carried out in an auger reactor, which has been described in section *2.2.2. Experimental setup: pyrolysis in an auger reactor*. In short, it comprises four main parts: the feeding system, the reactor, the vessel for solids and the condensing system. Both the feeding system and the reactor consist of screws, which allow carrying out the process continuously. Woodchips move through the reactor while decomposing into a solid residue and a gaseous product. The solid residue leaves the reactor falling into a vessel for solids. The condensed fraction is recovered in a liquid collector after moving down by gravity. Non-condensable vapours at ambient temperature are conducted to a burner before reaching the atmosphere.

The experimental design, as introduced in the abovementioned section, consisted of ten experiments carried out under different conditions: reaction temperature (1073 K, 973 K, 873 K, 823 K and 773 K), solid residence time (5 min, 3 min, 2 min and 1.5 min) and mass flow rate (3.9 kg/h, 4.8 kg/h and 6.9 kg/h).

7.2.4. Product characterisation

As detailed in section *2.2.3. Analytical techniques*, liquid fraction was characterised by means of the determination of collective properties, simulated distillation and GC/MS. Solid fraction and gas fraction were characterised by proximate analysis and gas chromatography coupled with a TCD detector respectively. Further details of product characterisation are provided in the following section.

7.3. Experimental results and discussion of the biomass pyrolysis in an auger reactor

The research described in this section was performed at two different levels. In the first level, the raw material behaviour under pyrolysis conditions was assessed in a thermobalance. In this first study, the temperature window to carry out the devolatilisation was established. In the second level a continuous auger reactor was used to study the influence of the operation parameters on the conversion yields and properties of the products. In this way not only the results found in the thermobalance were confirmed but also the yields to solid, liquid and gas products, the gas composition and product properties were obtained. All these experimental results are discussed in the following section.

7.3.1. Thermogravimetric analysis

A through study on thermogravimetric analysis has been presented in section *6.3.2. DAEM application* in the previous section. In Figure 30 and Figure 31 the fraction of mass remaining versus temperature and the rate of mass loss versus temperature can be observed for different heating rates.

Higher biomass volatilisation rate occurs at higher heating rates, since the biomass devolatilisation rate increases in a shorter range of temperatures. Wood devolatilisation occurs between 400 K and 800 K. Temperature ranges slightly depend on the heating rate used. Wood decomposition takes place, as the above-mentioned study showed, mainly in three steps: first lignin decomposition, which lasts until 800 K, followed by hemicellulose decomposition and, finally, cellulose decomposition. Lignin is the compound with longer decomposition times, since its decomposition starts at the same time of hemicellulose and can last until 873 K. It can be observed that working temperatures higher than 773 K will ensure total biomass conversion. Lower reaction temperatures could lead to incomplete pyrolysis of the wood samples, especially when large biomass particle size such as woodchips are used compared to particle size less than 0.2 mm analysed in the thermogravimetric analysis. Particle size is a key variable involved in heat transfer between gas and solid. It is widely recognised that for large particles, convective heat transfer between two phases become controlling and the low biomass thermal conductivity introduces significant internal heat transfer limitations [6].

7.3.2. Effect of temperature on pyrolysis products

The pyrolysis reaction was carried out at five different temperatures ranging from 773 K to 1073 K and different product yields were obtained depending on the reaction temperature (see Table 19). As it is showed, the maximum liquid yield (57 wt %) at this set of experiments is obtained at low reaction temperature (773 K), since severe cracking of the primary pyrolysis products occurs at higher temperatures [38]. Liquid yields of the experiments carried out at 773 K ranged from 45% to 59%, which is slightly higher than the yields obtained in other auger reactors. For instance, Mohan [25] reported liquid yields in auger reactors from 30 to 50%, and M. García-Perez and co-workers achieved up to 50.4% of liquid yield from pine chips in their batch reactor at 773 K [36]. Comparing the liquid yield obtained with pine pellets, Ingram and co-workers achieved a liquid yield up to 55.2% using ground-pellets [29] while M. Garcia-Perez reported a 57.8% liquid yield [36]. Comparing to other reactors, the yield of bio-oil obtained is similar to the reported in a bubbling fluidized bed reactor [39] or to some extent low (60-80 wt %) [25,40], although the improvement in this study is the mild biomass pre-treatment since the particle size of biomass fed into the reactor were woodchips instead of sawdust. Considering that the size reduction of biomass feedstock is a very energy-intensive and non-trivial operation due to the fibrous nature of most biomass materials, the capability of using large particles to achieve high yields of quality bio-oil would be advantageous [40]. It is reported that pyrolysis of large particle size biomass leads to pyrolysis secondary reactions, such as homogeneous and heterogeneous reactions, which include processes such as cracking, partial oxidation, re-polymerization and condensation [6]. It has also been suggested that these reactions lead to an increase in the yield of char [36] that can be mitigated by reducing the particle size, although this variable has not been evaluated. For this process to be widely applicable and flexible, minimal pre-treatment has been applied to the woodchips to keep the process as simple as possible. In addition, no specific drying treatment was carried out either since the woodchips were air-dried.

Accordingly, gas yields increase with higher reaction temperatures, similar to what it is stated in previous literature [24,41]. Solid yields, however, range from 26 to 19 wt % due to the different biomass devolatilisation rate achieved.

Table 19. **Experimental conditions studied in the auger reactor with pine woodchips as feedstock and product yields.**

Temperature (K)	Solid residence time (min)	Mass flow rate (kg/h)	Liquid yield (% wt)	Solid yield (% wt)	Gas yield (% wt)
Reaction temperature					
1073	5.0	3.9	36.6	19.0	44.4 [a]
973	5.0	3.9	37.2	21.3	41.6[a]
873	5.0	3.9	45.1	23.7	31.2[a]
823	5.0	3.9	51.4	25.7	22.9[a]
773	5.0	3.9	52.5	26.4	24.0
Solid residence time					
773	3.0	3.9	57.0	26.0	18.0
773	2.0	3.9	53.2	28.8	16.7
773	1.5	3.9	45.0	41.5	15.0
Mass flow rate					
773	5.0	4.8	56.4	27.8	22.5
773	5.0	6.9	58.7	25.8	24.7

[a] Calculated through mass balance

Effect of temperature on liquid properties

The influence of temperature on the bio-oil properties has been studied by the determination of collective properties, simulated distillation and GC/MS.

Bio-oil collective properties

Ultimate analysis, density and water content of the bio-oil samples are shown in Table 20. No significant differences can be observed in the ultimate analysis of the bio-oil at the different temperatures tested. Comparing to literature, the analysis results are similar to typical values reported by other authors [29,38,42].

Density values are similar in all the bio-oil samples and vary between 1.05 and 1.17 g/cm^3 and water content ranges from 11 to 19 wt %. These values are similar to those reported in other works [29,33,42,43].

Table 20. Collective properties of the bio-oil samples: ultimate analysis, density and water content.

	Ultimate analysis (%wt db)				**Density (g/cm^3)[b]**	**Water content (%wt)**
	Carbon (C)	Hydrogen (H)	Nitrogen (N)	Oxygen (O)[a]		
Reaction temperature (K) (mass flow rate = 3.9 kg/h, residence time = 5.0 min)						
1073	63.0	5.9	0.6	30.5	1.05	11.2
973	64.3	6.2	0.4	29.1	1.06	19.5
873	63.8	6.7	0.4	29.2	1.13	12.2
823	62.3	6.0	0.2	31.5	1.19	13.2
773	61.1	7.0	0.1	31.8	1.17	10.8
Solid residence time (min) (T = 773 K, mass flow rate = 3.9 kg/h)						
3	61.5	7.1	0.1	31.3	1.13	15.9
2	60.8	7.2	0.1	31.9	1.14	12.5
1.5	60.5	7.0	0.1	32.4	1.13	19.4
Mass flow rate (kg/h) (T = 773 K, residence time = 5.0 min)						
4.8	60.4	7.2	0.1	32.3	1.13	16.7
6.9	63.3	7.2	0.3	29.2	1.13	16.6

[a] Calculated by difference
[b] T = 296.7-297.3 K

Simulated distillation

This method is used to determine the boiling point distribution of different fuel fractions. Three ranges of temperature have been differentiated (see Table 21) in order to compare the bio-oils with gasoline and gasoil. The simulated distillation corresponding to the pyrolysis liquids with boiling points comprised in the gasoline interval (lower than 473 K), which ranges from 20.0 to 26.2 % mass, does not show any clear tendency according to temperature. The same tendency can be observed in the performance of the pyrolysis liquids compared to the gasoil fraction (with boiling points above 473 K).

Table 21. Simulated distillation of the pyrolysis oil obtained under different operational conditions.

	Boiling point distribution (% mass)		
	< 473 K	**473-623 K**	**> 623 K**
Reaction temperature (K) (mass flow rate = 3.9 kg/h, residence time = 5.0 min)			
1073	21.1	41.0	37.9
973	26.2	46.9	26.9
873	23.2	45.6	31.2
823	16.1	36.7	47.2
773	20.0	37.7	42.3
Solid residence time (min) (T = 773 K, mass flow rate = 3.9 kg/h)			
3	29.3	41.2	29.5
2	31.3	40.1	28.6
1.5	17.8	30.0	52.2
Mass flow rate (kg/h) (T = 773 K, residence time = 5.0 min)			
4.8	18.5	33.8	47.7
6.9	15.4	32.3	52.3

Gas Chromatography/Mass Spectrometry (GC/MS)

Pyrolysis oils are a complex mixture of water, higher molecular weight lignin fragments and lower molecular weight organics. Oxygen is present in most of the compounds identified in the bio-oil [44], due to the high amount of oxygen contained in the bio-oil (up to 32%, see Table 20) and the initial raw material. This high amount of reactive oxygen-containing compounds implies instability in pyrolysis oils [45]. Thermal cracking reactions on biomass pyrolysis generate the following products: primary products (cellulose and hemicellulose-derived products, and lignin derived methoxyphenols); secondary products (phenolics and oleofins); alkyl tertiary products (methylderivates of aromatics); and condensed tertiary products (PAH). Thus, thermal analysis performed by GC/MS of the wood reflects the sum of the thermal response of its three main components (cellulose, hemicellulose and lignin). The experiment carried out at 773 K, in which the solid residence time was 5 min and the mass flow rate was set at 3.9 kg/h, achieved the maximum bio-oil yield in the auger reactor. An example of the Total Ion Chromatogram of this sample is shown in Figure 41. More than 150 compounds were detected and among them, 64 compounds were identified by comparison with spectra from the NIST mass spectral library. The identified compounds listed in Table 22 included carboxylic acids, alcohols, aldehydes, ketones and phenolic compounds. The most abundant species, according to the percentage of area of the chromatogram, are: 4-methyl-1,2–benzenediol (7.2%); 1,2-benzenediol (5.7%); 2-methoxy-4-methylphenol (5.1%); D-allose (3.4%); 2-methoxyphenol (3.5%); and acetic acid (3.3%).

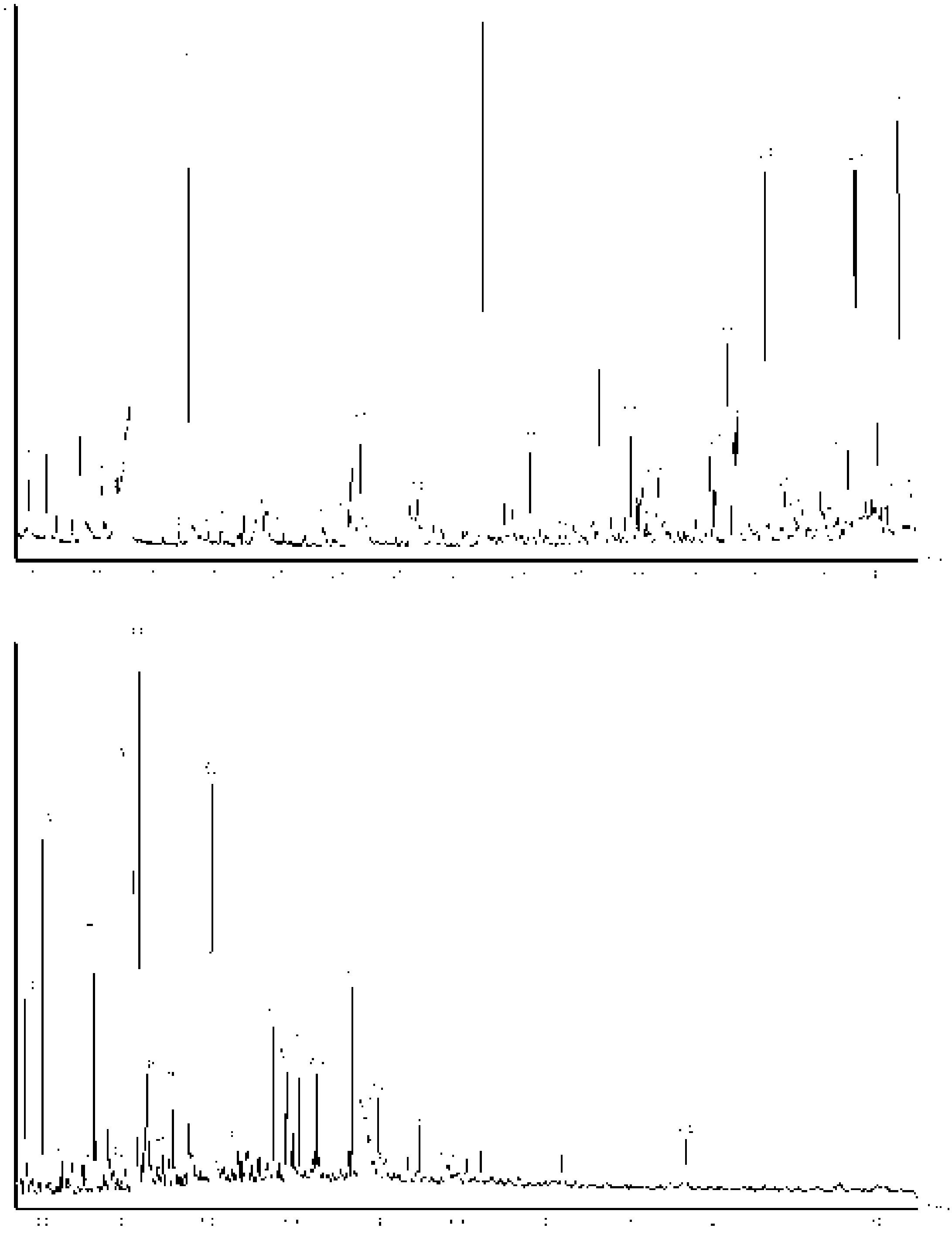


Figure 41. **Total Ion Chromatogram of bio-oil produced from pine woodchips at 773 K, 5 min of solid residence time and 3.9 kg/h of mass flow rate. Numbering of compounds is according to Table 5.**

In this bio-oil sample, the functional groups distribution is divided into mostly phenols (47.5%); followed by ketones (10.0%); acids (7.0%); aldehydes (4.0%); polycyclics (1.0%) and other functional groups, which represent the 0.1% of the total area. Table 23 summarises the identified compounds classified into functional groups. The influence of reaction temperature on the composition of bio-oil can be observed in Figure 4. Reaction temperature was noted to be the most important operational parameter that affects bio-oil composition. The influence of reaction temperature on the bio-oils results in a higher amount of polycyclic compounds, an increase that results from the further reaction of primary products [46], which increases from the 1.0% of the total area of the chromatogram at 773 K to 10.6% at 1073 K, as shown in Figure 42. It has been reported that at very high temperatures, dehydrogenation/ aromatization reactions can eventually lead to larger polynuclear aromatic hydrocarbons and, eventually, increases in carbonization [25,36,47,48]. It should be noted that aromatic compounds, especially naphthalene and heavier PAHs, cause technical problems for engine combustion or for advanced catalytic gas conversion [49]. Overall, the proportions of phenolic compounds do not show significant variations between the temperatures studied. However, the presence of aldehydes and ketones is substantially higher in the samples prepared at lower temperatures. These ranged from 0.8% and 4.0% in the case of aldehydes and between 5.8% and 9.9% for ketones, with decreasing temperature of pyrolysis.

A further analysis of the reaction temperature dependence of the chemical composition of the bio-oils has been performed. The bio-oil fractions have been represented previously as a mixture of eight macro-families [50], designated as: volatile non-polar compounds, volatile polar compounds, monolignols, polar compounds with moderate volatility, sugars, extractive-derived compounds, heavy non-polar compounds and heavy polar compounds. The volatile non-polar compounds are mainly formed of alkenes and aromatics. Bio-oil derived volatile polar compounds include compounds with 1-5 atoms of carbon with boiling points up to approximately 423 K, which include mainly ketones such as 2-cyclopenten-1-one. The monolignols and polar compounds with moderate volatility are present in bio-oils as phenols and benzenediols, guaiacols and syringols. The extractive-derived compounds are fatty and resin acids, paraffins and phenanthrenes.

Table 22. **Main compounds identified in the bio-oil in the experiment ran at 773 K (solid residence time = 5.0 min; mass flow rate = 3.9 kg/h).**

Id	Compound	MW	Formula	Rt (min)	Area (%)[a]	Id	Compound	Mw	Formula	Rt (min)	Area (%)[a]
1	acetate-1-propen-2-ol	100	$C_5H_8O_2$	12.388	0.45	33	2-hydroxy-2-cyclopenten-1-one	126	$C_7H_{10}O_2$	41.778	0.26
2	2,3-butanedione	86	$C_4H_6O_2$	14.840	0.30	34	3-methyl-phenol	108	C_7H_8O	42.408	2.57
3	acetic acid	60	$C_2H_4O_2$	15.772	3.27	35	2-methoxy-phenol	124	$C_7H_8O_2$	43.527	3.46
4	2-butenal	70	C_4H_6O	17.374	0.09	36	2,5-dimethyl- phenol	122	$C_8H_{10}O$	44.590	0.23
5	2-acetate-1,2-propanediol	118	$C_5H_{10}O_3$	17.684	1.95	37	maltol	126	$C_6H_6O_3$	44.745	0.54
6	2,2-dimethoxy-propane	104	$C_5H_{12}O_2$	18.362	0.05	38	3-ethyl-2-hydroxy-2-cyclopenten-1-one	126	$C_7H_{10}O_2$	45.227	0.41
7	3-methyl-3-buten-2-one	84	C_5H_8O	18.779	0.08	39	2-ethyl-phenol	122	$C_8H_{10}O$	45.938	0.18
8	2-pentanone	86	$C_5H_{10}O$	19.417	0.10	40	2,5-dimethyl-phenol	122	$C_8H_{10}O$	46.617	2.69
9	propanoic acid	74	$C_3H_6O_2$	20.177	0.54	41	2,6-dimethyl-phenol	122	$C_8H_{10}O$	48.211	0.17
10	2,5-dimethyl-furan	96	C_6H_8O	20.880	0.06	42	4-methoxy-3-methyl-phenol	138	$C_8H_{10}O_2$	48.546	0.31
11	(e)-3-penten-2-one	84	C_5H_8O	22.179	0.15	43	1,2-benzenediol	110	$C_6H_6O_2$	48.905	5.66
12	(acetyloxy)-acetic acid	118	$C_4H_6O_4$	23.021	0.15	44	2-methoxy-4-methyl-phenol	138	$C_8H_{10}O_2$	49.273	5.10
13	1-hydroxy-2-butanone	88	$C_4H_8O_2$	23.405	0.57	45	5-(hydrxymethyl)-2-furancarboxaldehyde	126	$C_6H_6O_3$	49.739	1.38
14	butanoic acid	88	$C_4H_8O_2$	25.342	0.62	46	3,4,5-trimethyl-phenol	136	$C_9H_{12}O$	49.902	0.44
15	3-methyl-2-butanone	86	$C_5H_{10}O$	29.077	0.49	47	3,4-dimethoxytoluene	152	$C_9H_{12}O_2$	51.039	0.54
16	2-cyclopentene-1,4-dione	96	$C_5H_4O_2$	30.246	0.06	48	2-ethyl-5-methyl-phenol	136	$C_9H_{12}O$	51.325	1.10
17	2-methyl-2-cyclopenten-1-one	96	C_6H_8O	32.412	0.51	49	3-ethyl-5-methyl- phenol	136	$C_9H_{12}O$	51.553	0.07
18	1-(2-furanyl)-ethanone	110	$C_6H_6O_2$	32.633	0.18	50	4-(2-propenyl)-phenol	134	$C_9H_{10}O$	51.856	0.07
19	2,5-hexanedione	114	$C_6H_{10}O_2$	32.919	0.05	51	hydroquinone	110	$C_6H_6O_2$	52.060	0.14
20	2-hydroxy-2-cyclopenten-1-one	98	$C_5H_6O_2$	33.360	0.63	52	4-methyl-1,2-benzenediol	124	$C_7H_8O_2$	53.662	7.23
21	1-(acetyloxy)-2-butanone	130	$C_6H_{10}O_3$	35.199	0.23	53	2-methoxy-4-vinylphenol	150	$C_9H_{10}O_2$	55.231	0.48
22	5-methyl-2-furancarboxaldehyde	110	$C_6H_6O_2$	35.665	1.02	54	4-(2-propenyl)-phenol	134	$C_9H_{10}O$	56.073	0.32
23	2-cyclopenten-1-one, 3-methyl-	96	C_6H_8O	35.943	1.19	55	2-methoxy-3-(2-propenyl)-phenol	164	$C_{10}H_{12}O_2$	57.389	1.39
24	phenol	94	C_6H_6O	36.875	1.85	56	2-methoxy-4-propyl-phenol	166	$C_{10}H_{14}O_2$	58.018	0.44
25	2,5-dihydro-3,5-dimethyl 2-furanone	112	$C_6H_8O_2$	37.528	0.40	57	4-ethylcatechol	138	$C_8H_{10}O_2$	58.182	1.48
26	3,4-dimethyl-2-cyclopenten-1-one	110	$C_7H_{10}O$	37.904	0.07	58	vanillin	152	$C_8H_8O_3$	58.901	1.25
27	2-cyclohexene-1,4-dione	110	$C_6H_6O_2$	39.294	0.18	59	(e)-2-methoxy-4-(1-propenyl)-phenol	164	$C_{10}H_{12}O_2$	59.923	1.04
28	4-methyl-5h-furan-2-one	98	$C_5H_6O_2$	39.653	0.43	60	(z)-2-methoxy-4-(1-propenyl)-phenol	164	$C_{10}H_{12}O_2$	62.105	1.85
29	2-hydroxy-2-cyclopenten-1-one	112	$C_6H_8O_2$	39.882	2.13	61	d-allose	180	$C_6H_{12}O_6$	62.865	3.93
30	2,3-dimethyl-2-cyclopenten-1-one	110	$C_7H_{10}O$	40.642	0.42	62	1-(4-hydroxy-3-methoxyphenyl)-ethanone	166	$C_9H_{10}O_3$	63.666	0.91
31	2-hydroxy- benzaldehyde	122	$C_7H_6O_2$	40.937	0.17	63	1-methyl-7-(1-methylethyl)-naphthalene	184	$C_{14}H_{16}$	72.019	0.34
32	2-methyl-phenol	108	C_7H_8O	41.321	2.36	64	4-hydroxy-2-methoxycinnamaldehyde	178	$C_{10}H_{10}O_3$	82.047	1.32

[a] Calculated by dividing each product peak area by the sum of areas of all product peaks; MW: Molecular Weight; Id: Identification number; Rt: Retention time.

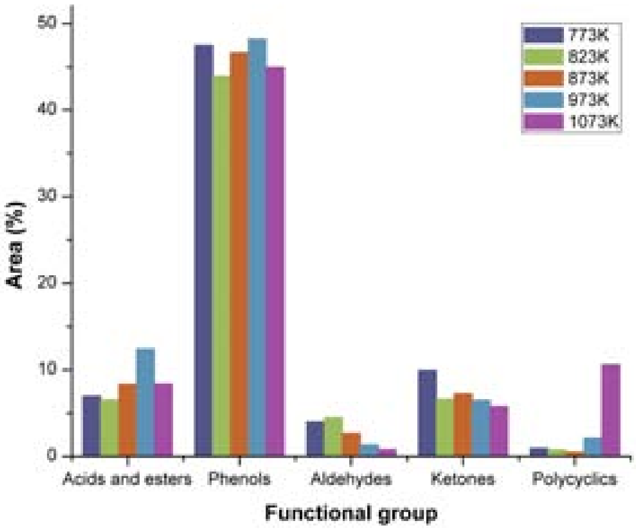


Figure 42. **Functional groups identified in the bio-oil obtained at different operational conditions, expressed as function of reaction temperatures (solid residence time = 5 min; mass flow rate = 3.9 kg/h).**

The sugars present in bio-oils are mainly polysaccharides, although they could not be identified in the bio-oils obtained in the auger reactor. This fact coincides with results presented by Wang and coworkers [51], even though levoglucosan is regarded to be a primary pyrolysis product of holocellulose (hemicellulose and cellulose), which increases with temperature [52]. The monosaccharide D-allose was identified in the bio-oil samples obtained at temperatures ranging from 773 K to 973 K, but it was not present at 1073 K. This might be explained by the complete degradation of holocellulose at high temperatures. In this study, heavy non-polar compounds and heavy polar compounds could not be determined due to the temperature limitation of the GC column used.

It can be observed that the presence of acids, such as propanoic acid or acetic acid, and esters in the samples rises moderately at increasing reaction temperatures (see Figure 43). Phenolics in pyrolysis oils are originated from the degradation of lignin present in the feedstock [52,53,54]. Although no significant differences can be seen among the samples in relation to the occurrence of phenols, the amount of phenol and 3-methylphenol (m-cresol) increases with preparation temperature, indicating that they are also formed from secondary degradation reactions (see Figure 44). Since the liquid reaction products were recovered altogether, the effect of side reactions is important, for example, phenolic compounds tend to polymerize with aldehydes under acidic conditions [55]. Given that the experiments were run at temperatures above 623 K, secondary pyrolysis products, mainly catechols, could be observed. The presence of these compounds increased with longer holding times, due to demethylation of methoxy phenols rather than dehydration reactions [55].

Table 23. Summarised classification of compounds by functional groups identified in the bio-oil samples.

ACIDS AND ESTERS	PHENOLS	ALDEHYDES	KETONES	POLYCYCLICS
Acetic acid	Phenol	2-butenal	2-methyl-2-cyclopenten-1-one	Styrene
Propanoic acid	2-methylphenol	5-methyl-2-furancarboxaldehyde	3-methyl-2-cyclopenten-1-one	Benzofuran
Acetate-1-propen-2-ol	3-methylphenol	2-hydroxybenzaldehyde	1-(2-furanyl)-ethanone	2-methylindene
Acetate-1,2-propanediol	2,5-dimethylphenol	5-hydroxymethyl-2-furancarboxaldehyde	1-(acetyloxy)-2-butanone	Naphtalene
Butanoic acid	Pyrocatechol		2,3-dimethyl-2-cyclopenten-1-one	Biphenyl
(acetiloxy)-acetic acid	4-Ethylcatechol			Biphenylene
				Acenaphthene
				Phenanthrene
				Anthracene

In accordance with previous literature [52], the increased yield of furans (5-methyl-2-furancarboxaldehyde and 5-hydroxymethyl-2-furancarboxaldehyde) observed at low temperature can be attributed to hemicellulose decomposition (see Figure 45), given that the subsequent dehydration of levoglucosan yields substituted furan and pyran derivatives [29].

Finally, as the temperature is increased, early increases in the production of ketones (see Figure 46) can be observed, reflecting the primary degradation of wood components (cellulose, hemicellulose and lignin) [52]. At higher temperatures dehydration reactions occur and their occurrence decreases, as the formation of phenols is favoured.

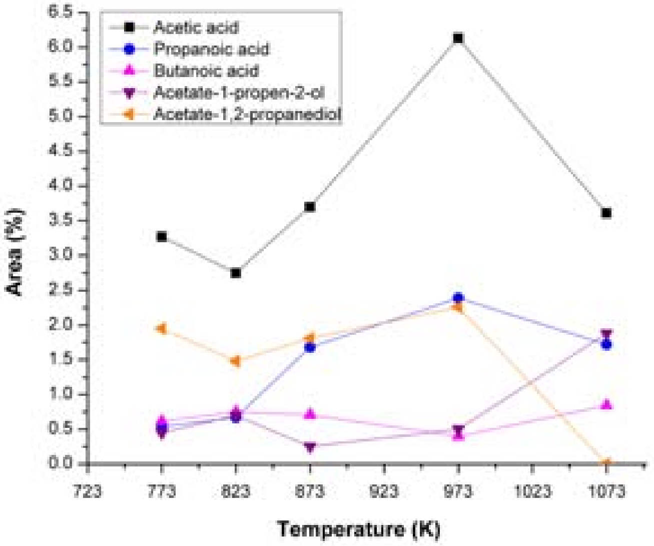


Figure 43. Presence of acids and esters expressed as percent of the area of the chromatogram as function of the reaction temperature (solid residence time = 5.0 min; mass flow rate = 3.9 kg/h).

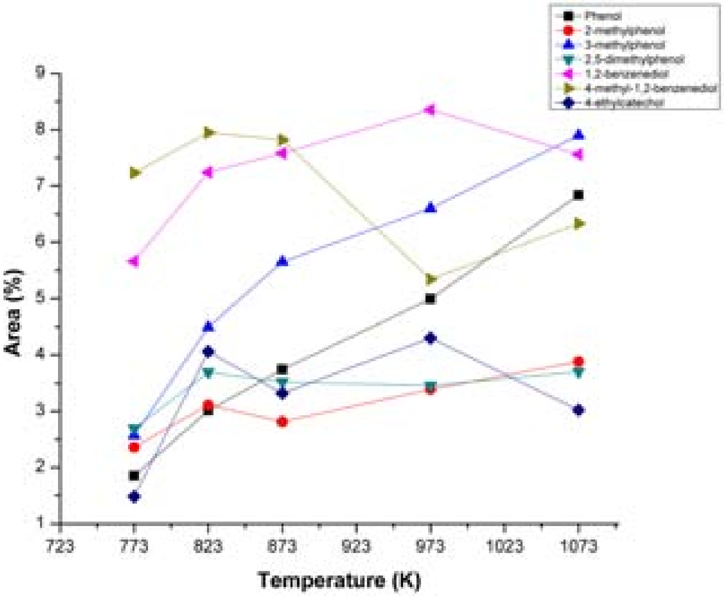


Figure 44. Presence of phenols expressed as percent of the area of the chromatogram as function of the reaction temperature (solid residence time = 5.0 min; mass flow rate = 3.9 kg/h).

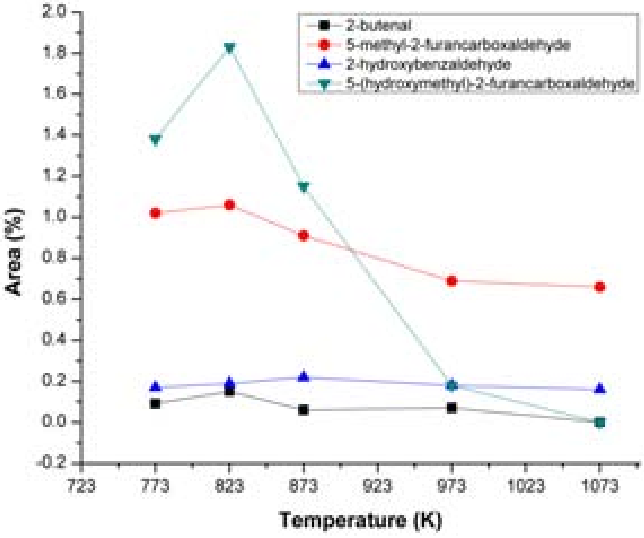


Figure 45. **Presence of aldehydes expressed as percent of the area of the chromatogram as function of the reaction temperature (solid residence time = 5.0 min; mass flow rate = 3.9 kg/h).**

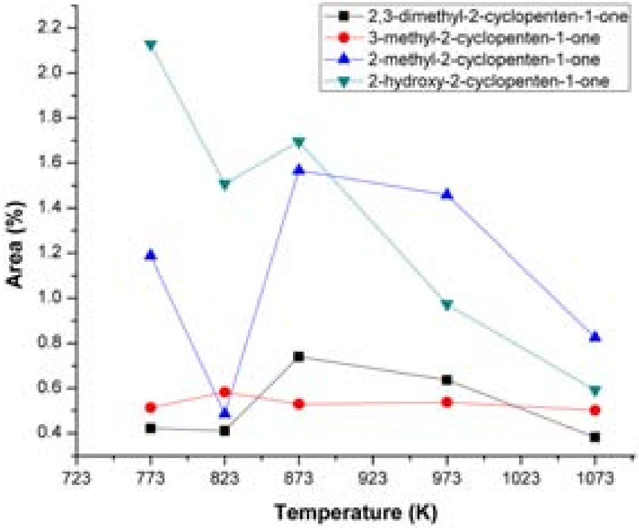


Figure 46. **Presence of ketones expressed as percent of the area of the chromatogram as function of the reaction temperature (solid residence time = 5.0 min; mass flow rate = 3.9 kg/h).**

Effect of temperature on char properties

Table 24 shows the char proximate analysis where it can be observed that although reaching reaction temperatures of 1073 K, the volatile matter remains above 10%. In the thermobalance essays almost complete devolatilisation was achieved for temperatures around 773 K. This difference can mainly arrive from the influence of three operational parameters changed from one system to the other: heating rate, solid residence time and particle size. In the auger reactor the particle will suffer a change in temperature from room temperature to 773-1073 K in minutes that produces a much higher heating rate and a subsequent shift of the pyrolysis reaction to higher temperatures. This influence of the heating rate in the pyrolysis process has been previously reported and modelled for different kinds of biomass and for the biomass components cellulose, hemicellulose and lignin [56]. The particle size (thermobalance 0.2 mm, auger reactor 1-2 cm) can also have a negative impact in the devolatilisation reached in the process since higher particle sizes above 0.2 mm produce higher char yields [48] due to the temperature gradient effect on the primary product distribution produced in processes with internal and external heat transfer control. Finally, the solid residence time is much shorter in the auger reactor than in the thermobalance. For example, in the fastest thermobalance experiment (20 K/min), the solid residence time at reaction temperature (between 450 K and 975 K) was around 41 min (26 min during the heating up period and 15 min at the final temperature) much longer than the 5 minutes in the auger reactor.

Table 24. Char proximate analysis at different process variables.

	Moisture (%wt)	Ash (%wt)	Volatile matter (%wt)	Fixed carbon (%wt)
Reaction temperature (K) (mass flow rate = 3.9 kg/h, residence time = 5.0 min)				
1073	0.8	7.4	11.0	80.8
973	1.4	7.7	14.6	76.3
873	2.4	6.0	18.5	73.1
823	2.5	3.6	19.0	74.9
773	2.4	2.8	24.8	70.0
Solid residence time (min) (T = 773 K, mass flow rate = 3.9 kg/h)				
3	2.7	2.9	29.5	64.9
2	2.2	2.2	39.1	56.5
1.5	1.9	1.5	56.8	39.9
Mass flow rate (kg/h) (T = 773 K, residence time = 5.0 min)				
4.8	1.7	3.1	31.9	63.4
6.9	2.0	3.9	27.9	66.3

Effect of temperature on gas properties

The gas composition for the reaction temperatures studied can be observed in Figure 47. The composition has been expressed in terms of yield to the different gas compounds since gas yield differs depending on each temperature. It is observed that higher reaction temperature produces a higher cracking, depolymerisation, decarboxylation and oxidation in the gas phase [57]. Therefore, not only the total gas yield is increased but also the fraction of light gases in the mixture, such as hydrogen and methane. Referring to CO_2 and CO, which are the main gas products depending on the oxygen present in the fuel, while the concentration of CO increases according to temperature, CO_2 concentration keeps almost constant. The behaviour of CO, with an increasing concentration related to temperature can be explained because an increase of C=O bond breakage [58]. The behaviour of CO_2 with temperature can be characterised by a slight increase or even a decrease [59] attributed to the fact that CO_2 is a product of the pyrolysis of cellulose and hemicellulose by a path less favoured by increasing temperature [60]. The behaviour of CO_2 with temperature can be also explained as the oxidation of CO, which competes with the kinetically favoured oxidation of hydrocarbons into CO. Hydrocarbon formation increases with temperature therefore there will be less oxygen available to produce CO_2 [58]. In relation to C_2-C_4 compounds, it can be observed that these concentrations increase with temperature, although they remain relatively constant from 873 K.

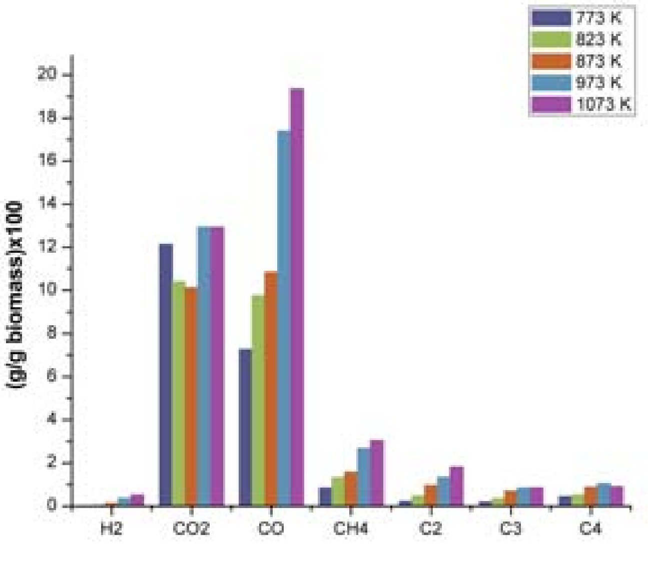


Figure 47. Composition of the gas fraction obtained at different reaction temperatures (solid residence time = 5 min; mass flow rate = 3.9 kg/h).

7.3.3. Effect of solid residence time on pyrolysis products

The solid residence time is an important variable since it is a key factor in order to scale up an industrial process. Higher solid residence times entail higher reactor volumes and, in consequence, higher costs of the overall plant. To study the influence of the solid residence time, pyrolysis was performed at different solid residence times: 1.5, 2.0, 3.0 and 5.0 min (see Table 19). It can be observed that there is a significant decrease in the solid yield obtained between the solid residence time of 1.5 and 2 min. Therefore, at 1.5 min of solid residence time, char still can undergo some further devolatilisation and a minimum solid residence time of 2 min is required to achieve the complete reaction. In terms of liquid conversion, the highest yields are obtained with 3 min of reaction time.

Referring to liquid characterisation, the variation of solid residence time does not have a significant influence on the overall chemical composition of bio-oil samples as it is shown in Table 20 and neither significant differences can be observed in terms of the simulated distillation (Table 21). However, longer solid residence times seem to lead an increase of phenols and a decrease of acids and esters, aldehydes, and ketones (see Figure 48). In relation to the solid product characterisation, no major differences can be observed in the char proximate analysis at different solid residence times (see Table 24).

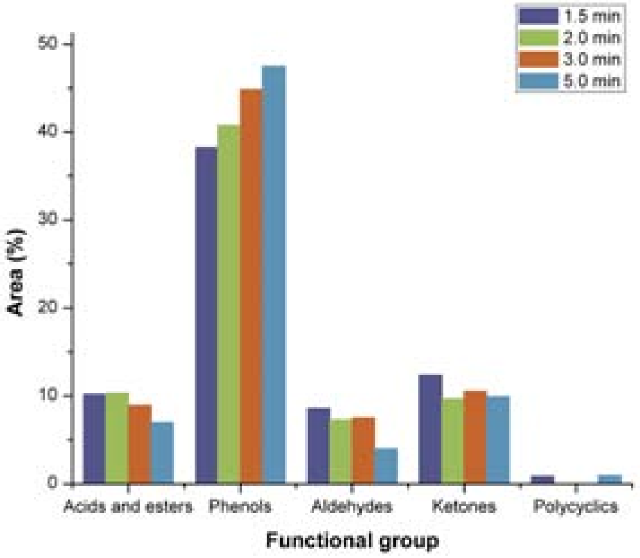


Figure 48. Functional groups identified in the bio-oil obtained at different operational conditions, expressed as function of solid residence time (T = 773 K, mass flow rate = 3.9 kg/h).

At lower residence times, the volatile matter of the char increases since the reaction time is not long enough to perform the complete reaction, as it was stated above. Solid residence time does not affect in such influence as it was with temperature on gas composition. Figure 49 shows the composition of the gas fraction obtained at different solid residence times. As it can be observed, the major fractions are CO_2 and CO, which slightly decrease when lowering the residence time for CO_2 and keep constant for CO.

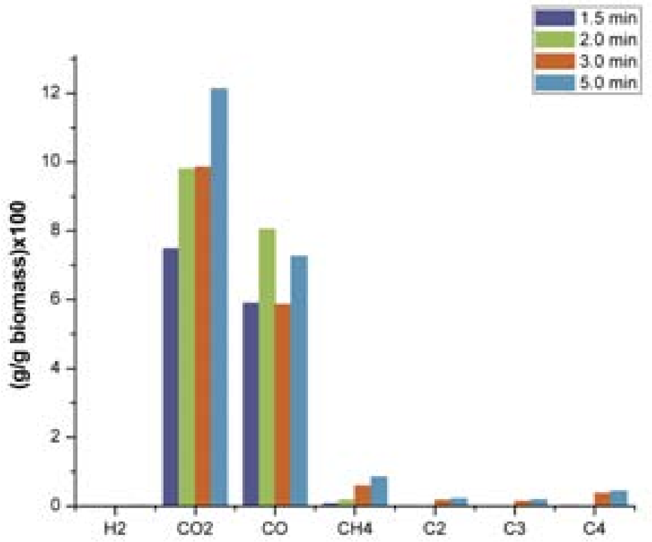


Figure 49. **Composition of the gas fraction obtained at different solid residence times (T = 773 K, mass flow rate = 3.9 kg/h).**

7.3.4. Effect of mass flow rate on pyrolysis products

The mass flow rate was studied on the reaction product yields and properties. Three experiments (3.9, 4.8 and 6.9 kg/h) were performed to analyse this variable. As it can be observed in Table 19, bio-oil yields show a continuous rise when mass flow rate is increased. Increasing the mass flow rate, the gas residence time decreases, consequently causing a lower cracking of the products.

The properties of the bio-oil obtained at different mass flow rate does not show significant differences between the samples, as it was observed with the variation of the solid residence time (see Table 20 and Figure 50). On the other hand, some differences can be observed in the simulated distillation curves (see Table 21). When the biomass flow rate is increased, the gasoline percentage in the liquid yield decreases from 20% to 15% and the gasoil percentage varies from 42% to 52% in the studied range. Again, no significant differences can be observed between the three mass flow rates studied; neither on the char characterisation, nor on the composition of the gas fraction (see Figure 51 and Table 24).

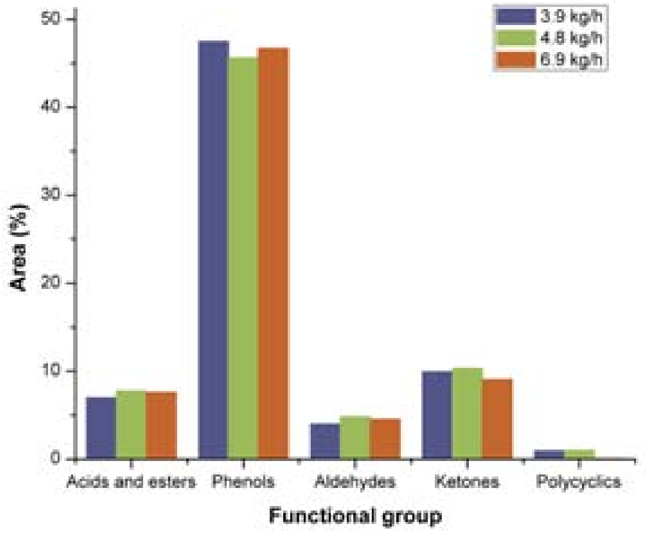


Figure 50. Functional groups identified in the bio-oil obtained at different operational conditions, expressed as function of mass flow rate (T = 773 K, solid residence time = 5.0 min).

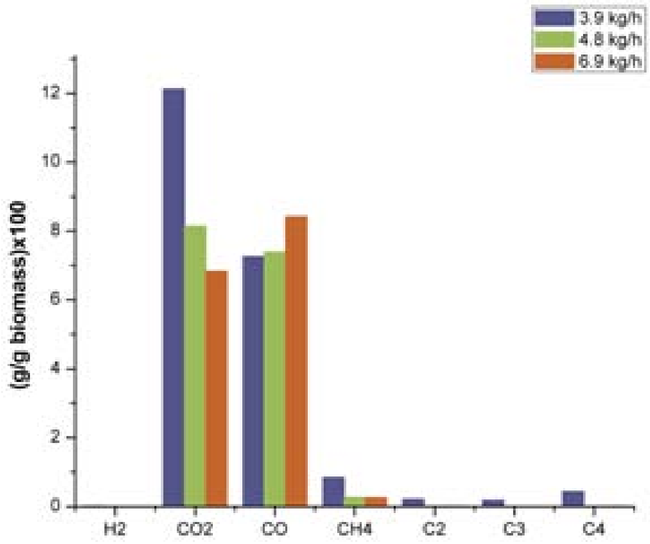


Figure 51. Composition of the gas fraction obtained at different mass flow rates (T = 773 K, residence time = 5.0 min).

7.3.5. Comparison of the auger reactor with other reactors

The properties of pine wood bio-oil from this auger reactor compared to other auger reactors and to a fluidized bed reactor, as well as a compilation of typical values from pine wood bio-oil from literature, are shown in Table 25. The bio-oil obtained from the auger reactor presents similar characteristics to the bio-oil produced in the other reactors. However, in this auger reactor the oils have less water and oxygen content. The results obtained in this study are similar to the auger reactor studied by Ingram et al. [29] in relation to the ultimate analysis and density determination, with the exception of the water content, which is lower in this study. The comparison between the auger reactor studied and other reactors shows similar density and hydrogen and nitrogen content, but to some extent with lower oxygen content and higher carbon content, which can be explained by the different reactor configuration. One of the advantages of the auger reactor is its simplicity, which facilitates its installation on a mobile platform. This fact creates the opportunity to process seasonal biomass in remote locations, such as forestry residues that are presently not being used owing to their expensive harvesting and transport costs [26]. Further, the lower need for less pre-treatment to be applied to the biomass (larger particle size and no drying process were used) prove that working with this pilot plant is possible without incurring high costs of customizing the feedstock.

Table 25. Comparison of the properties of the bio-oil obtained from pine wood and typical bio-oil values.

	Auger reactor in this study[a,b]	**Auger reactor[b] [29]**	**Fluidized bed reactor[b] [42]**	**Typical values wood bio-oil [33]**
Carbon (C)	61.1	61.0	43.5-46.7	54-58
Hydrogen (H)	7.0	7.0	6.7-7.1	5.5-7.0
Nitrogen (N)	0.1	0.0	≤ 0.1	0.0-0.2
Oxygen (O)	31.8	32.0	46.0-49.0	35-40
HHV (MJ/kg)	25.5	21.9	17.8-19.0	16-19
Density (g/cm^3)	1.17	1.19	n.d.	1.21-1.24
Water content (wt %)	10.8	16.0	17.0-21.4	15-30

n.d.: not determined

[a] T = 773 K; solid residence time = 5 min; mass flow rate = 3.9 kg/h

[b] Feedstock: Pine wood

7.4. Process scaling up: mass and energy balances

It has been demonstrated during this research that woodchips pyrolysis can be performed in an auger reactor obtaining similar yields and product characteristics as other types of reactors such as fluidized beds [25,39]. Around 250 kg of woodchips were processed during the whole experimental campaign and, once all the devices were adapted for biomass processing, no significant incidences were detected. This proves that the design is robust and appropriate for this process. Valuable information for scaling up to a large-scale plant has been found. It can be stated that a larger reactor based on this technology could be designed whenever a minimum solid residence time of 2 minutes is ensured in order to have full biomass devolatilisation. In addition, it is important to highlight the larger particle size of the woodchips fed into the pilot plant (between 1 cm and 2 cm) comparing to the sawdust used in fluidized bed reactors. This fact provides lower energy and economic costs of biomass pre-treatment since it is an industrial product that is currently used in biomass boilers. It has also been proven that 773 K could be used as design temperature since the highest bio-oil yield is obtained and because of the non-condensed gases have a calorific value high enough to provide the energy for the pyrolysis reaction even with a slightly positive energy balance.

However, before the development of a full-scale reactor there are some points that have to be demonstrated in an intermediate scale that could not be proven in the current pilot plant. The first one is the heat transfer to the reactor. Pyrolysis is a thermal process that requires a significant amount of energy to run. In the proposed system, the indirect heating of the woodchips through the reactor wall is performed. This heat transfer mechanism can be appropriate for pilot reactors but it has to be proven for large reactors where the amount of energy to be transferred is considerably higher but the increase of the area for heat transfer is not so high due to geometrical constraints. The second issue that has to be addressed is the moisture content of the raw material. During the experimental campaign it was possible to have stabilised biomass with low moisture content (around 7%). However, in a full scale plant the inlet biomass will have a higher moisture content that not only will consume energy during the evaporation process but also it will be transferred to the bio-oil decreasing its calorific value. Therefore, it is necessary to implement and integrate appropriate drying system to ensure low moisture content in the feedstock. Once these two issues could be demonstrated, it could be concluded that the biomass pyrolysis process based on auger reactors could be a strong competitor of the current fluidised bed reactors used in biomass fast pyrolysis.

Hence, in order to address these concerns, mass and energy balances of the pyrolysis process in the present auger pilot plant and in a scaled-up plant (1500 kg/h) are carried out in the following section using Aspen HYSYS® simulation software [61].

7.4.1. Mass and Energy Balances

Process mass and energy balances are carried out to compare the energy inputs and outputs from the pyrolysis process performed in the pilot plant. As stated in section *2.2.4. Experimental modelling*, several objectives are aimed with these simulations:

- to determine the mass and energy balances in the present auger reactor pilot plant (15 kg/h)
- to design a scale-up pyrolysis plant with a capacity of 1500 kg/h of biomass; and, consequently:
- to determine the energy and mass balances of the 1500 kg/h pyryolsyis plant
- to evaluate the process performance varying the moisture content of the biomass, the drying efficiency and changing the carrier gas from nitrogen to air, as sensitivity analysis.

To simulate biomass pyrolysis in HYSYS®, it is necessary to insert empirical formulas, molecular weights and enthalpies of combustion and formation for the biomass and the products obtained from the process (solid, liquid and gas fractions). The experiment basis to perform the process simulation was the one carried out at 773 K, with a mass flow rate of 3.9 kg/h and a solid residence time of 5 min. Table 26 shows the bio-oil ultimate analysis and char proximate analysis used to calculate the empirical formulas.

While the empirical formulas of the biomass, the solid fraction and the bio-oil were calculated from the chemical composition (ultimate and proximate analysis), the gas composition was determined by gas chromatography coupled with a TCD. Table 27 shows the gas composition of the non-condensable gases.

Molecular weights were determined by the empirical formula. Enthalpies of combustion were calculated from the molecular weight and the heating value of each fraction, which was determined experimentally. Finally, the enthalpy of formation was calculated from the enthalpy of combustion and the empirical formula (see Table 28).

Table 26. Proximate and ultimate analyses and calorific value of bio-oil and bio-char samples.

	Biomass	Bio-oil	Bio-char
Ultimate analysis (%wt db[1])			
Carbon (C)	46.5	61.1	77.7
Hydrogen (H)	6.2	7.0	3.3
Nitrogen (N)	0.1	0.1	0.3
Oxygen (O) [2]	47.2	31.8	18.8
Proximate analysis (%wt db[1])			
Moisture	9.4	-	2.4
Ash	0.9	-	2.8
Volatile matter	73.5	-	24.8
Fixed carbon	16.1	-	70.0
LHV (MJ/kg)	18.0	23.9	27.3

[1] Dry basis

[2] Calculated by difference

Table 27. Composition of the non-condensable gases.

Compound	(g/g biomass)*100
H_2	0.02
CO_2	12.13
CO	7.26
CH_4	0.84
C_2	0.22
C_3	0.19
C_4	0.44

Table 28. Empirical formulas, molecular weights and enthalpies of combustion (H_{comb}) and formation (H_{for})for the biomass, bio-oil and char.

Compound	Empirical formula	H_{comb} (MJ/kg)	H_{for} (MJ/kg)
Biomass	$C_{469}H_{659}O_{287}N$	-19.1	-5.2
Bio-oil	$C_{571}H_{624}O_{132}N$	-26.8	-4.4
Char	$C_{336}H_{155}O_{45}N$	-28.8	-1.9

Once the mass flows are determined, the pilot plant design is modelled (see Figure 52) with the objective of performing the simulation. As mentioned above, an initial 3.9 kg/h mass flow rate was set, which consists of organic matter (93.40%); moisture content (6.21%) and ash (0.39%). The pyrolysis reactor was set to produce the following yields at 773 K: 57% of bio-oil and 26% of char (according to the experimental results, see Table 19), and the gas yield at 17% (calculated by mass balance). A water flow of 0.25 m^3/h is used to condense the bio-oil. Non-condensable gases are burnt in the combustor, where the temperature of the flue gas after combustion was fixed at 1073 K. Considering that the reactor is kept at a constant temperature of 773 K, it is assumed that the gases that have been used to heat the reactor are at a temperature at least 300 K above it. Subsequently, both the energy required to perform the pyrolysis and the energy from the exhausting gases are obtained from the energy flows. The difference between these two values ($E_{balance}=E_{gascombustion}-E_{pyrolysis}$) results in the energy balance of all the process. Should be noted that in the existing plant, and thus in the simulation process, the flue gas from the gas combustion chamber is not recirculated into the process, generating a loss of a potential energy flow.

The results obtained from the HYSYS® process simulation showed that the energy required in the pyrolysis reactor is 5230.77 kJ/kg, while the energy released from the combustion gases is 832.05 kJ/kg. This fact means that the calorific value that can be obtained from the combustion gases is not enough to provide the sufficient energy to the pyrolysis process. Thus, extra energy requirements must be fulfilled in order to perform the process and this should be addressed in further industrial developments. As it was stated before, recirculating the gas flow is one of the major issues that must be addressed, even though the energy that can be obtained from the gas is not enough to maintain the energy balance positive of the overall process.

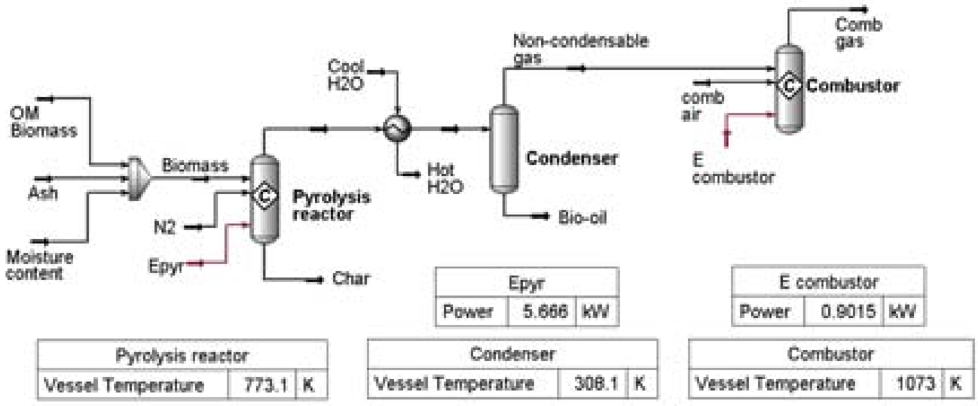


Figure 52. HYSYS® simulated installation diagram.

7.4.2. Design and simulation of a 1500 kg/h mass flow rate pyrolysis plant

Following the simulation of the original pilot plant, additional simulations have been carried out in order to evaluate the process performance of a larger plant (1500 kg/h). Extra requirements are planned in this new design, such as a drying unit or a char combustor, which are further described in this section. The new design also incorporated all the equipment necessary, such as induced draft fans, pumps and coolers and a heater, to perform the simulation as real as possible. Moreover, energy integration was one of the key parameters considered in the new design.

A drying unit was designed since the objective of the mobile plant is to use it in remote locations and to be fed with forest biomass. The moisture content of the biomass considered was 30 %, which corresponds to the amount of moisture that the biomass has once harvested from the forest and air-dried for three months [8]. The ash content of the biomass was 0.39 %. After the drying unit, the pyrolysis reaction was fixed at 773 K and applying the same product yields from the previous section. The nitrogen flow was set at 15 kg/h to avoid reflux, although the gas fraction moves by natural convection with the help of a fan. The char obtained from the pyrolysis was set to be cooled to avoid reactivity. The refrigerator used in the condenser is water, which is refrigerated by means of an air cooler. Besides the drying unit for biomass and the refrigeration unit for char, the flue gas produced in the combustion of non-condensable gases was set to be recycled to take advantage of its energy. The temperature of the non-condensable gases was 323 K and 440 K in the inlet of the gas combustor. The gas flow from the combustion gases is recirculated into the drying unit, previously being cooled by air to decrease the initial temperature of 923 K to 503 K.

Owing to the pilot plant showed not to be thermally autonomous, the new design was planned to incorporate a char combustor to supply the energy requirements of the process (see Figure 53). The char is a by-product of the process that does not have such high value-added properties as bio-oil. Hence, it is the best option to provide the energy to achieve process self-sufficiency. The temperature of the char combustor was set at 1125 K.

Thus, taking into account all the flows, the intention was to simulate a process as real as possible, which will help to the future design of the plant.

Results showed that, assuming all the conditions explained above, it is necessary to burn at least the 31% of the char produced to make the process thermally autonomous. If the percentage of char combusted is 31 %, the difference between the energy required for the pyrolysis and the energy released from the gases combustion and, therefore, the energy balance is 33 kJ/kg.

In addition, even the process being thermally autonomous, an additional amount of power would be needed in order to supply the energy consumption associated with auxiliary equipment for the pyrolysis plant (pumps, fans, etc.). This energy consumption is estimated as 43.6 kW of power, which represents 105 kJ/kg of biomass. An auxiliary generator, probably linked to the machinery involved in the process, could provide this power.

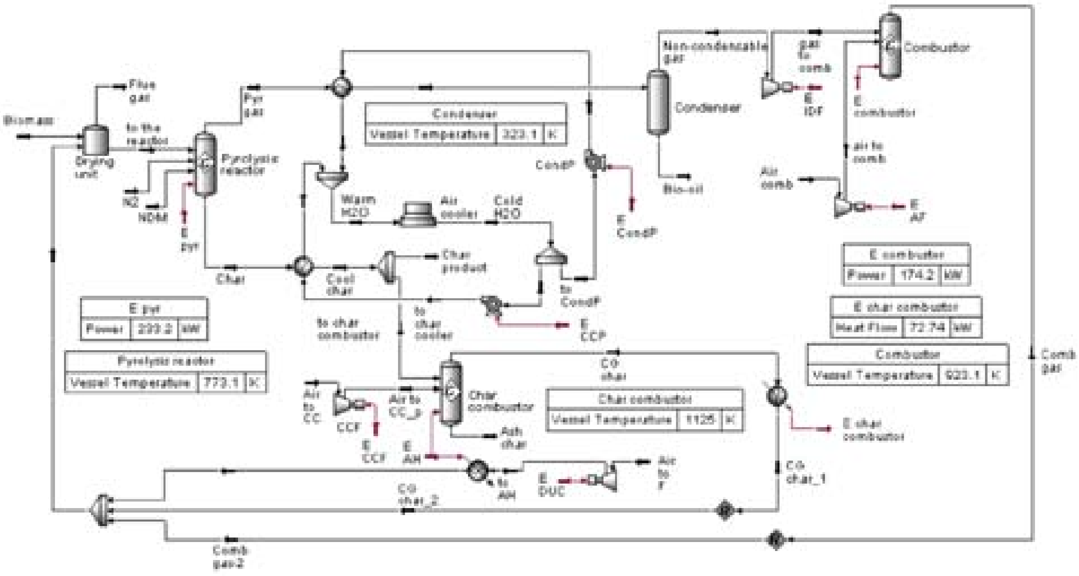


Figure 53. HYSYS simulation of a 1500 kg/h plant.

Furthermore, three sensitivity analyses were performed to assess the effect of the moisture content, the drying efficiency and the use of air instead of nitrogen on the overall process.

Figure 54 shows the sensitivity analysis of the effect of the moisture content on the pyrolysis products. Processing biomass with moisture content equal to or less than 6 % would not require using the char combustor. This relatively low amount of moisture content could only be achieved in very dry and windy zones. For instance, the samples pyrolysed in the pilot plant (see section 7.2.1. Feedstock) were air-dried and had 6.2% moisture content. As it can be observed, when the moisture content is up to 45 %, the amount of char needed to be burnt in the combustor to achieve thermal self-sufficiency is 52%. In the likelihood of having 30 % of moisture content, the 31 % of the char produced would be needed. This fact allows strategies as bio-char bioenergy, since an extra amount of char (up to 69%) can be used as carbon sink [3].

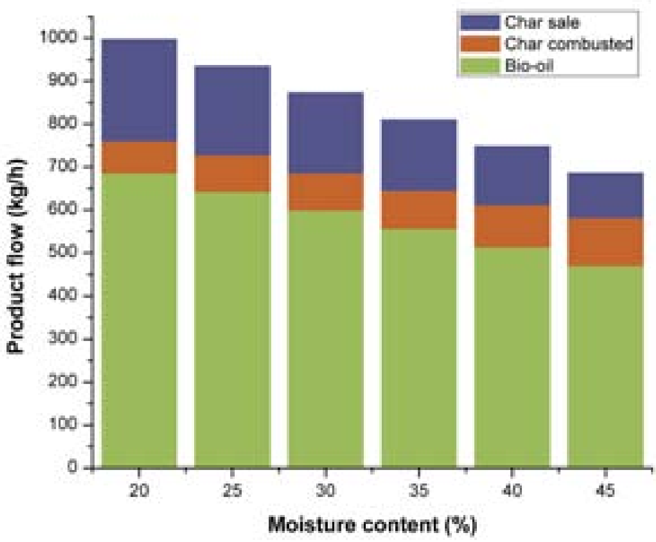


Figure 54. Sensitivity analysis of the effect of the moisture content on the pyrolysis product yields.

Next step was to study the efficiency of the drying stage, assuming a 30 % of moisture content and hence, a 31 % of char combusted. Results showed (see Table 29) that below the 97.2 % of drying efficiency, there is not enough energy to perform the process. If drying efficiency is 95%, it would be needed to combust 34% of char.

Table 29. Effect of the drying efficiency to the pyrolysis process. ***(E_{pyr}: Energy required to perform the pyrolysis; E_{comb}: Energy released from the gas combustion).***

Drying efficiency (%)	$E_{gas\ comb}$ (kJ/kg)	$E_{char\ comb}$ (kJ/kg)	E_{pyr} (kJ/kg)	$E_{balance}$ (kJ/kg)
100.0	418.19	174.57	559.67	33.08
97.5	410.73	174.57	581.63	3.66
95.0	403.26	174.57	603.59	-25.76

Finally, changing the carrier gas from nitrogen to air is evaluated. No significant differences can be observed from changing nitrogen to air as carrier gas and the energy balance at 100% of drying efficiency is 33.3 kJ/kg of biomass (see Table 30). The drying efficiency threshold is the same that using air than nitrogen (97.1%).

Table 30. Effect of the drying efficiency to the pyrolysis process changing the nitrogen to air as carrier gas. ***(E_{pyr}: Energy required to perform the pyrolysis; E_{comb}: Energy released from the gas combustion).***

Drying efficiency (%)	$E_{gas\ comb}$ (kJ/kg)	$E_{char\ comb}$ (kJ/kg)	E_{pyr} (kJ/kg)	$E_{balance}$ (kJ/kg)
100.00	418.28	174.57	559.58	33.26
95.00	410.81	174.57	581.54	3.84
90.00	403.35	174.57	603.50	-25.58

7.5. Economic feasibility of bio-oil production

In this section an economic assessment of the scaled up of the pilot plant (1500 kg/h) is carried out by means of cost and benefit analysis and economy indicators explained in section *2.1.3. Economic tool: cost and benefit analysis* from Chapter I.

The scenario that is going to be evaluated is shown in Figure 55 and consists of harvesting the forest biomass, which comprises three stages (felling, delimbing and hauling), transporting the logs to a buffer storage where the mobile pyrolysis plant would be located, chipping the biomass and finally converting it to bio-oil.

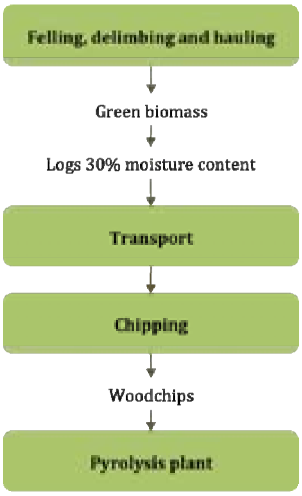


Figure 55. Biomass system analysed to perform the economic assessment.

7.5.1. Forest harvesting costs

Forest harvesting is performed by three stages:

(1) Felling: is the process of downing individual trees.

(2) Delimbing: is the process of removing branches from the stem of a felled tree.

(3) Hauling: is the pulling stage to collect and locate the biomass next to the forest road.

In this case, a Mediterranean typical procedure is accounted. It consists of a total of 3 workers, 2 of which work with a chainsaw to process the biomass (felling, delimbing and hauling). The other worker is engaged respectively to operate the skidder.

Table 31. Main economic parameters taken into account in this analysis.

Component	Parameter	Units	Chainsaw	Skidder
Model			STIHL MS 360	TIMBERJACK 360D
Purchase price	P	€	666.38	142740.00
Resale price	RP	€	0	28548
Depreciated price	Pa	€	-	121329
Machinery life time	H	hours	2500	10000
Machinery lifetime in years	N	years	3	6
Interest rate	ir	per unit	0.04	0.04
Engine power	Ne	CV	4.6	127
Gasoline price	p	€/l	1.00	-
Gasoil A price	p*	€/l	-	0.91
Fixed Cost				
Amortization	D	€/h	0.27	9.28
Interest	I	€/h	0.02	2.03
Insurance and Taxes	IT	€/h	0	0.12
Variable Cost				
Fuel cost	F	€/h	1.71	13.90
Lubricant oil	O	€/h	0.51	2.08
Spare pieces	S	€/h	0.12	1.58
Maintenance	M	€/h	0.21	5.71
Labour cost	**LC**	€/h	**9.14**	12.91
TOTAL COST	**TC**	**€/h**	**11.98**	**47.61**

Source: Purchase prices and variables from [62]; oil prices from [63].

Taking into account the working processes, the total cost of harvesting biomass per hour is 71.57 €/h (see Table 31). This price represents **22.90€/green ton**, considering the average amount of biomass that can be harvested per day (25 green ton/day). This data is similar to the data published for the Forest Technology Centre of Catalonia, which sets a range from 20-24 €/green ton [64]. This price does not include any of the transportation stages, so it is considered stacked wood located roadside.

7.5.2. Supply and logistics

a) Forest biomass required as fuel for a pyrolysis plant

Biomass requirements to feed into the pyrolysis plant of 1500 kg/h are 12 tons/day (30% of moisture content) considering 8 hours of labour per day. The total amount of biomass required in the plant is 3600 tons the first year (300 working days per year) and 3840 tons the following years (320 working days per year).

b) Forest biomass area required to provide 12 tons/day

To calculate the forest biomass area that can supply the biomass requirement for the pyrolysis plant, it is considered that an average of 25 tons of fresh biomass can be harvested for each hectare in Mediterranean forests [64]. This means that 10 km^2 is the optimum forest area necessary to be harvested. That makes, considering an optimum circle, a radius of 1.8 km, which is quite small. An average journey of 5 km is taken into account to assess the transport costs of transporting logs from the forest to the mobile plant.

c) Number of trucks and trips required to feed the pyrolysis plant

The biomass transport considers the transport from roadside to the buffer storage, where the mobile pyrolysis plant will be located.

The number of trucks needed daily to supply a biomass plant is defined by the bulk density of the material transported. In the case of the logs the density is approximately 580 kg/m^3 (30% moisture content) [65]. The type of truck normally used in forests to transport biomass is a three-axle rigid truck with a maximum permissible mass of 26 tons and a payload of 16 tons[1]. For this reason, when transporting logs, the weight is the limiting factor.

Less than one truck is needed to feed the pilot plant (12 Tons/day), taking into account the limiting payload of 16 tons. This makes a need of 225 trips per year to feed the plant. The distance is assumed to travel off-road and it is considered a return trip time of 30 min, a loading time of 48 min and unloading time of 20 min.

To calculate the fuel consumption of the vehicles the mathematical expressions detailed in section *4.3.2. Biomass transport* are used (see Equation 21 and 22). Applying maximum payloads for this truck, the average fuel consumption is 0.33 l/km for transporting logs. Next, this fuel consumption has been applied to the software ACOTRAM 2.2.1, from the Development Ministry of the Spanish Government [66]. ACOTRAM is a computer application that offers the calculation of operating costs of vehicles transporting goods by road, taking into account all the parameters need. The fuel price is obtained from the average price published by the Development Ministry [63], which is 0.912 €/l in 2009. The variables and the price of transporting biomass can be observed in Table 32.

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[1] **Maximum permissible mass** according to Spanish legislation R.D.2822/1998 (BOE num. 22, art.14 "masas y dimensiones" (anexo 9, pg.146)).

Table 32. Economic values for the transport of logs.

Component	Unit	
Purchase price	€	72329.46
Working days	Days	300
Working hours per year	hours	2000
Annual mileage	km	95000
Lifetime in years	year	10
Fuel consumption	l/km	0.33
Insurance and taxes	€/year	5811.37
Maintenance	€/km	0.0356
Labour cost	€/year	**25580.41**
TOTAL COST per truck	**€/h**	**48.19**

Source: Data from [66], fuel consumption own data.

7.5.3. Mobile pyrolysis plant

The mobile pyrolysis plant should be located in buffer storage next to the forest, in order to minimize the biomass transport costs. Once the surrounding biomass would be harvested, the mobile plant would change its location. Following it is presented the economic assessment of the buffer storage, where the biomass would be converted to woodchips, and of the mobile pyrolysis plant.

a) Buffer storage

The buffer storage allows first drying the biomass. Then, the logs are chipped and stored under cover to finish the drying stage and ensure supply. A tractor and a chipper are needed to perform the chipping stage. Their economic values are shown in Table 33. This price per hour, assuming a chipper performance of 40 m^3/h, represents 2.4 €/ton of biomass, which are similar to the ones reported in literature [67].

Table 33. Economic values for the chipping in the buffer storage.

Component	Parameter	Units	Tractor	Chipper
Model			Valtra Mega 8150	Jenz Hem 561Z
Purchase price	P	€	52637	145000
Depreciated price	Pa	€	-	116000
Resale price	RP	€	10527.4	0
Machinery life time	H	hours	10000	10000
Machinery lifetime in years	N	years	6	6
Interest rate	ir	per unit	0.04	0.04
Engine power	Ne	CV	240	-
Gasoil B price	p*	€/l	0.62	-
Fixed Cost				
Amortization	D	€/h	4.21	11.6
Interest	I	€/h	0.21	1.1
Insurance and Taxes	IT	€/h	0.12	-
Variable Cost				
Fuel cost	F	€/h	9.96	0.00
Lubricant oil	O	€/h	1.46	1.05
Spare pieces	S	€/h	0.93	0.40
Maintenance	M	€/h	3.68	8.41
Labour cost	**LC**	€/h	**12.91**	
Operative cost		€/h	34.52	21.06
TOTAL COST	**TC**	**€/h**	**55.6**	

Source: Purchase prices and variables from [62] and [68], oil prices from [69].

b) Energy conversion: mobile pyrolysis plant

The typical yields assumed of the mobile pyrolysis plant in this study are 57% for bio-oil production, 17% of non-condensable gases and 26% of charcoal and obtained from the experimental tests (see Table 19). The plant lifetime is accounted as 15 years and, as mentioned above, 8 working hours per day, 300 working days the first operational year and the rest of the lifetime 320 working days per year. The production of bio-oil would be the first year of 1753 m^3 and the following years 1871 m^3 per year.

A compilation of pyrolysis plant costs has been described by Bridgwater et al. [70] and follows the equation:

$$TPC = 40.8 \times (Q_h \times 1000)^{0.6194} \qquad \text{(Eq. 26)}$$

where, TPC is the total plant cost of the pyrolysis reactor system (€) and Q_h is the mass flow rate of prepared wood feed into the reactor (odt/h)

Moreover, the costs of the pyrolysis liquid storage tanks and transfer pumps must be taken into account, which have been described by Bridgwater et al. [70]:

$$TPC_{storage} = 119 \times (Q_h)^{0.4045} \qquad \text{(Eq. 27)}$$

where TPC is the total plant cost of liquids storage (€) and Q_h is the mass flow rate of prepared wood feed into the reactor (odt/h)

Heat for the process is supplied by combustion of the part of the char and off-gas in an external combustion chamber. It is considered that the 50% of the gross char production is consumed to provide the heat demand for the process and the 100% of the non-condensable gas production supplies the heat demand of the pyrolysis process (see section simulation).

Labour requirements are calculated from Bridgwater et al. [70], which in turn, adaptated from Beckam and Graham the following equation based on the estimates for the operation of an Ensyn transported bed fast pyrolysis plant:

$$Labour = 1.04 \times (Q_h)^{0.475} \quad \text{(Eq. 28)}$$

where Q_h is the mass flow rate of prepared wood feed into the reactor (odt/h).

A total of two workers are considered in this study for safety reasons, although only one person is required to carry out the process.

A 2% of operation and maintenance (O&M) of the capital costs is assumed, which is widely reported in literature [70].

7.5.4. Final biomass cost

Biomass harvesting, transportation and chipping costs are shown in Table 34. The biomass cost at plant is of 42.53 €/ton of 30% moisture content biomass.

Table 34. Feedstock cost at plant.

Operation	€/year	€/ton biomass (30% moisture content)
Harvesting	126839	35.23
Transport	17710	4.92
Chipping	8624	2.40
Total	**153172**	**42.55**

7.5.5. Economic assessment of the mobile pyrolysis plant

Table 36 shows the cost assessment of the pyrolysis plant at 5% interest rate, taking into account all loan refunds, financial costs at 5% interest rate, insurances (1% of the immobilized capital) and taxes (30% of the benefits without taxes). These variables are set considering the most conservative hypothesis to avoid overestimation. Fixed costs consist of the sum of depreciation, insurance and loan refunds. Variable costs include labour, operational and maintenance costs and the cost of the biomass.

The plant capital costs are 3155157 €, which is calculated from Equation 26. This investment cost is considered to be a good approximation, since it is close to a budgetary price for an auger reactor pilot plant built by Spirojoule, although the data is proprietary and cannot be reproduced.

Bio-oil revenues are calculated assimilating bio-oil as fuel oil. The heat content of bio-oil (23.94 MJ/kg, see Table 26) is 59% that of fuel oil (40.90 MJ/kg). Therefore, one must burn 1.7 kg of bio-oil to obtain the same amount of energy as released when burning 1 kg of fuel oil. Considering the current price of fuel oil (data of June 2010 in Catalonia), the price of bio-oil is accounted as 422.13 €/m^3.

First, a scenario without any debt and any financial charges is considered. The results of this scenario, where the investor assumes all the investment costs, are shown in Table 35. As it can be observed, the pilot plant is economically feasible at all biomass costs since NPV and IRR values are positive, although somewhat low so the investment is not really attractive considering the fixed revenue price.

Table 35. Economic assessment of the 12 Tn/day pyrolysis plant under a no-debt scenario.

		Biomass cost				
		10 €/ton	20 €/ton	30 €/ton	40 €/ton	50 €/ton
Capital cost	€/year	3155157	3155157	3155157	3155157	3155157
Fixed Costs						
Depreciation	€/year	210344	210344	210344	210344	210344
Insurance costs	€/year	15776	15776	15776	15776	15776
Variable costs						
Labour costs	€/year	60000	60000	60000	60000	60000
O&M	€/year	63103	63103	63103	63103	63103
Total costs	€/year	387633	426023	464423	502823	541223
Total costs	€/m^3	207	228	248	269	289
Revenues	€/year	789703	789703	789703	789703	789703
NPV	€	1918260	1640855	1363450	1086044	808639
IRR	%	13.0	11.9	10.8	9.7	8.6

Moreover, in a more likely scenario where the investor assumes 30% of the investment cost and the rest is financed by a bank, the feasibility assessment is more positive (see Table 36). The IRR at 40 and 50€/ton of biomass cost range from 20 to 17%, so the investment is attractive from the point of view of the investor. Under these considerations, the maximum price at which the biomass can be purchased is 72 €/ton, which is higher than the assessed one (42 €/ton).

Table 36. Economic assessment of the 12 Tn/day pyrolysis plant assuming a leverage investment.

		Biomass cost				
		10 €/ton	20 €/ton	30 €/ton	40 €/ton	50 €/ton
Capital cost	€/year	3155157	3155157	3155157	3155157	3155157
Fixed Costs						
Depreciation	€/year	63103	63103	63103	63103	63103
Insurance costs	€/year	15776	15776	15776	15776	15776
Loan refunds	€/year	147241	147241	147241	147241	147241
Variable costs						
Labour costs	€/year	60000	60000	60000	60000	60000
O&M	€/year	63103	63103	63103	63103	63103
Total costs	€/year	387633	426023	464423	502823	541223
Total costs	€/m^{3}	207	228	248	269	289
Revenues	€/year	789703	789703	789703	789703	789703
NPV	€	2122351	1844945	1567540	1290135	1012730
IRR	%	28.5	25.7	22.9	20.0	17.0

In addition to the cost accounting of the pyrolysis plant, the break-even point (BEP) is calculated in the scenario of 50 €/ton of biomass. The break-even point is the point at which cost and revenue are equal or, what is the same, there is no net gain or loss. Figure 56 shows the BEP for different bio-oil prices when the cost of the biomass purchased is 50 €/ton. In order to study the BEP and see the influence in the cost assessment of the bio-oil price and the plant capacity, several assessments with two plant capacities (1500 and 2500 kg/h) are carried out. In the case of the 1500 kg/h pyrolysis plant, the cost per barrel of bio-oil should be 116 €/barrel, while in the case of the 2500 kg/h pilot plant, the cost per barrel is 100 €/barrel. When the biomass is purchased at 40 €/ton, the BEP in a 1500 kg/h pyrolysis plant is at 108 €/barrel and in a 2500 kg/h plant at 91 €/barrel (see Figure 57). Therefore, the price of the biomass is not the most important variable in cost accounting, since depreciation and loan refunds are the most influential parameters in the final cost.

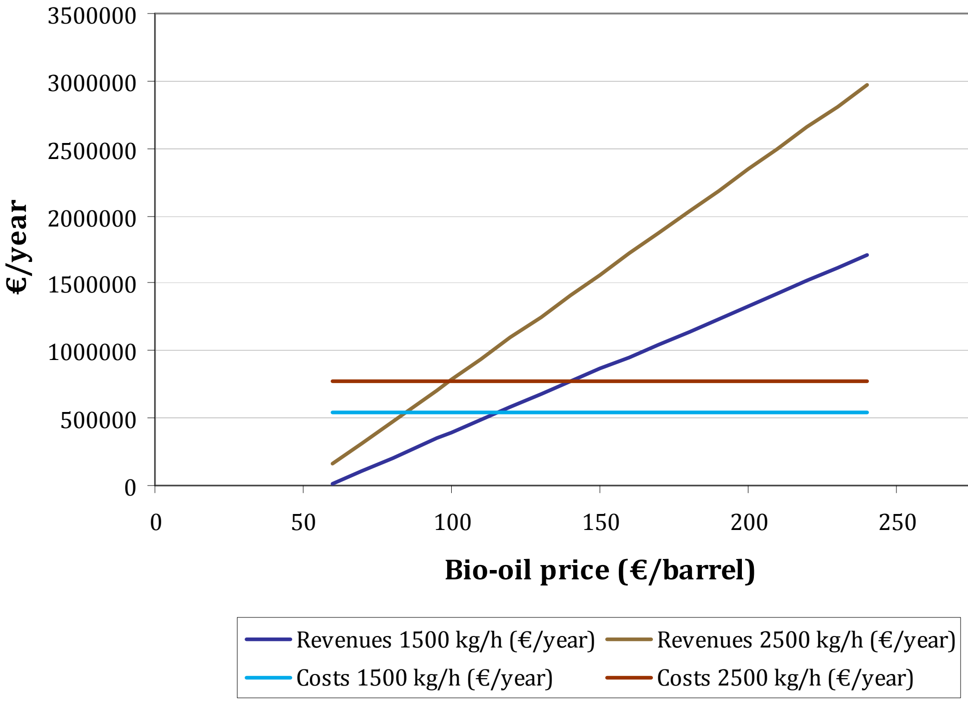


Figure 56. Break-even point of the pyrolysis plant with different capacities when biomass is purchased at 50 €/ton.

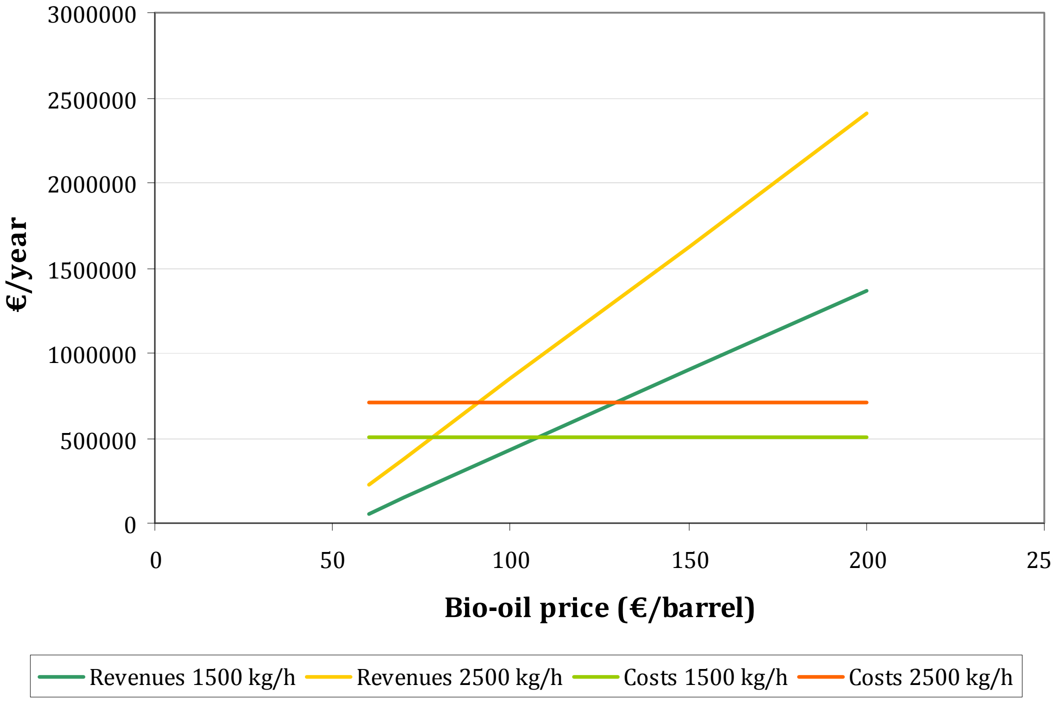


Figure 57. Break-even point of the pyrolysis plant with different capacities when biomass is purchased at 40 €/ton.

In Figure 58 the BEP can be observed when different capacities (kg/h) of pyrolysis plants are considered when the biomass is purchased at 50 €/ton and the bio-oil price set at 116 €/barrel. In this case, the capacity of the plant should be larger than 1500 kg/h to avoid net loss. Thus, higher capacities than 1500 kg/h should be considered under these considerations, due to the above-mentioned BEP for bio-oil prices.

As it can be observed, the bio-oil price is still not comparable to the Brent crude oil barrel, which in 2009 cost 48.80 €/barrel and neither it is when compared to 2008 oil prices, when the barrel cost 76.95 € [63]. However, it should be noted that bio-oil is susceptible to be subsidized due to it is obtained from renewable sources, a fact that has not been taken into account in the conservative hypothesis followed in the assessment.

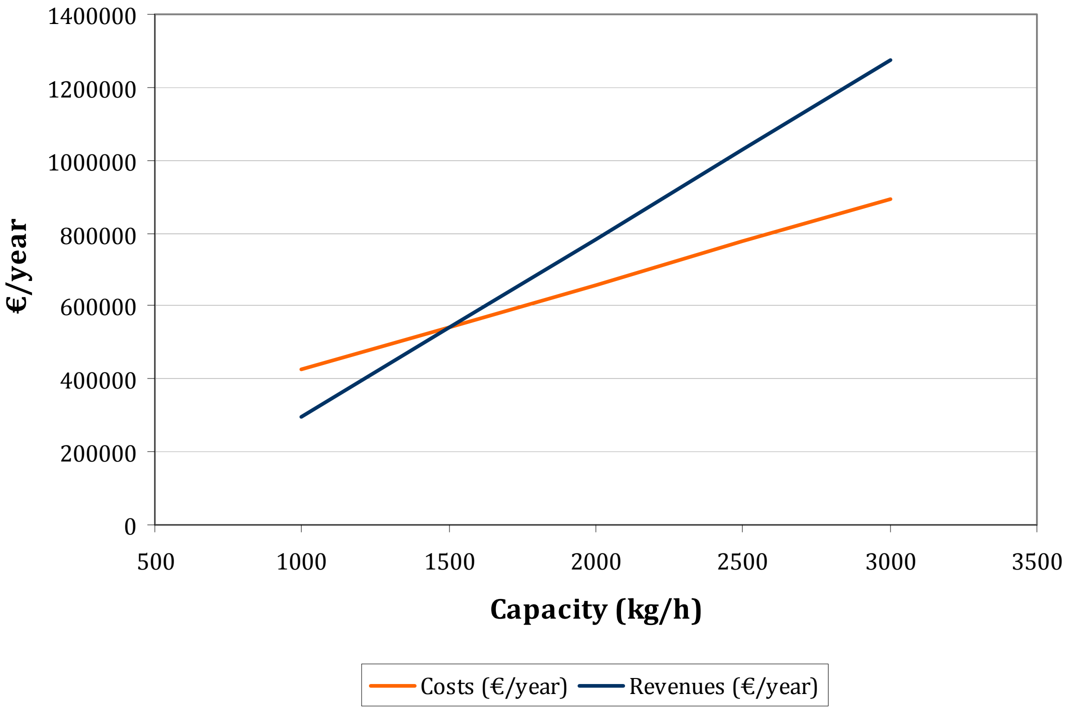


Figure 58. Break-even point of a pyrolysis plant with different capacities when bio-oil is purchased at 116 €/barrel.

7.5.6. Sensitivity analysis

A sensitivity analysis is performed in order to study the option of operating the plant with two shifts, that is, 16 working hours per day, and the influence of the bio-oil price on the feasibility of the plant (see Table 37). This analysis is carried out under the consideration that the 30% of the investment is assumed by the investor and the rest by financing entities.

Even though the main purpose of the plant is operating it as a mobile plant, there is the possibility of installing medium-scale pyrolysis plants scattered in the territory. This plants, could operate in two shifts, so four people would be needed for operating the plant. These plants could process 24 tons of biomass/day, which is a total amount of 7680 tons per year, and produce 3742 m^3 of bio-oil per year. This possibility increases outstandingly the profitability of the plant, as Table 37 shows. The internal rate of return is from 55.6% when the biomass is purchased at 50 €/ton and rises onwards when the biomass purchase price decreases. In this scenario, the break-even point is 85 €/barrel when the biomass is purchased at 50€/ton and 77 €/barrel when it is purchased at 40 €/ton. This fact reveals the highest profitability compared with the scenario of 8h per day operating plant, as well as a closer price to the Brent barrel.

The bio-oil price plays a fundamental role on the overall assessment. The initial bio-oil price was set at 422.13 €/m^3 according to the hypothesis above-mentioned. If the bio-oil price is increased 20%, the biomass can be purchased up to 144 €/ton. Considering the realistic scenario of 40-50 €/ton, the IRR would rang between to 32% and 29% respectively.

Table 37. Sensitivity analyses on the economic assessment of the 12 Tn/day pyrolysis plant.

		Biomass cost				
		10 €/ton	20 €/ton	30 €/ton	40 €/ton	50 €/ton
Two-shift operating plant						
Revenues	€/year	1579408	1579408	1579408	1579408	1579408
NPV	€	7113894	6559084	6004273	5449463	4894652
IRR	%	77.0	71.7	66.3	60.9	55.6
Increase 20% bio-oil revenue						
Revenues	€/year	947645	947645	947645	947645	947645
NPV	€	3263329	2985924	2708519	2431114	2153709
IRR	%	39.8	37.0	34.3	31.6	28.8

7.6. Conclusions for the biomass pyrolysis in an auger reactor

The objective of this section was to assess the performance of an auger reactor pyrolysis plant using forest woodchips as feedstock and to determine the yields and properties of liquid, char and gaseous products obtained under different reaction temperatures (from 1073 to 773K), solid residence times (5, 3, 2 and 1.5 min) and mass flow rates (3.9, 4.8 and 6.9 kg/h). It has been demonstrated that biomass woodchip pyrolysis can be successfully achieved in an auger reactor under experimental conditions close to the operation range of parameters of possible industrial scale plants (continuous operation, moderate temperature and low solid residence time). Results showed that, comparing temperature, solid residence time and mass flow rate; temperature was the most influential parameter.

In the range studied, 773 K offers the most valuable yields and product characteristics for liquid production. It has been confirmed that solid residence times longer than 2 minutes are needed in order to reach complete conversion. This lower temperature implies lower energy and environmental costs, which were high when performing forest biomass gasification, as it was studied in Chapter III.

No significant differences were found between the various operational conditions studied, on the collective physical properties of the bio-oils analysed, neither after changes in the reactor temperature nor in the solid residence time or the mass flow rate. Qualitative identification carried out by GC/MS showed that the most abundant compounds are volatile polar compounds, which mainly included carboxylic acids, ketones, aldehydes and monolignols, which were formed of phenols and benzenediols (pyrocatechol). A higher reaction temperature in the pyrolysis process led to an increase of aromatic compounds, mainly formed by PAH such as naphtalene or biphenyl. It was also observed that longer residence times influence the char characteristics. On the other hand, it has been observed that biomass flow rate slightly affects the process in the range studied.

Finally, this study shows that the auger reactor produces a standard bio-oil comparable to other auger reactors and similar to other bio-oils from other reactors. This bio-oil can be used as an energy vector and, in a future biorefinery scenario, to produce chemicals such as acetic acid or levoglucosans.

Relating to the mass and energy balances, taking into account product yields and compositions from experiments carried out at 773K and at a mass flow rate of 3.9 kg/h, simulation results show that the pyrolysis process is not thermally autonomous, since the energy of the released gases is not sufficient to fulfil the pyrolysis energy requirements. In order to have a positive energy balance, a new design of the pilot plant is conceived and simulated. The new design incorporates a char combustor to supply the energy needs of the process and a drying unit since the biomass fed into the reactor is intended to be forest biomass, which has at least 30% of moisture content. Simulations show that the amount of char needed to burn to have a positive energy balance is at least 31% of the char produced. If biomass has moisture content lower than 6%, the process is energy-independent and the char combustor is not necessary.

Sensitivity analyses show the moisture content of the biomass should not exceed the 45%, since from this quantity value the biochar for sale as charcoal or value-added strategies such as using the bio-char as carbon sink would not be recommended. The drying efficiency should be above 97% to maintain the process energy positive. On the other hand, using air as carrier gas instead of nitrogen shows no significant differences in terms of energy balance and, thus, would be worthy using air due to nitrogen costs.

Finally, this study shows that the scaling-up of the pilot plant is only feasible when an additional char combustor is incorporated in order to keep the energy balance positive. This fact sheds light on the future designing of the mobile plant and gives valuable information for the further steps that are going to be considered.

The economic assessment of the 1500 kg/h pyrolysis plant shows that this plant is profitable when the biomass cost is purchased at prices up to 72 €/ton. The total costs of producing bio-oil ranged from 207 to 289 €/m^3 depending on the biomass cost (10-50€/ton). The break-even point of the pyrolysis plant is between 108 and 116 €/barrel of bio-oil when the biomass is purchased at 40 and 50 €/ton respectively. When higher capacities are considered, such as 2500 kg/h, the break-even point ranges between 91 and 100 €/ton respectively. Setting the bio-oil price at 116 €/barrel, the capacity of the plant should be larger than 1500kg/h to avoid net losses. Moreover, if the 1500 kg/h pyrolysis plant is operated in two-shifts, that is, 16 hours per day, the profitability of the overall investment improves strikingly. The break-even point of the bio-oil price per barrel reaches 85 €/barrel when the biomass is purchased at 50 €/ton and 77 €/barrel when the biomass price is 40 €/ton. Another value-added product is the excess of bio-char that has not been used to dry the biomass (more than the 50% of the production), since it can be sold as charcoal or even used as a fertilizer, although further studies about this must be addressed.

In addition, it must be noted the lesser biomass pre-treatment needed since the particle size of biomass fed into the reactor are woodchips (2-3 cm of nominal size) and the compact design of the reactor that operates continuously with low maintenance operations. In addition to the lower energy and economic costs of biomass pre-treatment, forest woodchips with these characteristics are already an industrial product currently used in biomass boilers and no further expensive industrial developments are needed. Afterwards, the bio-oil produced as an energy vector with reduced transport costs could be directed to a centralized warehouse and initially converted into electricity and heat, but in future it also could be the input of a biorefinery.

8. A novel approach for greener processing technologies: microwave assisted dissolution of wood in ionic liquids

A novel approach for greener processing technologies is presented in this section. While pyrolysis offers significant advantages as the multiple products obtainable, other routes to process wood are foreseen in this chapter in order to study them and see the prospects of the biorefinery concept, at least in terms of using green chemistry principles. In this case, the use of ionic liquids to dissolve wood is presented.

8.1. Introduction to the microwave assisted dissolution of wood in ionic liquids

Up to the 19th century mankind used renewable resources not only for food but also for functional applications. At the turn of the century the situation changed completely, as coal became the key raw material for the production of coke, ammonia, tar, and gas. Finally, the developments and improvements in the area of fossil oil processing resulted in today's chemical industry mainly based on oil and natural gas.

Apart from thermochemical processes, such as gasification or pyrolysis that have been previously studied in Chapter III and in the preceding section respectively, another parallel strategy is converting biomass into value-added products [71-74]. More than 300 compounds have been identified from the basic components of biomass: phenolic fraction; acetic acid, acetone and liquid alkans. Thus, obtaining chemicals from biomass resources is one of the most interesting ways of applying the framework of environmental-friendly biorefineries. It is necessary to develop sustainable sources to compensate for a future shortfall and for increasing costs of petro-derived aromatic platform molecules. Shifting society's dependence away from petroleum to renewable biomass resources is generally viewed as an important contribution to the development of a sustainable industrial society and effective management of greenhouse gas emissions [72], as it has already been discussed in the previous chapters.

Hence, a first step is to separate the biomass components (cellulose, hemicellulose and lignin) to make use of them individually later on. In this respect, ionic liquids are considered biomass green solvents that can offer large opportunities for pulp and wood industries. The potential of ionic liquids as environmentally-friendly solvents is being studied widely and it has been reported that they can dissolve cellulose and partially wood [75-79]. Ionic liquids are liquids at a relatively low temperature (<373 K) and they have many interesting properties such as chemical and thermal stability, non-flammability and immeasurably low vapour pressure [80,81]. Ionic liquids have also been studied as green solvents for lignin [82]. Although in the last years criticism about ionic liquids has gained ground in terms of environmental issues such as toxicity [83-88], there is much effort to achieve greener reactions with this solvent.

From both economic and environmental points of view, the magnitude of the wood conversion industries to paper and related products imposes serious challenges in the development of green processing technologies for wood and other lignocellulosic materials [89]. Therefore, fractionation of lignocellulosic materials is essential for applications such as paper-making and in their conversion into basic chemical feedstocks or liquid fuels. In this sense, the use of ionic liquids as green solvents provides a new method of fractionation [90,91], as well as chemical modifications of wood based lignocellulosic materials [92,93]. Under conventional heating methods, it has been reported that [C$_4$mim]Cl (see Figure 59) can effectively dissolve cellulose, wood and other lignocellulosic materials [75,78,89,94], which represents an opportunity for such industries to achieve cleaner and more efficient strategies.

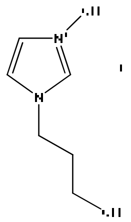
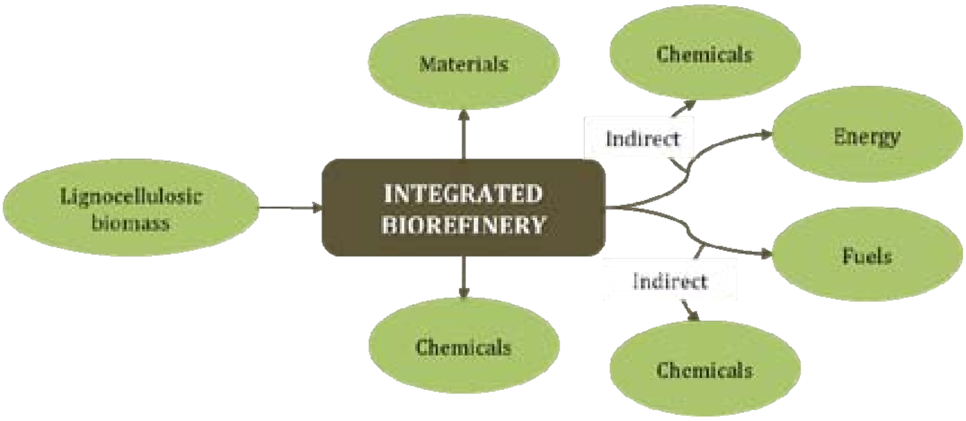


Figure 59. Structure of 1-butyl-3-methylimidazolium chloride ([C$_4$mim]Cl).

In this section it is presented the novel approach of dissolving wood using the ionic liquid 1-butyl-3-methylimidazolium chloride ([C$_4$mim]Cl) by means of microwave activation at laboratory scale. The solubility of wood under microwave activation with conventional heating methods is also compared. Finally, the recovery of cellulose from the wood sample dissolved in the ionic liquid is analysed.

8.2. The biorefinery concept

A biorefinery can be considered as an integral unit that can accept different biological feedstock and convert them to a range of useful products including chemicals, energy and materials (see Figure 60) [95]. Biorefineries are the application of green chemical technologies with the aim of developing new, genuinely sustainable, low environmental impact routes to important chemical products, materials and bioenergy.



Source: Adapted from [95].

Figure 60. The integrated biorefinery as a mixed feedstock source of chemicals, energy, fuels and materials.

Biorefineries produce different industrial products from biomass, which can be differentiated by low-value high-volume products (transportation fuels, commodity chemicals and materials) and high-value low-volume products (specialty chemicals such as cosmetics or nutraceuticals) [96]. Three different types of biorefinery have been described in the literature [96-98]:

- *Phase I biorefinery:* they use one only feedstock, have fixed processing capabilities (single process) and have a single major product. They are already in operation and are proven to be economically viable. Examples of this biorefinery are biodiesel production through transesterification; today's pulp and paper mills, and corn grain-to-ethanol plants.
- *Phase II biorefinery:* they can only process one feedstock, but they are capable of producing various end products (energy, chemicals and materials) and thus respond to market demand, prices, contract obligation and the plant's operating limits. Examples of this type of biorefinery are the plants which use corn starch to produce a range of chemical products (biodegradable polyesters and starch-derived thermoplastics), or the production of a multitude of carbohydrate derivatives.

- *Phase III biorefinery:* they are able to produce a variety of energy and chemical products (phase II biorefineries), and also use various types of feedstocks and processing technologies to produce the multiplicity of industrial products. Currently, there are four phase III biorefinery systems being pursued in research and development, which are lignocellulosic feedstock biorefinery, whole crop biorefinery, green biorefinery and two-platform concept biorefinery. The different types of phase III biorefineres are summarised in Table 38.

Table 38. Principal characteristics of Phase III biorefineries.

Biorefinery type	Feedstock	Principal technologies	Phase of development
Green biorefinery	Wet biomass: green grasses and green crops	Pre-treatment, pressing, fractionation, separation, digestion	Pilot plant (and R&D)
Whole crop biorefinery	Whole crop (including straw) and cereals (wheat, maize, etc.)	Dry or wet milling, biochemical conversion	Pilot plant (and Demo)
Lignocellulosic biorefinery	Lignocellulosic-rich biomass: e.g. miscanthus, wood, etc.	Pre-treatment, chemical and enzymatic hydrolysis, fermentation, separation	R&D/Pilot plant (EC), Demo (US)
Two platform concept biorefinery	All types of biomass	Combination of sugar platform (biochemical conversion) and syngas platform (thermochemical conversion)	Pilot plant
Thermochemical biorefinery	All types of biomass	Thermochemical conversion: torrefaction, pyrolysis, gasification, HTU, product separation, catalytic synthesis	Pilot Plant (R&D and Demo)
Marine biorefinery	Aquatic biomass: microalgae and macroalgae	Cell disruption, product extraction and separation	R&D (and Pilot plant)

Source: Adapted from [99].

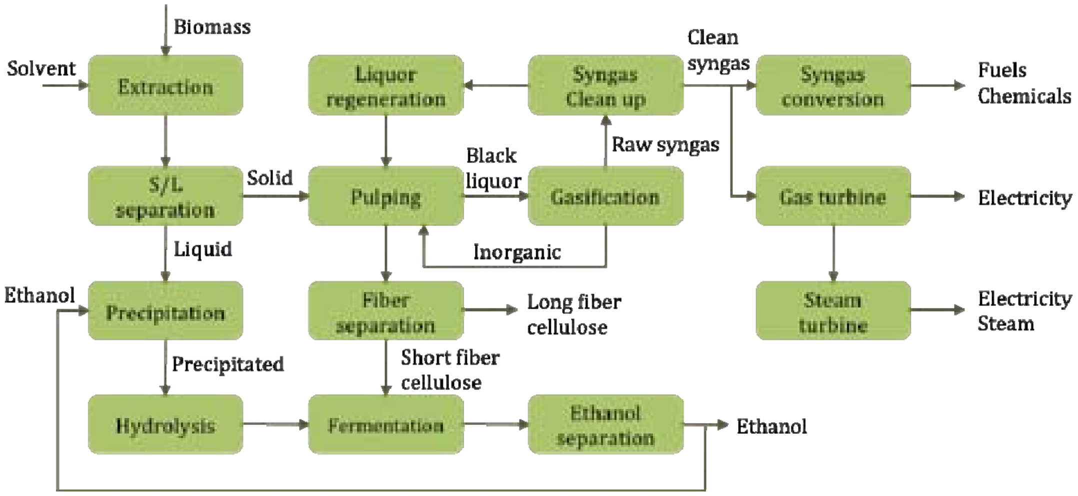
On the other hand, Dermibas 2009 [31] differentiates seven different types of biorefinerys according to their functions:

- Fast pyrolysis-based biorefineries
- Gasification based biorefineries
- Sugar based biorefineries
- Green biorefinery
- Energy crops biorefinery
- Oilseed biorefinery
- Forest based and lignocellulosic biorefinery

Regardless of the type classification of biorefineries, generally speaking they can be defined by their biomass transformation processes and the products obtained. In other words, it can be understood as a biorefinery if a pyrolysis process is applied to obtain chemicals.

If a gasification process is used within the biorefinery concept, the pyrolysis process can be continued with a Fischer Tropsch reaction (as in the case at Choren, Germany) or with hydrotreatment (as with Ensyn and Dynamotive, Canada) [100].

As described above, there are several biorefinery plants in different stage of development. In Figure 61 an integrated forest biorefinery based on the existing pulp mills is shown.



Source: [101].

Figure 61. Diagram of an integrated forest biorefinery.

Although the biorefinery concept has been widely discussed and defined, there is a need for further development of demonstration plants, which will require cross-sector collaborations and attract the necessary investors required for the construction of full-scale biorefineries [96].

Therefore, sustainable chemicals and materials can be produced applying green chemical technologies to transform biomass feedstock. The use of ionic liquid to dissolve biomass points to new opportunities in the processing wood industry, as well as a new challenge to fractionate the main constituents of biomass (cellulose, hemicellulose and lignin), which is approached in the following section.

8.3. Experimental of the microwave assisted dissolution of wood in ionic liquids

In the following section the materials and the experimental setting are detailed for the microwave assisted dissolution of wood in ionic liquids.

8.3.1. Materials

Pine wood chips of two different species: Scots pine *(Pinus sylvestris)* and Aleppo pine *(Pinus halepensis)* were used as raw material for the experiments, whose proximate and ultimate analysis and calorific values are shown in Chapter I. Ionic liquid 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) was used as green solvent.

8.3.2. Experimental for wood dissolution in ionic liquid

5 wt% suspensions of wood chips were prepared by combining 100 mg of wood chips and 1.6 g of [C_4mim]Cl in test tubes. Conventional heating at 313 K was applied with constant stirring for a period of 12h. Microwave assisted wood dissolution was conducted on a CEM Discover® Labmate microwave. This equipment consists of a continuous focused microwave-power delivery system with operator-selectable power output from 0 to 300W. Wood dissolution was performed in glass vessels (capacity of 10 mL) sealed with a septum. Temperature measurements were carried out using an infrared temperature sensor mounted under the reaction vessel. All experiments were performed using a stirring option whereby the contents of the vessel were stirred by means of a rotating magnetic plate located below the floor of the microwave cavity and a Teflon-coated magnetic stir bar in the vessel. The vessels were placed in the microwave oven and heated at 353, 373 and 403 K with constant stirring and applying an initial power level of 10 W. Samples were exposed during different periods of time, ranging from 30 minutes to 130 minutes.

8.3.3. Components recovery

Following the dissolution of wood, the ionic liquid based wood liquors were treated with the solvent extraction method shown in Figure 62. Resulting liquors obtained from the wood dissolution were filtered through a Büchner funnel to remove undissolved material. Cellulose was recovered upon adding water (30 mL) and subsequently filtered and washed repeatedly with water to completely remove [C_4mim]Cl. The aqueous fraction which contained lignin and the ionic liquid was separated by adding dichloromethane. The ionic liquid was extracted in the aqueous fraction, while the organic fraction contained lignin. Dichloromethane was evaporated (≤313 K) by means of a rotary evaporator in order to extract lignin.

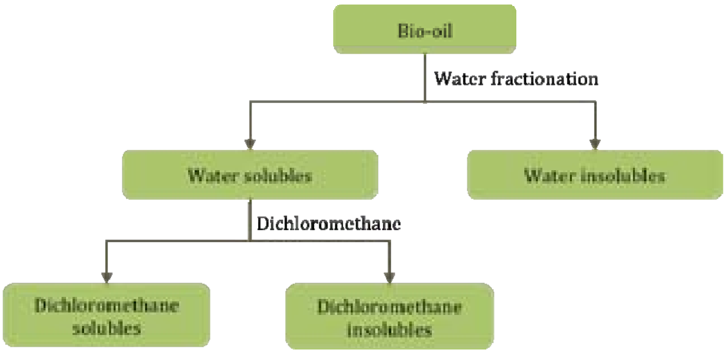


Figure 62. Solvent extraction method for the separation of the IL-based wood liquors.

8.3.4. IR spectroscopy

FTIR spectra were obtained by means of a Perkin Elmer spectrophotometer. Finely divided 9 mg samples were ground and dispersed in a matrix of 300 mg of KBr, followed by compression to form pellets. All the spectra were recorded at a resolution of 4 cm^{-1} and consisted of 100 co-added scans. Background spectra were obtained using pure KBr.

8.4. Results and discussion of the microwave assisted dissolution of wood in ionic liquids

In this section the results from the microwave assisted dissolution of wood in ionic liquids are presented.

8.4.1. Wood dissolution in ionic liquid

Dissolution of pine wood chips in [C_4mim]Cl was carried out applying two different heating methods: conventional heating and microwave activation. The ionic liquid worked as a solvent in the dissolution reaction and the starting temperature was settled in 353, 373 and 403 K during different periods of time ranging from 30 to 130 minutes. The samples consisted of 5 wt% suspensions of wood chips in a solution of the IL and were heated with constant stirring at different temperatures. Different grades of solubility were achieved, as it is shown in Table 39. In all cases, partial dissolution can be explained by the following parameters: particle size of the wood sample, temperature and time of the dissolution reactions.

Table 39. Dissolution parameters of pine wood chips in 1-butyl-3-methylimidazolium chloride.

Temperature (K)	Heating rate (min)	Time (min)	Solubility
353	10	30 min	Weak
353	10	75 min	Moderate
353	5	80 min	Moderate
353	5	2 h	Strong
373*	-	12h	Moderate
373	5	30 min	Weak
373	5	60 min	Weak
373	5	70 min	Strong
373	10	60 min	Strong
373	10	2h 10 min	Strong
403	5	30 min	Strong

*This sample was treated with conventional methods and constant stirring.

On one hand, the particle size of the wood sample plays and important role in the dissolution profiles. The complex and compact structure of the wood cell wall and between the lignin, cellulose and hemicellulose would essentially inhibit the diffusion of the ionic liquid inside it, resulting in only a partial dissolution of wood chips [89]. Comparing to previous studies carried out with wood chips under conventional heating [76] and our samples, our results show that faster dissolution profiles were obtained. Complete dissolution reported in literature was not achieved due to the greater particle size of the wood chips used compared with the reported wood powder or sawdust [89].

On the other hand, temperatures along with dissolution time play an important role in the kinetics of the process. At higher temperatures wood dissolution increased. Temperatures above 393 K are needed to solubilise the lignin from the cellulose fraction of wood [102]. However, a partial wood pyrolysis took place during the microwave activation, above all at 373 K and when reaction time exceeded 90 minutes.

On a qualitative scale, after the process, a dark and viscous solution similar to bio-oil was obtained. The appearance of this solution could be explained by the presence of lignin, due to its characteristic colour, and as a result of the partial wood pyroysis. In ionic liquids, both the cation and anion of the salt play a crucial role dissolving cellulose. Moreover, the viscosity of IL plays a role in the dissolution speed. The IL would disrupt the hydrogen-bonding interactions present in wood, allowing it to diffuse into the interior of the wood and resulting in a viscous but hazy solution [89]. In literature, 1-butyl-3-methylimidazolium chloride (BmimCl) has been described as the most efficient solvent to dissolve wood [76,89,101].

Finally, our results show that microwave activation enhances the rate of dissolution compared with conventional heating methods. In all cases, none of the samples dissolved completely even after extended periods of time. However, we achieved the same dissolution ratio described in previous literature [76,89,103] with lower periods of time (from 30 to 130 minutes) owing to microwave activation.

8.4.2. Properties of components recovery

Following the dissolution of wood, the ionic liquid based wood liquors were treated with the solvent extraction method explained. The resulting liquors were filtered through a Büchner funnel to remove undissolved material. Afterwards, upon adding water cellulose precipitated while the lignin containing fraction was in the aqueous solution. The solids were recovered by filtration and washed repeatedly with water to completely remove [C_4mim]Cl. Although much overlap of compound types exists in both fractions, as already reported [25], cellulose could be identified in the IR spectra (Figure 63) of the precipitated fraction. Subsequently, a further extraction of the water-soluble fraction, which contained the lignin-rich fraction and the [C_4mim]Cl, was carried out with dicloromethane. The aqueous phase contained the ionic liquid whereas the lignin was separated in the organic fraction. Dichloromethane was evaporated (≤313 K) resulting in a mixture of phenolic compounds from lignin.

Monitoring of the components recovery from the IL-based wood liquors was performed by means of Fourier Transform Infrared Spectroscopy (FTIR), a useful technique for analysing the structure of wood constituents and the chemical and structural changes taking place in wood components due to different treatments [104-107].

The original IR spectrum of the wood samples and their characteristic absorptions are shown in Figure 63 and in Table 40. The quantitative values of the characteristic bands of the IR spectra of the wood samples that appear in Table 40 are only used qualitatively and in order to compare the bands obtained from the reconstituted cellulose with those from the original wood sample.

Table 40. Characteristic bands of the infrared spectra of the wood samples.

Wavenumber	Assignment
1734	C=O stretching of acetyl or carboxylic acid
1636-1600	C=C stretching of the aromatic ring (lignin)
1512	C=C stretching of the aromatic ring (lignin)
1427	CH_2 bending (cellulose)
1374	OH in plane bending (cellulose)
1264	CH_2 wagging
1058	Asym. bridge C-O-C stretching (cellulose)
896	Asym. out of phase ring stretching

Source: Adapted from [105].

Finally, we investigated the cellulose recovery from the IL-based liquors. This reconstitution was achieved through the addition of an excess of water which acted as the nonsolvent. Figure 63 and Figure 64 show the IR spectra of both pure long fibber cellulose and the recovered cellulose.

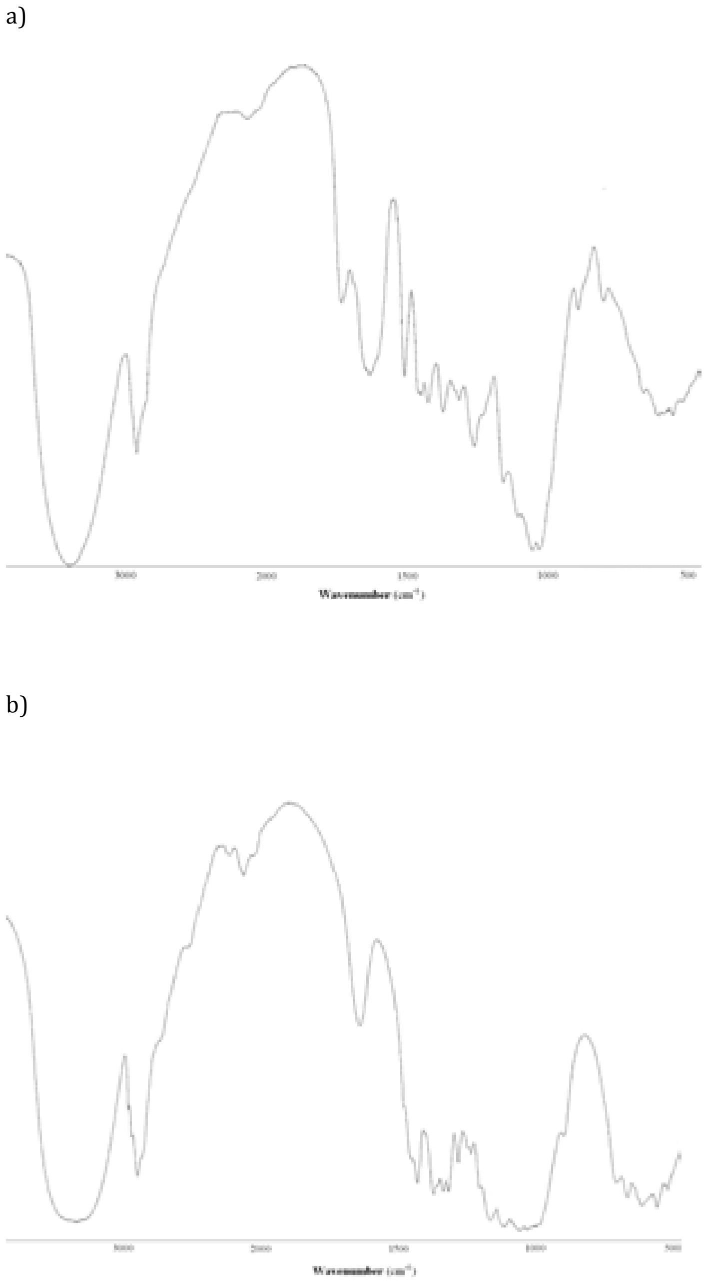


Figure 63. Infrared spectra obtained from KBr pellets pressed from (a) chopped samples and (b) long fibber cellulose.

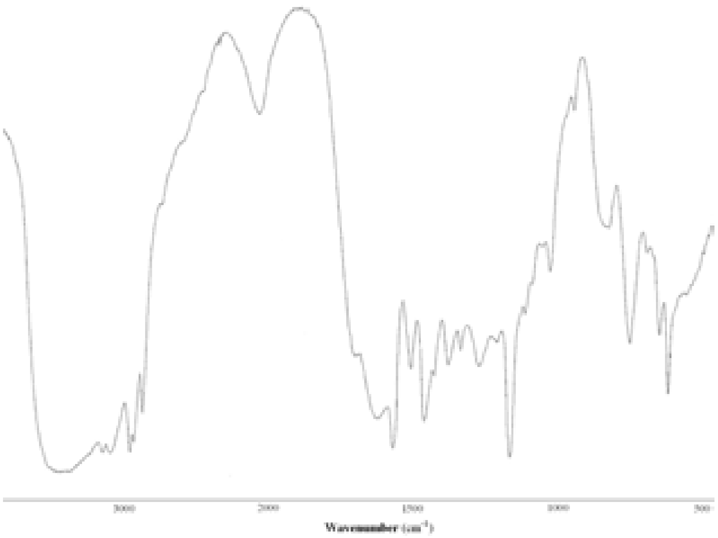


Figure 64.Infrared spectra of cellulose reconstituted from IL based pine wood liquors by the addition of water.

The IR spectra of cellulose reconstituted from IL based pine wood liquors (Figure 64) illustrates the disappearance of the internal hydrogen bonding band at 1641 cm^{-1}, which exists between OH-cellulose and water [108]. Beside this fact, the action of microwave activation also led to an increase in the absorption range between 1700 and 1000 cm^{-1}. Therefore, our findings show that, although microwave activation improves the rate of dissolution, it can also lead to delignification and to partial degradation of the wood components, as it was reported in previous literature [89,107]. From spectra comparison we can draw the conclusion that partial wood pyrolysation took place during wood dissolution since compounds such as aromatic hydrocarbons and carboxylic acids were found in the IL based pine wood liquors. The C=O stretching vibrations with absorbance between 1600 and 1750 cm^{-1} indicate the presence of ketones or aldehydes. The O-H stretching vibrations between 3200 and 3400 cm^{-1} indicate the presence of phenols and alcohols. The absorbance peaks between 1500 and 1636 are indicative of alkenes, while the presence of alkenes is attributed to the C-H deformation vibrations between 1350 and 1450 cm^{-1}.

Although low temperatures were settled (353, 373, 403 K) comparing to conventional pyrolysis temperatures, which range up to 773 K, pyrolysis took place. Most processes that convert biomass into liquid fuels begin with pyrolysis, followed by the catalytic upgrading of the resulting biocrude liquids [25], as it has been shown in the previous section in the pilot plant experiments. Bio-oil is similar to the IL-based wood liquors obtained. Bio-oil can be burned in an engine or used as a feedstock for chemical plants and it also can be easily transported due to the volume reduction achieved by converting solid biomass to a liquid.

In addition to this opportunity to convert wood into bio-oil by means of microwave activation, another promising approach is to produce biochar bioenergy which is based on low-temperature pyrolysis of wood to produce biochar while lowering CO_2 in the atmosphere [109]. Biochar has been shown to persist longer and to retain cations better than other forms of soil organic matter and thus has the potential to provide an important carbon sink and to reduce environmental pollution by fertilizers [109]. Hence, microwave activation can help enhance low-temperature pyrolysis under controlled and faster conditions than the existing ones. In this respect kinetic models can help optimize thermal conversion performance of the different biomass components (cellulose, hemicellulose and lignin), as well as they can be used as a tool to control working conditions in future integrated biomass systems [56]. Nonetheless, using ionic liquids to pyrolyse wood with microwave activation is an approach that can be a possibility both for further research and future microwave assisted applications.

8.5. Conclusions for the microwave assisted dissolution of wood in ionic liquids

Microwave activation with ionic liquids provides a new platform for greener processing technologies, since fractionation methods can be performed on controlled operations. On one hand, dissolution of wood with ionic liquids can be an opportunity to convert biomass to valuable products and chemicals, not to mention the chance to separate the three main constituents of biomass (cellulose, hemicellulose and lignin). Results show that solvent systems based on 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) can partially dissolve wood. Lower dissolution times are achieved by means of microwave activation in comparison with conventional heating methods. Cellulose recovery is also demonstrated, although microwave activation lead to partial pyrolysation of wood components. This ‘greener’ way of separation can be the basis of innovative methods to extract chemical products from biomass such as vanillin from lignin [95], as well as converting extracted cellulose into ethanol which has a much higher yield comparing to other refined cellulose [78].

On the other hand, performing biomass pyrolysis using ionic liquids and microwave activation holds promise for obtaining energy and improving the environment in multiple ways, since pyrolysis has the potential to be carbon negative [109]. Pyrolysis products such as biochar and bio-oil can be obtained with lower times and temperatures and can be cracked to obtain chemicals and fuels. The use of raw biomass as a source of bio-oil should become more attractive within the biorefinery concept.

Besides, the fractional condensation of biomass pyrolysis vapors can be used to remove a portion of the water, thereby increasing the heating value and reducing the weight of oil per unit of heat generated upon combustion [25]. Hence, microwave activation with ionic liquids provides an array of future possibilities such as novel extraction and distillation methods, both for dissolving wood and to perform pyrolysis; otherwise as stepping stones to future biorefineries.

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V

Conclusions and future research

9. Conclusions

This dissertation presents an integrated sustainability analysis of innovative uses of forest biomass by means of a multidisciplinary approach. Taking into account the few studies that integrate, from a global perspective, social, environmental, technological and economics aspects, it helps to a better understanding and an enhanced knowledge of the implementation of bioenergy systems.

The main research findings from this dissertation are addressed in the following section for each chapter and section studied.

Social assessment: Integrated Assessment of forest bioenergy systems

- It is considered that the implementation of the forest bioenergy systems in Mediterranean regions such as Catalonia is a process soon to be developed and put into practice, not only for the global necessities of energy diversification, to foster new sources of renewable energies, but also for the high interest aroused in a great part of the society.
- The bioenergy sector in Catalonia (Spain) is characterized mainly by: a lack of economic profitability of forestry products; logistics and supply problems; biomass accumulation in forests that derivates to a dangerousness and fire risk; a lack of a real forestry market; a high fragmentation of forestry properties along with the conservative owners' character; and a lack of a well defined forestry policy.
- The analysis of scenarios demonstrated they should include other aspects such as social acceptability or supply and logistics since the technological variable is not the most important one in terms of feasibility of the implementation of bioenergy systems. It was also concluded that government plays a very important role in regulation and control of these experiences.
- Integrated Assessment methodology is regarded as a good approach to face up to sustainability problems, which involve a large number of issues intimately interrelated, associated to social structure, culture, political and economic aspects. It facilitates to implement and continue different processes of public participation and decision making, helping to meet all the actors involved in the process, and thus create a discussion forum which gathers the relevant views that needed to be considered in the establishment of these new energy sources.

Environmental assessment of a gasification bioenergy system

- The energy consumption in both urban wastes and forest residues pre-treatment and transport stages is low in comparison to the energy obtained from gasification in all three scenarios. Post-consumer wood from the collection from recycling points requires the 5% of the energy involved in the process, followed by the post-consumer wood from the collection of bulky wastes (7%), and, finally, forest residues that entail the 13% of the overall energy.
- The most appropriate biomass for the gasification plant is the biomass of post-consumer wood compared with forest residues, considering the high physical requirements (15% moisture content; homogeneity; chip section of 2 cm; etc.) of the gasification plant.
- Referring to the environmental analysis and from the different biomass analyzed, forest residues is associated to a greater impact in five of the six impact categories analyzed (within an increase of 22% and 72% in comparison to the other scenarios). Post-consumer wood from recycling points is associated to a lower contribution in all the impact categories (within 27% and 64% of the maximum impact), whereas post-consumer wood from bulky wastes has 30% to 93% of the maximum impact.
- In relation to the stages, biomass pre-treatment is associated to a significant impact in two impact categories: Abiotic Depletion (AD) and Ozone Layer Depletion (ODP), calculated as 71% and 98% of the overall impact. The transport stage is of no significant influence either in the scenarios or in the impact categories (< 24% of the overall impact). Gasification represents an overall impact up to 78% of the different impact categories. In reference to Global Warming (GW), the impact percentage is between 26 and 52%, although the CO_2 balance is considered neutral.

Technological assessment: experimental, simulation and economic study on biomass pyrolysis; along with a green chemistry approach in the biorefinery context for processing biomass

From a general perspective, the following research findings can be mentioned regarding technological aspects:

- Pyrolysis offers significant advantages regarding the multiple products obtainable, since bio-oil can be used as an energy vector, the bio-char and the recyclability of the non-condensable gases produced. When bio-oil is the product that is most aimed, there are byproducts such as biochar that can be used to supply energy to the pyrolysis endothermic process and non-condensable gases that can be recirculated to contribute to the heat the reactor. Moreover, it has the potential of deployment on small and medium-scale in a local and regional scale.

- Bio-oil, along with the possibility of using it as an energy vector, can be used as a chemical platform due to its diversity of compounds. For instance, by extraction processes, compounds can be recovered such as phenols that are used to produce resins; organic acids used in defrosting; other products used to manufacture synthetic fibers or fertilizers, as well as products that can be used in food and pharmaceutical industry.
- Regarding the biochar, the combination of porosity along with the amount of minerals enables to use biochar as fertilizer in the forest itself, which also retains moisture due to its high porosity. This fertilization has the potential to contribute to carbon sequestration, so that the global CO_2 balance may be negative, considering the sequestration undertaken by the biomass growing and the coal as fertilizer itself.
- There are still several challenges regarding the economics of a commercial pyrolysis plant. Carrying out a pyrolysis process to produce electricity is an option in a pre-stage of commercial availability, but the efficiency of the bio-oil cogeneration engine is still low. Bio-oil in a future scenario of upgrading it to fuel or being the feedstock into a biorefinery offers significant advantages since it is possible to take the most of all products and by-products compared to obtaining directly energy from it.

Distributed Activation Energy Model applied to biomass devolatilisation

- DAEM reproduces accurately the devolatilisation of different types of wood, so it helps to a better understanding of the wood decomposition when thermochemical processes are carried out. It can be used as a tool to control operation conditions in future integrated biomass systems.
- It is possible to predict the behavior of a certain wood under a pyrolysis process using DAEM from the cellulose, hemicellulose and lignin content of the feedstock.
- Moreover, this model was successfully validated using other types of biomass. This fact will allow knowing the biomass devolatilisation performance prior to experimental determination by means of thermogravimetric analysis.

Biomass pyrolysis in an auger reactor: influence of operational variables and properties of the products; energy, mass and economic balances of a scaled-up pilot plant

- It has been demonstrated that biomass woodchip pyrolysis can be successfully achieved in an auger reactor under experimental conditions close to the operation range of parameters of possible industrial scale plants (continuous operation, moderate temperature and low solid residence time). Results showed that temperature was the most influential parameter.
- In the range studied, 773 K offers the most valuable yields and product characteristics for liquid production. It has been confirmed that solid residence times longer than 2 minutes are needed in order to reach complete conversion.
- No significant differences were found between the various operational conditions studied, on the collective physical properties of the bio-oils analysed, neither after changes in the reactor temperature nor in the solid residence time or the mass flow rate. Qualitative identification carried out by GC/MS showed that the most abundant compounds are volatile polar compounds, which mainly included carboxylic acids, ketones, aldehydes and monolignols, which were formed of phenols and benzenediols (pyrocatechol).
- The auger reactor produces a standard bio-oil comparable to other auger reactors and similar to other bio-oils from other reactors.
- Simulation results showed that the pyrolysis process in the auger reactor pilot plant (15 kg/h), where the experiments were carried out, is not thermally autonomous, since the energy of the released gases was not sufficient to fulfill the pyrolysis energy requirements due to the moisture content of the biomass.
- The design of an scaled up pilot plant (1500 kg/h) must incorporate a drying unit since the biomass fed into the reactor is intended to be forest biomass, which has at least 30% of moisture content, and this drying unit is thermally fed by a char combustor. Simulations of this scaled-up pilot plant showed that the amount of char needed to be burnt to have a positive energy balance is at least 31 % of the char produced. If biomass has moisture content lower than 6%, the drying unit is not necessary so neither the char combustor.
- The total costs of a 1500 kg/h pyrolysis plant are 269 €/m^3 and 289 €/m^3 when the biomass is purchased at 40 €/ton and 50 €/ton respectively. The biomass price has been calculated as 42 €/ton and includes harvesting, transport and chipping operations. The break-even point of the pyrolysis plant is between 108 and 116 €/barrel of bio-oil when the biomass is purchased at 40 and 50 €/ton respectively. Moreover, capacities larger than 1500 kg/h should be considered to have net profits when the bio-oil price is set at 116

€/barrel. Finally, there is an excess of char that has not been used in the drying process and it is accounted more than half of the production, which can be sold as a value-added product such as charcoal or even fertilizer, although further studies about this option must be addressed.

- The possibility of operating the plant in two shifts instead of one, that is, 16 working hours per day, 7680 tons of biomass/year and producing 3508 m^3 of bio-oil; offers outstanding advantages in terms of profitability. Under this scenario, the internal rate of return is 61% and 56% when the biomass is respectively purchased at 40 and 50€/ton. The break-even point of the price per barrel of bio-oil decreases up to 85 €/barrel if the biomass is purchased at 50 €/ton and 77 €/barrel when it is purchased at 40 €/ton.

Greener processing technologies: microwave assisted dissolution of wood in ionic liquid

- Microwave activation with ionic liquids provides a new platform for greener processing technologies, since not only fractionation methods can be performed on controlled operations, but also pyrolysis as it has been demonstrated in this study.
- Dissolution of wood with ionic liquids can be an opportunity to convert biomass to valuable products and chemicals, not to mention the chance to separate the three main constituents of biomass (cellulose, hemicellulose and lignin).
- Results show that solvent systems based on 1-butyl-3-methylimidazolium chloride ([C4mim]Cl) can partially dissolve wood. Lower dissolution times are achieved by means of microwave activation in comparison with conventional heating methods. Cellulose recovery is also demonstrated, although microwave activation lead to partial pyrolysation of wood components. This fact foresees the possibility of performing pyrolysis using ionic liquids with lower times and lower temperatures.

10. Future research and improvement proposals

In this section improvement proposals and future research are addressed regarding each chapter of the dissertation.

Social assessment: Integrated Assessment of forest bioenergy systems

- Study the social perception to analyze the several outputs of this dissertation organizing another focus group, especially to study the use of mobile pyrolysis plants in forests.
- Research the social implications of different scenarios of pyrolysis plants; a local scenario consisting of mobile pyrolysis plants and a global scenario of medium-scale pyrolysis plants.
- Examine the possibility of implementing the mobile pyrolysis plants in a local cooperative context, for instance in a forest and/or farming cooperative with the help of forest and agricultural protection associations.

Environmental assessment of a gasification bioenergy system

- Improve separation and densification of the post-consumer wood in order to avoid energy and economic costs of pre-treatment and transportation.
- Research and select machinery adapted to the characteristics of Mediterranean forests, such as steep slopes and difficult accessibility.
- Use biofuels, such as biodiesel or in a long-term scenario bio-oil, in the machinery and transport to achieve a better environmental and energy balance, although further studies about the impact of using biofuels are also required.

Technological assessment: experimental, simulation and economic study on biomass pyrolysis; along with a green chemistry approach in the biorefinery context for processing biomass

- Perform the scaling up of the auger reactor pilot plant, which is on due course, to process 200 kg/h of woodchips. This is the intermediate scale to fulfill the final objective of a plant with a capacity of 1500 kg/h. An environmental assessment of the scaled-up pilot plant (200 kg/h) is already planned in the following months.

- Study in detail the effect of the moisture content and particle size of the forest biomass on the product yields and properties of the products. The process should be capable to work continuously with a biomass moisture content ranging from 20 to 40% to avoid energy expenditures of drying biomass, which is the moisture content of harvested biomass air dried in the forest.
- Use catalysts in the pyrolysis reaction to enhance the pyrolysis performance and decrease the oxygen content of the bio-oil as a first step for upgrading the bio-oil for transport fuels. This will be carried out via hydrotreating in presence of catalysts such as zeolites or sulfided nickel or molybdenum supported on alumina, which is planned to be studied in the following year.
- Study the catalytic activity and effect of nanomaterials, basically modified carbon nanotubes (CNTs), and combined with enzymes and photocatalysts on the properties of the bio-oil as a refining step for using it as fuel.
- Assess how to improve heat transfer to the reactor by means of improving the reactor configuration using sand to achieve a better heat transfer in the auger reactor or other reaction configurations such as using a heated auger conveyor electrically heated.
- Feed other types of biomass such as agricultural residues or lignocellulosic energy crops such as poplar in the pilot plant and study its influence on the operation of the auger reactor and the composition of the products.
- Carry out further studies about the use of biochar as fertilizer in forests to study its capability of CO_2 sequestration. Analyze additionally the environmental implications of such practice.
- Perform energy and environmental assessment of greener processing technologies to evaluate the real “greenest” of these approaches. More specifically, the difference of energy consumption between using microwave and conventional heating, as well as the environmental implications of ionic liquids.
- Study the pyrolysis performance and the properties of the products when microwave activation is applied on biomass, with the help of ionic liquids or other polarized compounds.
- Analyze the environmental, social and economic impacts of using the scaled-up pilot plant (1500 kg/h) in Mediterranean forests and compare the different options available in short and long term (electricity production, bio-oil as feedstock for a biorefinery, etc.).

- Research on application of bio-oil in a future scenario of a biorefinery for producing chemicals, taking advantage of its most abundant functional groups (eg. carbonyl, carboxyl and phenolic). For instance, specific chemicals such as vanillin or levoglucosan can be obtained, as well as phenolic compounds that can provide smoky flavours for the food industry.