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WOOD WASTE ENERGETIC RECOVERY: EXPERIMENTAL AND MODELING STUDY OF THE THERMAL DEGRADATION

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The biomass incineration for energy production and the waste managing are two environmental themes on which the research is focusing. This work has the aim to understand if the energetic recovery of the wood waste is a possible way of recovery. The research was started France, and, through a bibliographic work, it studies the availability of wood waste in the country and the legislation at the european and national level, regarding incineration of this kind of waste.

The wood waste was divided in four raw material waste types: packaging wood, furniture wood, demolition wood and others (utility poles, railway sleepers, etc…); for each one of them the immediate availability and the annual flux was accounted .

In the second part of this study the composition differences between wood waste with few addictives and natural wood was analyzed. At first a list of wood polluting compounds coming from the treatments was done, furthermore, through an experimental work of thermogravimertic analysis (TGA), some differences between the natural wood and the wood waste were found. One of the main differences is the presence of the melamine and the resins, especially in the furniture waste, which changes the thermal degradation behavior of the wood.

Since waste biomasses are several and very different, the CRECK Laboratory developed a model to characterize the biomasses biochemically and simulate their TGA.

A comparison of the TGA was done experimentally and then simulated to validate the model on non-natural biomasses, the results show that the model simulate with a good accuracy the real thermal behavior of the wood waste.

Considering that some biomasses (in which several wood waste biomasses) have an high hydrogen content because of the presence of hydrogen rich extractives as terpenes and they could not be characterized by the model, the last step of this study was a development phase, in order to comprise these biomasses.

A study on the terpenes was made to insert them in the model; moreover some TGA were simulated and compared to the former model simulation. The results of the comparisons show an improvement in describing biomass thermal degradation.

VALORIZZAZIONE ENERGETICA DEL LEGNO DI RIFIUTO: STUDIO SPERIMETALE E MODELLISTICO DELLA DECOMPOSIZIONE TERMICA

La valorizzazione energetica delle biomasse e la gestione dei rifiuti sono due tematiche su cui la ricerca si sta concentrando. Questo lavoro ha lo scopo di capire se la valorizzazione energetica del legno di rifiuto sia una via di recupero possibile. La ricerca è cominciata in Francia e, attraverso un lavoro bibliografico, si occupa di studiare la disponibilità del legno di rifiuto nel paese e il quadro legislativo a livello europeo e nazionale per quanto riguada questi tipi di rifiuto. Il legno di rifiuto è stato diviso in quattro tipi di materie prime: legno da imballaggio, legno da mobilio, legno proveniente da demolizioni e altro (pali telefonici e elettrici, traverse ferroviarie, ecc…); per ognuno dei quali si è valutata la disponibilità immediate ed il flusso annuo.

Nella seconda parte di questo studio sono state analizzate le differenze di composizione tra il legno naturale ed il legno debolmente trattato con additivi. Inizialmente è stato fatto un elenco di composti inquinanti presenti nel legno derivanti da specifici trattamenti, in seguito, attraverso un lavoro sperimentale di analisi termogravimetriche (TGA), sono state trovate delle differenze tra il legno naturale ed il legno di rifiuto. Una delle più grandi differenze è la presenza di melamina e resine, specialmente nel legno da mobilio, che cambia il comportamento di decomposizione termica del legno.

Dato che le molteplici biomasse sono molto differenti tra loro, il laboratorio CRECK ha sviluppato un modello per stimare le composizione biochimica delle biomasse e simularne la TGA.

Le TGA analitiche e quelle simulate sono state cofrontate al fine di validare il modello su biomasse non naturali, i risultati mostrano che il modello simula con buona accuratezza il comportamento di decomposizione reale del legno di rifiuto

In ragion del fatto che alcune biomasse (tra le quali molti tipi di legno di rifiuto) hanno un alto livello di idrogeno a causa della presenza di estrattivi ricchi in idrogeno come i terpeni e non possono essere caratterizzate dal modello, l'ultimo passo di questo studio è stata una fase di sviluppo modellistico, al fine di inserire queste biomasse.

E' stato fatto uno studio sui terpeni, al fine di inserirli nel modello; inoltre sono state simulate delle TGA e confrontate al modello precedente. I risultati dei confronti indicato un miglioramento nella descrizione del comportamento di degradazione delle biomasse.

«Il dubbio lo porto in me, talvolta anche in forma esagerata.
Sul dubbio, una volta, ebbi una polemica con Gramsci. E mi pare che lo dica anche
Renan: "Senza la presenza del dubbio, perdiamo l'esatta valutazione dei fatti e delle cose;
la mania della certezza è l'anticamera del fanatismo".
Con la mania della certezza si finisce sempre col non ammettere l'opinione altrui.
Io invece sono sempre pronto ad ascoltare le opinioni altrui e a cercare in esse gli
elementi positivi. Il dubbio mi si addice perché richiede libertà e non comporta
necessariamente la perdita della fede, della volontà di battersi.
Sia pure attraverso inevitabili errori.»

(Giorgio Amendola, Roma, gennaio 1974)

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• 1. The wood

Wood is a plant tissue that makes up the trunk of the plants. This tissue is used by man for multiple aims, currently it is well considered as building material, for its mechanical proprieties, and as combustible for its LHV (Lower Heating Value).

The french law “norme NF B 50-003” (which delineates the classification of wood) defines it as “a group of resistant secondaries tissues (of support, of conduction and of stock) which make up the trunk, the branches and the roots of the woody plants. It is placed between the vascular cambium and the nub”.

• 2. Sources of wood

The principal source of the wood is the forest resource, where the wood is put together by activities of cut and upkeep.

There are two kinds of exploitation: the former is in the wood industry, and the latter, in which the wood is transformed in pellets, is the energy production in the collective boiler rooms[1].

Another smaller source is the wood coming from the gardens and green spaces. The upkeeping of these areas produces biomass waste, like the pruning wood, that is mostly burned by the collectives boiler rooms.

Some other waste, coming from the upkeeping of the gardens and the green spaces, is composted, with the production of some the residuals.

The maintenance of beaches and of fluvial weirs brings some wood waste, mostly the driftwood, which is normally treated as Municipal Solid Waste (MSW) and buried or putted together in the wood containers in the recycling centres.

Most part of the wood is treated by the industry, which mainly produces building lumber, a wood exploited for its mechanical properties.

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[1] Collective boiler rooms, from the french term chaufferies collectives, or incinerators which burn natural biomass

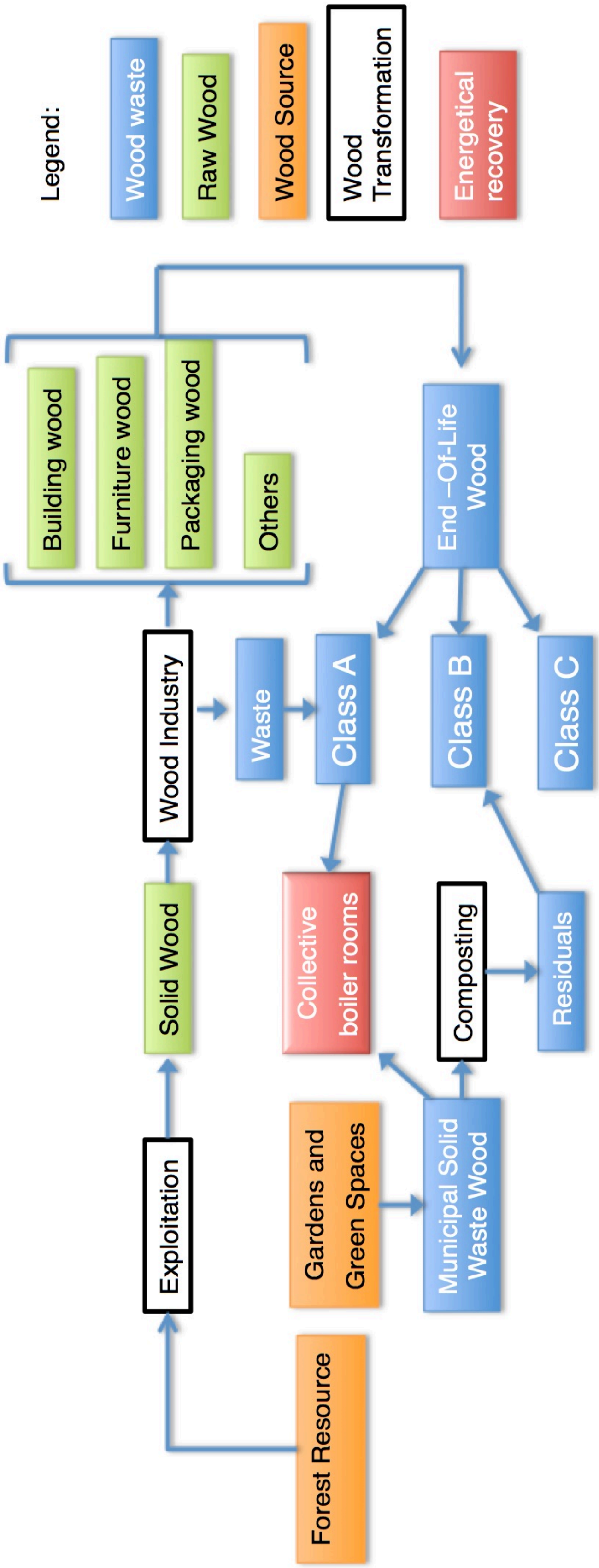

Fig. 1) Scheme of the sources, the uses and the waste of the wood.

The wood industry, through the operation of sawing, produces wastes, such as chips, sawdust and barks, which are burned in the collectives boiler rooms.

The lumber is used by the construction industry, by the public work sector, by the packaging industry and for the production of railway sleepers and utility poles.

The lumber, answering to some building and mechanicals criteria, is treated with conservative, insecticide, fungicide products and with peintures and varnishes; all of these treatments make the wood waste hardly treatable.

For this reason the wood waste is divided in three classes (A, B, C) by the french professionals of the sector, depending on the quantity and the danger of the treatments received. The class A wood, in other words the wood not treated with additives, may be burned in the collectives boiler rooms thanks to its similarities with natural biomass wood; in some classifications we can fund the natural biomass itself listed as class B wood. The class B wood, that is to say the wood treated with a few addictives, may be burned in France after the law “décret n° 2013-814 du 11 septembre 2013” [1]; on the contraty the class C wood cannot be burned for it is considered an hazardous waste.

The wood waste, like the lumber and all the treated woods (mostly the class B wood), the driftwood, the residual of the composting and the pruning wood make a deposit of wood waste currently poorly exploited, being considered as trash.

• 3. Waste recovery

Under the waste recovery sector we can gather all the processes which transform a waste material or an apparently useless product into a brand-new material or quality product or something of higher utility.

We can distinguish between two macro-typology of waste recovery: the materials recovery and the energetic recovery[2].

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[2] Energetic and material recovery, from the french terms “valorisation en energie” and “valorisation en matière”.

The materials recovery is made up of the waste treatments, which makes their reemployment, reusing and recycling possible. Consequently, the aim of these treatments is to handle the waste in order to reuse the composing materials.

The different typologies of materials recovery are:

- the recycling of the materials: the waste material(s), after a transformation, become the raw material for a new product;

- the reemployment: the used product, after being fixed or being brought to the original conditions, is newly used for the same or another use;

- the reutilization: the product is used several times for the same scope;

- the regeneration: the waste, after a transformation, finds the same physico-chemical proprieties and can be used as virgin material.

The energetic recovery involves the use of the waste's heating value, burning it and getting back the energy as heat or electricity. This it is a way of recovery whose aim is to transform the waste in order to produce energy.

The outgoing materials are generally ashes and gases, which must be treated.

The different typologies of energetic recovery are:

-Incineration: a combustion at variable temperature range (based on the nature of the waste) with the aim of getting back the heat and using it to produce electric energy. The outgoings are smoke filled with polluting elements (mostly dioxins and furans, the load in pollution depends on the nature of the waste), clinker and ashes (the load in pollution depends on the nature of the waste). The auxiliary treatments include a mandatory gas treatment stage to reduce the polluting load of the outgoing gases, an ash treatment stage and a sector for the material recovery of ashes and clinker.

The incineration is a process lead at high temperatures (around 800-1000 °C) and with air insufflation. This operation brings to growing gas volumes with the rising of the ARF (Air-Fuel Ratio), also the reaction is fast enough to release the heavy metals which are eventually contained in the gas.

The incineration is a very developed technology in the energetic recovery sector for the treatment of the Municipal Solid Waste (MSW), and preferably with the using of low or non pollution loaded waste, therefore the biggest part of the class A wood waste is burned in incinerators.

- Pyrolysis: a thermochemical decomposition process of the organic materials lead at a medium temperature range (400-800 °C) and in complete lack of oxygene.

The outgoings are syngases (H_2 + CO, that can be transformed in CH_4 by a Fischer-Tropsch process or directly burned), pyrolysis liquid and carbon to be purified.

Pyrolysis is, thus, a process typically endogenous. The applications of the pyrolysis are oriented to the alternative fuel production, although for the moment the quality of the outgoings is still too poor to consider industrial plants.

- Gasification: gasification is a chemical process which allows to convert carbon-rich materials, like coal, oil and biomasses into syngas.

The process is lead at high temperature (700-800 °C) with a nitrogen insufflation and a sub-stoichiometric percentage of oxygen.

Therefore there are three chemical processes, pyrolysis, combustion and gasification itself; the presence of three reactions in the same time allows the gasification to be a weakly exogen process.

In our project, using the wood treated with a few addictives, the gasification is the process chosen for its higher capacity to hold back the pollution (especially heavy metals) in the ashes, which are easier to treat.

• 4. Why recover in energy the class B wood?

According to the regulatory autorisation in France, the class B wood energy recover scenario became economically, energetically and environmentally interesting.

Here are several reasons for the energy recover:

- There is a high availability of the wood waste, it comes from several sectors like: furniture wood, wood outgoing from the construction industry and all the wood treated with glues and paints, etc…

- The availability of the class B wood is not totally collected, currently only 76% of the total, corresponding to 3,8 million tons, is collected, there is an availability of around 5 million tons [2];

- The class B wood is a waste, the recovery allows to avoid dumping; currently not recovering this material is a loss for the community;

- A recovery industry already exists for the class B wood, this is the material recover, especially for the panel production. The panel production sector needs several phases before being able to use the wood: cleaning phase, selection, grinding phase, trituration, sieving phase, and decontamination. The panels produced in France are sold in Italy and in Belgium for the half part. All the treatments on the wood and the exportations contribute to the CO_2 emissions, which can be considerably reduced if the consommation may be done nationally;

- The class B products, being dry, have a high LHV: comparing the same masses they produce much more energy than the natural wood, therefore they can be put in the mixes to improve the medium LHV;

- In other european countries, the combustion of the wood waste is now allowed, but only if there are a few preparatory stages (fine grinding, ridding to remove the dust) which don't burden the using cost;

- The gasification, with its low-combustion and oxygen-lacking process, enables the accumulation of the heavy metals like zinc, arsenic (that can be totally transformed in metallic arsenic, easier to handle) and chromate copper arsenate (CCA) in the ashes, this allows to handle these polluting elements easier compared to the incineration that scatter the pollution in the gas. It also enables the decrease of the production of dioxins and furans, the Volatile Organic Compounds (VOC) emissions and the unburned;

- The ashes are only the 2-3% of the wood volume after the gasification [3], this allows to save the landfill space and cost;

- The combination of gasification and combustion has a higher energetic efficiency (the total energetic yield is higher than 90%, especially because of the syngas combustion vapours, that contain only 6% of oxygen, unlike a direct combustion of wood, made with an higher Air Fuel Ratio (AFR), where the vapours exceed frequently 11% of oxygen: this brings a bigger vapour volume and therefore a bigger energetic loss) [3];

- The ratio of the production unit dimension and the energy produced favours the gasification compared to incineration;

- After the gasification process there is a lower vapour volume which needs to be treated;

- The gasification allows the production of the syngas, which being a secondary fuel may be transformed in synthetic fuels or directly burned;

- The wood gasification is a well studied issue, several publications have already studied the matter, like “Prediction of the working parameters of a wood waste gasifier through an equilibrium mode” (C.R. Altafini et al., 2002) [4], “Total recycling of CCA treated wood waste by low-temperature pyrolysis” (L. Helsen et al., 1998) [5] and “Experimental studies on producer gas generation from wood waste in a downdraft biomass gasifier” (P.N. Sheth, B.V. Babu, 2009) [6].

5. The wood classification

The wood waste categories consider all end-of-life materials and objects, in other words woody objects produced privately or by industries

The wood waste is collected, for the vast majority, by specialized enterprises and is grouped according to the treatments done for the primary use and according to the pollution received until the end of life.

The three wood classes considerated by the french sector professionals’ classification are:

- Class A: this category includes the wood which was not treated before the use, which has no polluting charge and which is very likely to the natural biomass; in general this wood is recovered and considered as biomass fuel to vurn in the collectives boiler-rooms

- Class B: this type includes all the woods treated with few additives; mostly they are woods containing glues or being treated with surface treatments like painting or varnishing. Low polluted wood belongs to this typology too, like wood used in building and the public work sector. The class B wood may be recovered by burning or by recycling the material according to the pollution level: currently the burning system of recovery is limited by the risk of liberating the pollution in the outgoings, especially in the gasses.

- Class C: this class represents the greatly polluted wood, like the railway crossings, utility poles or wood treated with chrome, chlorine, arsenic or boron. This category of wood is considered hazardous waste. The class C wood cannot be recovered by burning because of it's pollution content.

The table below shows the principal woody primary materials and their respective class.

Classes	Primary Materials
A	Forest, pruning and urban wood, sawmill linked products, second “clean” transformation linked products, boles, sawdust, barks, chips, wood industry residuals of lumber, others.
B	Furniture wood, wood with glues, paints, varnishes, pallets, crates, fireproof wood, wood outgoing from the building sector, wood outgoing from the public words, dismantlement wood, driftwood, outgoings from the composting, others.
C	Creosoted wood, wood impregnated with metallic salts, railway crossings, electric poles and telephone posts.

Table 1) Woody Primary Materials

• 6. French regulation

The objective of this chapter is to understand the state of the art of the european and french regulation regarding the energetic recovery of class B wood.

• 6.1 Normative classification

There are many wood classifications according to their pollution levels, the table below shows the definition of the woods which we can find in the european reference documents about the wood-energy sector.

Wood-Energy fuels

CEN TC 335	Not Treated	Treated	Out of CEN TC 335
Reference documents	Without addictives	Treated with a few addictives	Out of the reference documents

Definition	Without any chemical addition	Gluing without any other chemical addition	Gluing with low addition of preservation and completion products	Mixed with other materials, dirty, fireproof products and/or the addition of strong chemical products
Meaningful examples	Solid wood	Untreated panels, beams of glue-laminated structural wood	Laminated chipboard panels, treated pallets	wood treated by impregnation or fireproof
Traceability/ Composition	Traceability of all the product and the mixes	Traceability on the type of the glue and the quantity	Traceability on the type and the concentration of the glue/complention/preservation	Partial or complete absence of traceability
Parameters	Natural levels of chlore and nitrogen	Nitrogen level < 15% Natural level of chlore	Nitrogen level < 15% Heavy metals (HM) < 1000 ppm Halogenated organic compounds <10 ppm Boron< 1000 ppm	Nitrogen level >15% Heavy metals (HM) > 1000 ppm Organo-halogenated compounds >10 ppm Boron>1000 ppm

Table 2) Normative classification of wood

- 6.2 European framework

In the european framework we can find the following texts, framing the regulatory apparatus for every country about the waste managing:

- the 94/62/EC directive of the European Parliament and of the Council of 20 december 1994 about packaging and waste coming from packaging [7];

- the 2006/12/EC directive of the European Parliament and of the Council of 5 april 2006 [8] about the waste replace the directive 75/442/EC of 15 july 1975 [9]. This text set the politic of the European Union about waste managing.

Concerning the emission limits on the incineration plants and of the combustion in general we can find:

- the directive 2000/76/EC of the European Parliament and of the Council of 4 december 2000 on the waste incineration. About the wood, the following waste material are excluded form the dominion of this directive: “the wood waste, with the exception of the wood waste that may contain halogenated organic compounds or heavy metals as result of a treatment with wood preservative or coating, and which includes particular such wood waste originated from building and demolition waste” (art.2, §2, alinéa 1, iv) [10].

- the directive 2001/80/EC of the European Parliament and of the Council of 23 october 2001 about the emission limits of certain pollution compounds in the atmosphere coming from big incineration plants that receive waste free from heavy-metals and from halogenated organic compounds. By extension this enlarges the notion of biomass [11].

• 6.3 French framework

The french regulation of the wood waste is currently structured around the legislation of the Classed Insallation for the Environment Protection (Installation Classées pour la Protection de l’Environnement), but, until the “Décret n° 2013-814” of 11 septembre 2013 [11], it had been unclear concerning the energetic recovery of the wood waste, specifically about the woods treated with few additives.

The rubrique ICPE 2910 “Combustion exclusion the plants target of the rubriques 2770 and 2771” (“Combustion à l’exclusion des installation visées par les rubriques 2770 et 2771”) [12] rules the combustion processes, in particular:

- the rubrique 2910 A which concerns the plants that burn: “natural gas, oil, liquefied oil gas, domestic fuel oil, carbon, heavy fuel oil or biomass”, but the considerated biomass is defined as “at the natural state and neither permeated nor covered of any substance. It includes the wood in chips, boles, shred wood, sawdust, barks or products outgoing from the wood industry, of his transformation or of his handcraft.”:

- the rubrique 2910 B puts tighter the others fuels, in other words the fuels not defined in the rubrique 2910 A, but it gives the prescriptions about the plants where the power is lower than 20 MW.

ICPE 2910 A	**not treated biomass**
Power of the plant	regulation
< 2 MW	no prescriptions
2 - 20 MW	submitted to a declaration, simple gasses dust removal
>20 MW	submitted to an autorisation
ICPE 2910 B	**biomass treated with a few addictives**
Power of the plant	regulation
< 0,1 MW	no prescriptions
> 0,1 MW	submitted to an autorisation

Table 3) ICPE normative

- the rubrique 2910 C is referred to the plants that use biogas only.

The décret n° 2013-814 of 11 september 2013 [1] gives the autorisation and the public easement to burn a "quantity of hazardous substances or hazardous preparations, that may be inside the plant, higher or equal to the AS threshold of the using rubriques or the stockage of these substances or preparations", and it gives the autorisation to burn a "quantity of hazardous substances or hazardous preparations, which may be inside the plant, lower to the AS threshold and higher or equal to the A threshold of the using rubriques or the stockage o these substances or preparations" (rubrique 2717 1. 2.).

Concerning the atmospheric emissions, the installations where the power is lower than 2 MW are not concerned by any regulation (neither in the rubrique 2910 A nor in the 2910 B). Nevertheless the norm NF EN 30.5 [13] for the boiler rooms with a power lower than 300 kW is currently the reference for the CO emissions.

Today in France there are no limit values to rule the emission of dust in the plants with a power lower than 2 MW.

In the national regulatory context the directives are integrated to the french law by the environment code (article R. 541 and further), the law Grenelle 1 for the environment [14] and its evolution: the law project that brings a national duty for the environment (also known as Grenelle 2 for the environment) [15].

These texts add the following objectives:

- the obligation for the producers of furniture elements to assure (individual initiative or managing structures financing) the responsibility of their end-of-life products, starting from 2011 (article 78 quarter, Responsabilité Elargie Producteurs or REP);

- the obligation to start a plan for the managing of the construction sector waste (article 79, cf. details part 3.4);

- the recovery objective for the waste at 35% in 2012 and at 45% in 2015 (the recovery was at 33% in 2009)

- the packaging waste recovery at 75% in 2012;

- an encouragement to the energetic recovery of the waste;

- a re-evaluation of the re-using practices and of the environmental impacts of creosoted wood.

The ashes may be recovered either by spreading directly on the ground, or in the agriculture sector (spreading them in the forests is mostly common in nordic countries), or co-composting, in the road construction sector or still, marginally, as side raw material in the fabrication of ceramic. The main recovery sectors, that are the direct spreading in agriculture and the co-composting, aren’t ruled by a specific normative. Several logics can be followed, but the normative gaps subsist:

Product logic:

Ashes are considered as combustion by-products and can be considered as fertilizing matter for a direct or indirect return to the soil; several normative or regulatory options are available:

- approval;

- standardisation:

  - Norm NFU 42-001 (“vegetal ashes”): according to this norm the vegetal ashes go into the category of the composed P and K fertilizers, under particular conditions (minimal compounds content). After the experiences , most of the ashes produced by the boiler rooms in France can’t be considered as vegetal. This norm is now currently being reviewed.

  - Norm NFU 44-001 regarding basic emendations: the ashes contain the minimal content of CaO and MgO required, but they cannot be put in the standard because they are not in the norm field;

- Norm NF U 44-051, application report mandatory: the ashes can be putted in organic amendement in respect of the regulation, or in case of heavy metals concentration limit values not reached.

Waste logic:

- Spreading: this kind of recovery is not allowed for the boiler rooms considered by the order of 25 July 1997 (2910 A, power from 2 to 20 MW) [16], and the spreading conditions are not clearly defined for the boiler rooms concerned by the orders of 20 June 2002 [17] and 30 July 2003 [18] (2910 A, power higher than 20 MW). Furthermore nothng is previewed for the boiler rooms under 2 MW.

- Co-composting: the order of 7 january 2002 [19] concerning the rubrique 2170 set the requirements for the compost whose quantity is included between 1 and 10 tons/day, and for the compost activity done out of the agricultural exploitation and/or for not-agricultural products, specifically for he products containing ashes (in this case a innocuousness study is mandatory). A spreading plan is then necessary.

In summary in France, the regulation and the normative context are equally lacking about the management of the ashes, and it seems necessary to preview a regulation concerning all the power plant selection, and specify the sectors available for every kind of ash, based on the characteristic and, particularly in terms of heavy metals limit values.

• 7. Raw materials types

In this study, in order to have a precise overview, only the most available raw materials will be considered. Furthermore several treatment types will be introduced for every class, with the aim to find, for every type, the polluting compound coming from the treatment received.

We can distinguish several raw materials, the following ones are generally classified as class B wood:

- 7.1 Packaging wood (pallets, cages, cases, casks,..)

The packaging wood are wood products whose aim is to protect the merchandises from shocks which can occur during their transport, they are made up almost totally with solid wood. We can distinguish between two types of wood packaging (Fig.2)

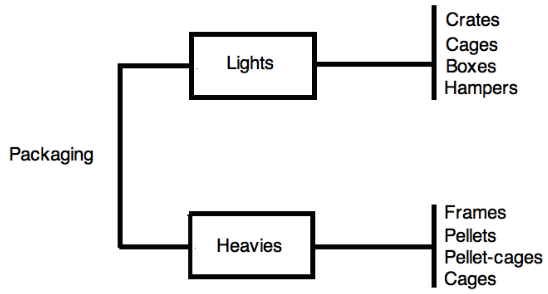


Fig. 2) Packaging wood outline.

Most of the packaging is not treated, although some treatment is previewed in order to massively reduce the spreading of damaging compounds integrated in the commercial trades.

The norm NIMP15 (ISPM N° 15) [20] that is applied to every wood packaging material (like pallets, boxes, packaging panels, embroidery frames, crates, etc...) establishes two possible treatments:

- Heat treatments (HT) lead at 56 °C during at least 30 minutes;

- CH_3Br (Bromomethane) fumigation on time, concentration and temperature control;

According to the norm NIMP15 after the packaging and energy recovery, the pollution compounds concentration is probably not higher than the one found after the class A wood incineration, except for the brome content and for the heat treatments which cause a small rise of the contents in the ashes.

Frequently foreign objects can be present (metallic objects, nails…) and they need specific equipment for the incineration in the boiler rooms. Currently it is difficult to eliminate all of these materials, they may eventually cause some problems after the combustion and create clinker. For this reason the packaging is collected by the enterprises specialized in recycling and waste managing.

It is not likely that the pallets, being not treated, contain a higher pollution content than the class A wood, but the presence of metallic object oblige to a pre-treatment to separate them before the gasification.

The collection of the packaging is often made by the enterprises specialized in recycling and waste managing.

Fig. 3) Standard pallet.

- 7.2 Furniture wood

The furniture wood is the constituent element of the furniture, a lot of qualitative varieties exist according to the aesthetic effect, the mechanical proprieties, the use, etc…

In this chapter, two main types are distinguished: solid wood and pressed wood.

The solid wood is extract from the trunk of a downed tree with the aim of the transformation. The furniture items made of solid wood are qualitatively and aesthetically better, for their realization the wood must be treated with chemical products for sealing, paints and varnishes for the conservation.
The wood, according to the treatment, can have a different composition, compared with the class A wood, especially if it is treated with chemicals products, for example the sealing, fungicide and insecticide treatments, it might contain a higher level of heavy metals, especially copper and zinc. On the other hand, if the solid wood is treated with natural products, the heavy metal compounds content is the same of the natural wood.

In the end the physical treatments, especially the heat treatments, can cause a small rise of the ash content.

The pressed wood is produced from wood fibres or particles which are compressed and kept together by a binder, pressure or heat.

The pressed wood sub-typologies are: Multy-Density Fiberboard (MDF), chipboard and Oriented Standard Board (OSB).

Fig. 4) Multy-Density Fibreboard (MDF).

Multy-Density Fibreboard panels (MDF) are a type of pressed wood with an average density of 800 kg/m^3 for the High Density Fiberboard HDF, 750 kg/m^3 for the MDF and 600 kg/m^3 for light MDF.

This panel, invented in the United States in 1966, is a valid alternative to solid wood, indeed its fine composition allows it to be virtually hysotrope, being easily decorated and, because of industrial production, it has a high resistance and it is cheaper compared to solid wood.

MDF is made from hardwood and softwood particles between 5 and 40 mm of dimension, the particles are treated with steam and glued with several additives and glues, dried and pressed.

The additives used are synthetic binders based on urea-formaldehyde compounds; these resin binders, of the family of aminoplasts, may increase its nitrogen content. In the end the panels are produced from agglomerated fibres and they contain formaldehyde, which might cause cancer in animals and is probably carcinogenic to humans. The use of these fibres is dangerous for operators during the storage and the grinding operation, where a large amount of dust is generated.

Chipboard is a wood-based panel, coated with a sheet impregnated with melamine. The chipboard is usually used as a carrier of an MDF panel or in solutions like the sandwhich panel arrangement.

The same technique is also declined on plasterboard for the realization of movable partitions.

The melamine resins come from the family of the aminoplasts such as urea-formaldehyde. They do not increase the heavy metal content of the wood, but they increase significantly the nitrogen content. The chipboard can also be treated with paints and varnishes, or glued to sheets of painted wood; it can bring the presence of heavy metals.

An oriented standard board or OSB, also known as oriented structural panel is a panel of wood from 6 to 25 mm thick, made of wood shavings oriented in specific directions, and glued together by a resin (95% of wood, 5% of waxes and resins) [21]. The resins used are those of the family of aminoplasts as Phenol-Formaldehyde (PF), Melamine-Urea-Formaldehyde (MUF) or isocyanate (PMDI), their contribution to the wood can increase the levels of nitrogen. Resins based on formaldehyde are hazardous to operators because they are probably carcinogenic for humans. During the storage and grinding operation a large amount of dust is produced; this dust is very dangerous if inhaled.

Fig. 5) Oriented Standard Board.

In France, the law Grenelle II, from 2012 [15], requires furniture manufacturers to establish a pathway for recycling of used furniture ("Art. Any natural or legal person, who manufactures, imports or brings in the market furniture elements, must provide support for the collection, the sorting, the reclamation and the disposal of such end-of-life products, either as individual initiative, or in the form of funding approved eco-organismes, which will manage them". Moreover: "any transmitter on the market who does not respect this obligation is subject to the general tax on polluting activities"); and: "building products and furniture as well as coatings wall and floor coverings, paints and varnishes, which emit substances in the environment, are subject to the mandatory labelling of volatile pollution from 1 January 2012".

- 7.3 Wood outgoing from the building and demolition sector

The wood waste outgoing from the building, demolition, construction, dismantling and rehabilitation sector is an important source, both for public and private works.

This category of wood comes from different origins, in fact we can find packaging, solid wood, chipboard and class C wood, as electric poles or railroad ties. The collection is made by enterprises specialized in the field of waste and recycling.

The two most used typologies for the building sector are solid wood and glued laminated timber.

The solid wood used in the construction sector is not different than the one used in the furniture industry, except that the construction needs to have a longer durability, to increase this durability some waterproofing, fungicide and insecticide treatments are done. With these treatments some pollution compounds are added to the wood and increase the content of heavy metals, especially copper, and they can bring the presence of halogeneted organic compounds; other treatments, especially the ones done with hazardous materials like creosote, are considered carcinogenic and banned in France today.

The glued laminated timber is made of wood slats bonded with the fibres in the same direction. This typology of wood is used in manufacturing large parts or particular shapes which could not be obtained differently with the same material, and furthermore for improving the mechanical strength.

For the manufacturing, the slivers are first dried, sorted (visually or by ultrasound) and purged from their defects, then glued end-to-end to obtain the desired length: this is what is called jointing. Afterwards the glue is placed on the obtained beams, then superimposed in the direction of the wood fibres and pressed. After the planing, we can apply some surface treatment or finishes to achieve the sustainability and the desired look.

In compliance with the European norm EN 14080: 2013 [22] glues must belong to the following types of binders:

- Urea resin glues and melamine adhesives, which have already exhibited the characteristics and potential contaminants (growth of nitrogen, formaldehyde);

- Phenolic resorcinol resins glues;

- Polyurethane glues.

These three compounds do not provide any heavy metals, moreover the use of these adhesives is a minor fraction of the mass of the wood.

In the energy recovery process the glued laminated timber is comparable to the natural wood, it does not have a different composition in terms of heavy metals or halogenated compounds.

The collection of the wood outgoing from the building and demolition sector is often made by professional recycling-waste companies, however a significant fraction is collected by the recycling centres which also accept the waste of the enterprises.

The wood waste treated with many additives as utility poles and railroad sleeper is now considered a non-recyclable hazardous waste, that is to say class C wood. The amount of waste of this typology is important, so the recovery cannot be overlooked.

- 7.4 Driftwood

Driftwood and, generally, floated waste is the waste dragged by the wind, the waves and the flow of water and collected on beaches or river dams.

Normally this type of wood can be recycled, in fact some large pieces of driftwood are sought for the construction, according to their relatively rot-proofing characteristics (if the wood has been a long time in the water, nutrients have been leached. This makes it difficult to be degraded by fungi, bacteria and insects). The driftwood found in the sea has a salt content which makes it less susceptible to fire. The river driftwood is treated as Municipal Solid Waste (MSW) and sent to the recycling centres or to the landfill sited, therefore it is a potential source of wood waste not exploited.

- 7.5 Pruning wood

Pruning wood is the wood outgoing from trees breeding, gardens and green spaces. It mostly wood comes from the crown of the tree.

This wood is being exploited in energy recovery in the collective boiler-rooms, treated as Municipal Solid Waste (MSW) and collected by the wood in waste containers.

The characteristics and composition of pruning wood are variable according to the considered species of tree, generally there are two types of wood: the hardwoods, from deciduous trees, and softwood, from pinophytes trees.

- 7.6 Wood outgoing from composting and others

The composting is a biological decomposition process that turns organic waste, including biomass, into compost, a hygienic and stabilized product, like a soil rich in humic compounds.

Composting and other activities generate wood waste currently non-exploited.

• 8. Wood treatment

The norms NF EN 335 [23] categorize the using field of the wood in 5 “using classes”:

- Using class 1: Wood under cover, protected from the weather and not subject of humidity;

- Using class 2: Wood under cover, protected from the weather, occasionally subject of humidity;

- Using class 3: Wood subject to the weather, or frequently subject to humidity but not in contact with the ground;

- Using class 4: Wood in contact with the ground or with fresh water;

- Using class 5: Wood in contact with salt water.

According to their uses the woods undergo treatments that can be of three types:

- 8.1 Mass treatments

Mass treatments are done primarily for the preservation, involving the mass of the material

They are divided into three categories:

- Physical treatments (drying, steaming, etc...): these treatments do not involve the addition of any particular chemical compounds, except in some particular cases, in order to make the timber waterproof. They are impregnated with vegetable oils, which reduce the moisture content by evaporation of the water.

- Treatments with natural products (linseed oil, shellac glaze, beeswax, rosin, etc...): they do not raise the heavy metals content of the wood;

-Treatment with chemicals products: pesticides containing heavy metals such as copper chromium arsenic (CCA) where organic molecules (creosote and PAHs, halogenated organic).

Some of these additives give the wood, especially the end of life, toxicity problems and inside pollution, wich is dangerous for operators and possible precursor of by-products during the gasification.

The principal preservative products are:

- Cromated copper arsenate (or CCA)

This product is very effective for the preservation of wood, especially wood used outdoor, but very toxic (and carcinogenic) because of its use as a biocide prevail; in addition, the CCA was thought theoretically to fix itself in the membranes of the cells, leaving only some traces of residual product in the wood and on its surface. It is a source of serious diseases (including neuropathy and neuropsychological problems) for people exposed to the gases in case of fire or accidental burning. The factories workers, as those exposed to dust in factories which use the pre-treated wood, are also involved.

The aim of the gasification is to concentrate the content of heavy metals in the ashes, avoiding the dispersion of metals in the gasses.

Since the 1990s, the product was gradually banned by a growing number of countries and a growing number of uses. In Europe, several texts (eg Directive 76/464/EEC and following) prohibit the use of creosote. In France, a decree of November 17, 2004 specifies the conditions for the marketing and the use of arsenic and its deriveds; arsenic is still allowed for the treatment of wood, but with many exceptions.

Commercial solutions of these components are either using oxides, CrO_3, CuO and As_2O_5, or salts, e.g., $CuSO_4$, H_3AsO_4 and $Na_2Cr_2O_7$.

Finally the waste CCA-treated wood is considered a toxic and hazardous waste, that is to say Class C wood currently not recoverable.

- Ammoniacal copper arsenate (ACA)

The combination of arsenic and copper in ammoniacal copper arsenate (ammonia facilitates the penetration into the wood) makes this product effective against fungi, bacteria and insects, but these two components are eco-toxic and non-degradable. In particular, they cause problems in the end of life of the object, they are specifically responsible of the growth of the heavy metals content and they need dangerous treatments. The wood waste treated with ACA is considered a hazardous toxic waste and so is classed as a Class C waste, currently not recoverable.

- Preservatives products without arsenic or chromium

These products are often based on copper ethylamine (eco-toxic for many aquatic organisms) with the addiction of co-biocide with a low toxicity to mammals.

Ex: ACQ (copper quaternary amine compound) and CBA (compound of nitrogen and boron copper type) were used in Europe and Japan for several years. They are not as attached at the wood or as stable as the CCA, and their history is less documented. They are also more expensive than CCA, however the wood treated with these products is considered a toxic and hazardous waste, therefore is classed as a Class C waste, currently not recoverable.

- Creosote and coal tar distillates (or wood)

Creosote and coal tar distillates or similar products (generally referred as "creosote") cannot be used excep for certain conditions (if concentration of benzo [a] pyrene B [a] P is lower than 0.005 % in weight, or 50 ppm, and if the concentration of extractable phenols is below 3% in weight, 30 g/kg). [24] In France, following an order of June 2, 2003 the use of creosoted railway sleepers by privates is forbidden; These products are still legal for some industry, which use them for wood treatment (if the benzo [a] pyrene (B[a]P) and extractable phenols content do not exceed certain levels), but the sale of CCA-treated wood was forbidden.

The mixture is relatively complex, rich in phenolic compounds, pyrimidine and polycyclic aromatic hydrocarbons: naphthalene, fluorine and anthracene in particular.

The wood treated with creosote does not have a higher heavy metals content, but is very dangerous for the operators because of the by-products which the combustion generates.

The CTBA (Centre Technique du Bois et de l'Ameublement, Technical Centre of the Furniture Wood) classes preservation products in six families following the different using classes:

- Non-fixing metal salts: mono-component salts (essentially boron, but also phosphate, magnesium oxide, aluminum or antimony) used in the water.

- Fixing metal salts: complex metal salts containing chromium to fix active metals (mainly CCA).

- Organic solvents: tebuconazole, propiconazole, fipronil, melamine, lindane, aldrin, dieldrin azaconazole, Dichlofluanid chloroparaffins and pentachlorophenol (PCP, now banned).

- Emulsions: they use water as a vehicle for the substances and are associated with water-dispersible synthetic substances.

- Other Products: combine metal compounds (copper, boron) with synthetic molecules (CBA, ACQ, copper bis (N-cyclohexyldiaze-niumdioxy) (Cu-HDO), methyl bromide, mainly pyrethroids).

- Creosotes: outgoing from the distillation of coal.

Product Type	Using Classes				
	1	2	3	4	5
Non-fixing metal salts	yes	no	no	no	no
Fixing metal salts	yes	yes	yes	yes	yes
Organic solvents	yes	yes	yes	yes	no
Emulsions	yes	yes	according to the treatment	no	no
Other Products	yes	yes	yes	yes	no
Creosotes	yes	no	according to the case	yes	no

Table 4) Using classes of the preservation products.

- 8.2 Surface treatments

These are the treatments for the aesthetics and the protection of the wood against external aggressions (UV, rain, biodegradation, scratches, etc...).

- Paints, stains and varnishes. They consist mostly in binders (alkyd resin acrylic resins, polyurethane resins, epoxy resins), pigments (zinc oxide (white), Litophone (BaSO4 and ZnS, white), CdS (orange), iron oxides and $Pb_2CrO_4.PbO$ (red) etc…), fillers (calcium carbonate (chalk), magnesium silicate (talc), silica, calcium sulfate), of solvents (ketones, toluene, xylene) and other additives (cobalt);

- The thick plastic coatings, thick plaster mortar cement, whitewash or gypsum;

- Melamine (see below);

- Creosote and coal tar distillates;

- Organo-halogenated compounds such as pentachlorophenol (PCP);

- Sealants and other coatings.

- 8.3 Resins for bonding

These treatments are designed to glue the pieces and the parts of the chipboard. Glues are used as assemblers of solid wood or wood products, including panels. These glues are based on synthetic aminoplast or phenol resins, made of formaldehyde. Epoxy adhesives, glues protein (casein), the starch pastes (dextrin) or glues a rubber (neoprene, acrylonitrile-butadiene rubber) are less used. They provide high levels of formaldehyde and they are potentially dangerous for operators.

The resins and waxes used for bonding wood chipboard are:

- Phenol-formaldehyde (PF)

These polymeric resins are obtained from a reaction between phenols and formaldehyde, they are also called phenolasts.

Phenoplasts show a good heat resistance. They have a dark color, good dimensional stability, and they are less hard and less fragile than aminoplasts.

The use of these resins containing formaldehyde can cause cancer in animals and probably in humans. Such resins are dangerous for operators, mostly during the treatments, especially the storage and the grinding, where a large amount of dust is generated.

- Melamine-urea formaldehyde (MUF)

Used for the agglomeration of wood glued laminated timber, Medium Density Fibreboard (MDF) and Oriented Strand Board (OSB).

Wood treated with MUF is hard, rigid and it has a high resistance to abrasion.

Their mechanical properties make them suitable in continuous processes up to 100 °C. The products have good resistance to most solvents, and they are very sensitive to hydrolysis and to light.

Melamine, as urea-formaldehyde (UF), is a resin of the aminoplasts family, it is not likely to provide the timber a higher heavy metals content, but it provides significant nitrogen content.

The use of these resins containing formaldehyde can cause cancer in animals and probably in humans. Such resins are dangerous for operators, mostly during the treatments, especially the storage and the grinding, where a large amount of dust is generated.

- Isocyanate (PMDI)

An isocyanate is a chemical compound containing the isocyanate functional group N=C=O.

Isocyanates are generally toxic and reactive compounds, which must be handled with care. Exposure to isocynates is dangerous for operators and professionals.

- 8.4 Polluting Compounds

Understanding the wood treatments is useful to us to assume the existence of certain pollutants.

A non-exhaustive table is shown below [24]

Polluting Compound	Treatment(s) that may provide the compound to the wood
Ca	Drying
S	Pesticide, Glues, Paints
Cu	Pesticide, Glues, Paints, Complention
Zn	Pesticide, Glues, Paints, Complention, Preservation, Galvanization
Mn	Pesticide, Drying, Completion
Cl	Paints, Glues, Preservation, Completion, Plastic
N	Paints, Glues, Fire-proofing
B	Preservation, Fire-proofing
Al	Glues
Cr	Glues, Paints, Preservation, Completion
P	Glues, Fire-proofing
Fe	Paints, Assembling, Handling
Pb	Drying, Paints, Completion, Plastics
Cd	Paints, Completion, Plastics
Ti	Paints
Co	Drying
Mg	Glues
Al	Paints
As	Preservation
F	Preservation
Ba	Paints
Sn	Preservation
I	Fungicide

Hg	Paints, Preservation
Ni	Assembling, Concrete

Table 5) Polluting compounds and treatments susceptibles of providing them.

• 9. Characterization

• 9.1 Average elemental and biochemical composition

The elemental chemical composition of wood varies according to species. The timber consists of about 50% carbon, 42% oxygen, 6% of hydrogen, 1% nitrogen and 1% minerals (mainly Ca, K, Na, Mg, Fe, Mn). There is also sulphur, chlorine, silicon, phosphorus, and other elements in small quantities [25].

Wood mainly composed of organic materials (cellulose, hemicellulose, lignin, phenols, terpenes, fatty acids, etc…) and a small percentage (1 to 1.5%) of mineral elements. It also contains a variable amount of moisture and ash [25].

The biochemical compostion gives an indication of the content of the three major molecules (cellulose, hemicellulose and ligning), and the extractives.

- Cellulose (about 50%)

Cellulose is an organic polymer composed of glucose monomeric units (or rather β-D-glucopyranose, formula $C_6H_{12}O_6$), a monosaccharide which is synthesized through the photosynthetic activity of plants from CO_2 in the atmosphere.

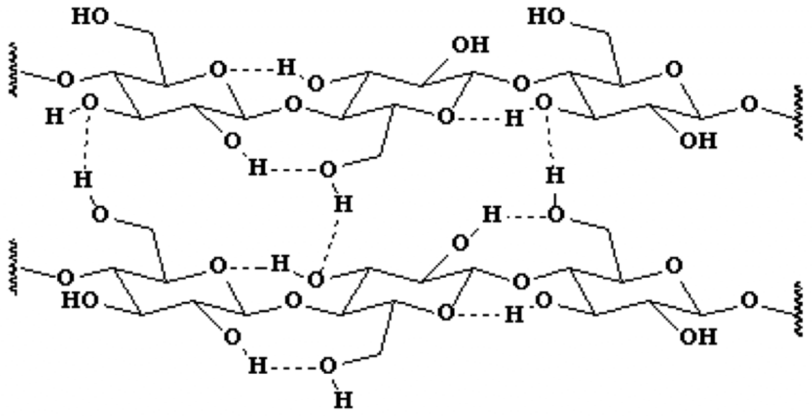


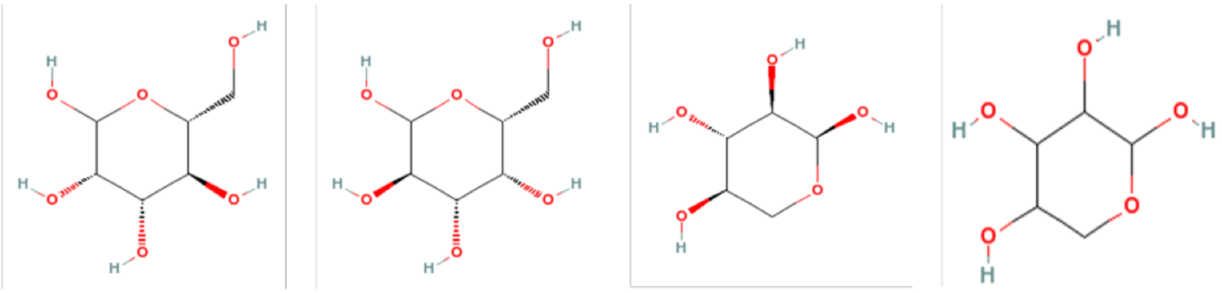
Fig. 6) A representation of two linear chains of cellulose, interconnected by hydrogen bonds.

The above molecules are linked together by appropriate enzymes to form a long, thread-like chain, in which the bond between two of them (which gives rise to the dimer known as cellobiose) is of the 1,4 β-glucoside type, since it involves a carbon atom in position 1 of a molecule and one in position 4 of the other. This results in a rotation of 180 ° for each molecule, which gradually adds to the chain following the elimination of a molecule of water. The linear arrangement of glucose units in cellulose involves a uniform distribution of -OH groups directed toward the outside of each chain. This enables for the formation of hydrogen bonds between adjacent chains.

- Hemicellulose (15-25%)

Hemicellulose is an irregular polymer, chemically similar to cellulose as both constituted of carbohydrates (chemical compounds made of carbon, hydrogen and oxygen in which the last two elements are present in the same proportions in which they appear in the formula of water). While cellulose is crystalline, however, and resistant to hydrolysis, hemicellulose has an irregular and amorphous structure, characterized by little resistance, and is readily hydrolyzed and devolatilized by a dilute acid or base, as well as many enzymes. Hemicellulose is constituted of long chain molecules, like cellulose, but their degree of polymerization is very low and on average about equal to 150-200 monomer units. Hemicellulose chains are often branched. Unlike cellulose, which is a homopolymer, hemicellulose includes several monomeric units, from the chemical group of monosaccharides: six-carbon sugars (mannose, galactose) and five-carbon sugars (xylose and arabinose). The monomeric units are reported in figure 5.

Hemicellulose mainly contains pentose D-sugars and occasionally even small amounts of L-saccharide. Xylose saccharide is always present in higher quantities, but glucuronic acid and galacturonic acid can also be found.



mannosio galattosio xilosio arabinosio

Fig. 7) major monomeric units in hemicellulose.

- Lignin (20-30%)

Lignin is not a carbohydrate, but it has a predominantly aromatic nature and can be seen as an irregular three-dimensional polymer from racemic and relatively complex structure consisting of monomers linked together through a variety of chemical bonds. The type of chemical structure and its reactivity are not, however, completely understood and its isolation remains a problem not entirely solved.

- Estractives:

These compounds are the complementary part of the biochemical composition, they are mainly organic compounds which are extracted together and, thus, grouped together.

In this category there are more than 100.000 compounds that can be grouped in three categories:

Phenols, terpenes and fatty acids.

- 9.2 Heavy metals content of wood waste

The characterization of wood waste has the objective of finding the main pollutants in class B wood.

A precise characterization is difficult to do because wood can be considered class B after several different treatments. This wood includes many different wastes, such as furniture or waste from the construction sector. It is clear that the treatments of the wood in the several sectors have a different purpose and it is reasonable to think that it may be loaded with different pollutants.

Worldwide, the wood preservation industry handles over 30 million m^3 of wood, and it consumes more than 500,000 tons of chemicals.

The physico-chemical characterization of wood waste analysed in this study was based on the work undertaken by the CTBA (Centre Technique du Bois et de l'Ameublement, Technical Centre of the Furniture Wood) [26] and by the CSTB (Centre Scientifique-Technique du Bois, Technical-Scientific Centre of the Wood). [27]

For a complete overview of the pollutants in wood, the table below shows the average polluting compounds contents in the natural biomass and the maximal polluting compounds content, proposed by the FCBA (Institut Technologique Forêt Cellulose Bois-construction Ameublement; Technological Institut of the Forest, the Cellulose, the timber and the Furniture).

Polluting Compound	Content in the natural biomass [*mg/kg*]	Maximum content proposed by FCBA [*ppm*]
Arsenic	1,4	10
Cadmium	0,7	10
Chrome	22,6	100
Copper	21,9	400
Tin	1,7	10
Manganese	180,6	1000
Lead	29	
Zinc	228	200
Heavy-metals total	485,9	1000
Chlorine	1100	6000
Fluorine	40	5000
Organo-halogenated compounds total	4,05	10

Glues and resins	0	150000

Table 6) Concentration of polluting compounds in natural biomass according to the CTBA report and maximum contents according to FCBA.

It is remarkable that the zinc content in the natural biomass is over the limit proposed by FCBA.

The table below shows the minimum, the average and the maximum content of polluting compounds on each class B wood sample studied in the CSTB and CTBA reports, and the maximum contents.

Polluting Compound	Minimal content [*ppm*]	Average Content [*ppm*]	Maximum content [*ppm*]	Maximum content proposed by FCBA [*ppm*]
Arsenic	4	9,9	27,6	10
Cadmium	2	2	2	10
Chrome	2	22,1	230,5	100
Copper	2	153,4	445	400
Tin	3	3,9	43	10
Manganese	17	80,2	213	1000
Lead	2	165,4	1642	
Zinc	7,5	315,3	2896	200
Heavy-metals total		680,3		1000
Chlorine	49	283	553	6000
Fluorine	1	4,32	25,5	5000
Glues and resins	0,1	15,3	78	150000

Table 7) Concentration of polluting compounds in class B wood.

The tests show that there is a considerable heterogeneity in the samples and, therefore, these values should not be taken as reference values.

We list five elements as the main responsible for the levels of the wood pollution: lead, zinc, arsenic, organo-halogenated and chromated copper arsenate (CCA).

Lead and zinc are especially responsible for 70-85% of the trace metal elements contamination and the zinc has a higher content in the natural biomass (228 mg / kg) compared to the limit (200 ppm).

- 9.3 Composition of the ashes

For the characterization of the ashes several studies are compared. The contents of the main compounds increase with the growth of the number of the treatments received. The Cu, Pb, Zn, and Hg content are significantly different between the treated biomass and clean.

But the results have to be treated with care, for example: for the same type of fuel, with wood chips, the values obtained by different organizations are very different.

Compound	Natural Wood [*mg/kg*] [28]	Wood waste [*mg/kg*] [28]	Wood with few addictives [*mg/kg*] [24, ADEME]	Non-Hazardous Industrial Wood waste [*mg/kg*] [24, ADEME]
As	< 1	< 2	132,8	61,5
Cd	< 1	< 5	6,8	7,5
Co	6 - 27	< 10		
Cr	< 10	16 - 810	1150	568,5
Cu	99 - 498	43 - 1450	827,1	994,4
Ni	20 - 250	18 - 235	4,9	84,3
Pb	9 - 450	49 - 7300	1461,5	506,3
Zn	54 - 1900	18 - 6200	1169,4	1655,3
Hg				0,3
Se			2,2	2,3

Table 8) Metallic compounds in the wood ashes.

- 9.4 Comparison with the Refuse-Derived Fuels (RDF)

One of the current energy recovery processes for the class B wood is the use as Refuse-Derived Fuels (RDF), typically used by cement producers.

A comparison is made to better understand the difference between the standards of an average cement producer and the French regulatory values on the RDF.

The French norm CEN/TS 15357, published in 2006, deals with the terminology and definitions for Refuse-Derived Fuels (RDF).

According to this norm there are five categories of RDF classified according to their LHV, chlorine, and mercury.

Parameter	Measure	Unit	Class				
			1	2	3	4	5
LHV	Average	[*MJ/kg dry*]	25	20	15	10	3
		[*kWh/t*]	6960	5560	4170	2780	830
Clorine	Average	% sur sec	< 0,2	< 0,6	< 1	< 1,5	< 3
Mercury	Median	[*mg/MJ dry*]	< 0,02	< 0,03	< 0,04	< 0,05	< 0,06
	80th percentile	[*mg/MJ dry*]	< 0,04	< 0,06	< 0,16	< 0,3	< 1

Table 9) Classification of the RDF according to the norm CEN/TS 15357

Parameter	Cement producer	Class of the norm CEN/TS 15357
PCI	> 12 MJ/kg dry	4
Grading	< 20/40 mm according to the use	
Moisture Content	> 20 %	
Ash Content	5% - 20%	
Chlorine	< 0,5%	1

Table 10) Comparison between the quality request of a cement producer on the RDF and the norm CEN/TS 15357 classes

• 10. Availability of the recoverable wood waste in France

The resource of wood exploitable in energy in France has a strong growth potential, according to the availability in the different sectors. The exploitation of the French forest promotes the local economic activity, thereby contributing to sustainable regional development.

For class A wood, several resources are exploited:

- Wood forest residues: This resource is relatively unexploited, and it is abundant. In 2004 around 9,2 million Tonne of Oil Equivalent (TOE) were used, mainly for domestic use. The forest residues are by far the biggest deposit [29].

- Clean wood from the processing of wood industries: The wood industry, sawmills, furniture and other sectors of the wood industry, generate by-products at each stage of processing. Some of these products are exploited in the same activities, mainly for heating. Sawmill waste is recycled by grinding industries but also by energetic recovery.

The aim of this work is not to account the availability of calls A wood, but these values are important because the wood waste takes clearly origin from the exploitation of the natural wood, and we can imagine that a growth of the natural wood exploitation could came first a growt of the wood waste.

To estimate the class B wood availability is complicated, especially because this kind of wood follows different paths of collection, in fact it can be collected by the recycling centres (e.g.: in the case of furniture wood) or can be collected by specialized enterprises if coming from a specific sector (including wood from construction sector and public works).

The energy recovery of class B wood was not widely practice before the nomenclature 2013-814 of 11 September 2013 [1] because the regulatory norms did not allow it, excep for some cases.

Class B wood is currently recycled mainly for the production of particle board for the domestic and European markets.

To evaluate the deposit several reports and publications were considered:

According to a CTBA report (Centre Technique du Bois et de l'Ameublement, Technical Centre of the Furniture Wood, April 2003 "Valorisation énergétique des déchets de bois faiblement adjuvantés") [26], the availability of wood waste generated by the first and second transformation (in total, activity logs, packaging, construction and furnishing, suddenly wood waste including wood of class A) is estimated to be about 12 million of tonnes.

According to the report by Pollutec, FCBA (Institut Technologique Forêt Cellulose Bois-construction Ameublement; Technological Institut of the Forest, the Cellulose, the timber and the Furniture) and Federec [2], the national class B wood availability is 5 million tonnes, of which 3,8 million tons are collected.

Among these 3,8 million tons: 3 million tons are recovered and 0,8 million tons are eliminated.

The origin of these 3 million tonnes is estimated to be 60% (1,8 million tons) of wood waste from construction and 40% (1,2 million tonnes) of furniture wood [2].

For a complete and updated overview, and to check the consistency of the data, we have made a study on the availability of different raw materials, that is to say: packaging, furniture and wood coming from the contraction sector.

- 10.1 Packaging wood

Collection of packaging is characterized by large leaks, including the lack of data collection on the part of the reused packaging, especially the pallets. If there is a growth of the reuse, however, it is not possible to estimate this growth or even check this trend without getting into a detailed survey. Thus, the output flow of the reuse circuit is determined by considering that the flow of new pallets placed on the market is the same amount of pallets discarded.

The table below shows the different flow packaging France, the data are in units of pellets and all the packaging types are single use only.

Packaging type	Pallets, Pallet-Cages	Cases, Boxes, Crates	Reel and Bobbins	Light Packaging	Total
Empty packaging products placed on the market in France	576518			433486	1010004

Empty packaging products made in France and exported	189214	13546	3161		205921
Empty reusable packaging products placed on the market in France	563388				563388
Empty packaging products imported	696791	24203	203		729483
Full packaging products placed on the market in France	1273309			466178	1739487
Full packaging products imported	110000				110000
Packaging waste outgoing from the French market	1273309	466178			3588974

Table 11) Fluxes of packaging products in France [30], data from INSEE-SSNE (Service de Statistiques Nationales d’Entreprises, National statistic service for enterprises, 2008).

For conversion in volume (data INSEE-SSNE 2008):

- mono rotation palettes: 0,026 m^3 sawn / unit;
- reusable pallets: 0,035 m^3 sawn / unit;
- pallet-cages: 0,09 m^3 sawn / unit;
- reusable pallets-cage 0,12 m^3 sawn / unit;
- Handling platform: 0,02 m^3 sawn / unit;

For conversion to mass the average density retained at 15% humidity is 555 kg/m^3 (estimation by CTBA, confirmed by the FCBA 2010 for the incomings).

The report by ADEME [30] counted a total wood packaging products of 2,5 million tons, 670 thousand tons recovered, the most part of recovery is recycling (460 thousand tons).

Packaging waste	Mass [tn]
Packaging wood waste produced	2.412.875
Energy recovered	460.000
Recycled	213.214
Total of recovery	673.124
Packaging wood input to the collection	1.001.319
Packaging waste collected but not recovered	3.28.105
Packaging waste ot collected: lack of collection or reuse	1.411.556

Table 12) Packaging waste according to the ADEME report [30].

The data found show the existence of an immediately exploitable potential of 328 thousand tons of packaging, in which it is possible to add the resource currently not collected. The probem with the flux of non-collected material is that the lack of data makes impossible to estimate the reused flow. The exploitable potential of packaging wood waste in France is between 328 thousand tons and 1,74 million tons. According to the report of ADEME Anfor (Anfor, 2002) [31] to estimate emissions from the combustion of wood with few additives, the availability of the packaging wood is quantified as:

- Between 100 and 200 thousand tons of boxes and cages

- Between 1 and 2 million tons of pallets.

From this study we can say that the data is consistent and the availability currently collected is 328 thousand tons, but exploitation can be up to 1,74 million tons (with a percentage of collection of 100% and a percentage of reuse 0%).

- 10.2 Furniture wood

Most of the collection of furniture waste is made in recycling centres, following the studies of foreshadowing conducted by ADEME in 2010 [32], the sector of furniture produce, adding together households and professionals, between 2,2 and 3,2 million tons of waste. The average availability of household and non-household furnishings is 2,7 million tons, in which:

- the availability of household furniture and related is 2,1 million tons, or 33 kg/capita/ year; 88% of total availability (estimated in 2009, based on 63,4 million of inhabitants);

- the professional furniture availability is 600 thousand tons, 22% of the total deposit (2009 estimate).

Only 40% of this furniture waste was recycled in France in 2012.

Today it is estimated that only 45% of the total can be recycled, and 35% can be recovered for energy.

The table below shows the current scenario.

Origin	Tons/year	Percentage	Percentage of collected wood	Mass of collected furniture wood [tn]
Household furniture	2100000	88%	35%	735000
Professional furniture	600000	22%	35%	210000

Table 13) Furniture wood waste, current scenario.

The deposit of recoverable wood today is 945 thousand tons.

Furniture producers may organize themselves individually, or collectively within one or more certified eco-organizations, respecting the recycling specifics given with the inter-ministerial decree.

The REP (Responsabilité élargie producteurs, extended producer responsibility) aims to achieve 75% of recycling and re-use in 2015 on furnishing professionals' waste, and 45% on households furnishing waste. Considering that the estimated life for furniture is 15-20 years, the availability of furniture waste for energetic recovery will decrease from an estimated mass of 1.095.000 tons/year (in which 945 thousand tons from household furnishings waste) to 150 thousand tons of professionals' furniture waste.

The table below shows the scenario in 15-20 years

Origin	Tons/year	Percentage	Percentage of collected wood	Mass of collected furniture wood [tn]
Household furniture	945000	86,3%	35%	330750
Professional furniture	15000	13,7%	35%	52500

Table 14) Availability of furniture wood waste in the medium term future.

The availability of exploitable wood in 15-20 years will be 1,095 million tons, but if the percentage of collection is the same as today only 388,25 thousand tons will be recoverable.

As in other sectors, the sorting, collection and processing of used furniture has been entrusted to an eco-organization, created by the industrials of the sector and the law requires that they manage their waste.

It was decided that there would be two environmental organisms, one for households furniture waste (Eco-Mobilier) and another one, Valdelia, for enterprises, local communities (hospitals, schools, etc.), stores bars, hotels and restaurants.

The aim of Eco-Mobilier is to achieve by the end of 2017 a recycling rate of 75% of professionals' waste furniture, whose current availability is 600 thousand tons. For Valdelia the goal is the collection of 87 thousands tons.

According to the report of ADEME Anfor (Anfor, 2002) [31] to estimate emissions from the combustion of wood with few addiitives, the availability of the furniture wood waste is about 1 million tons.

From this study we can say that the data is consistent and the current wood furniture availability is 945 thousand tons.

- 10.3 Construction and dismantling wood waste

A building consists in a large number of materials that can be very different depending on the use of the building, the year of construction or the location and origin of the materials.

The wood is only one part of these materials and it can be a non-hazardous waste (if wood Class A or B) or a hazardous waste (case of wooden class C).

For the evaluation of the availability of such waste several studies have been done, the first study takes back to 1994 (ADEME) [33] and evaluates the deposit of waste from demolition and dismantling of 24 million tons, of which only 10,2 million tons generated by the demolition were categorized in:

- Inert waste: 64,7% or 6,6 million tons;

- Non-hazardous waste: 33,3% or 3,4 million tons;

- Hazardous waste: 18,6% or 1,9 million tons;

A reassessment of the availability was carried out in 1999, the entire waste of buildings was estimated at 31 million tons (ADEME, FFB, 1999) [38], including 17,3 million tons coming from the demolition only. According to the waste categories defined by the regulations, the total amount of construction and dismantling waste is divided as so (ADEME, FFB, 1999) [38]:

- Inert waste: 65,1% or 20,15 million tons;

- Non-hazardous waste (ex-industrial waste): 28,4% or 8,804 million tons;

- Packaging: 1% or 310 thousand tons;

- Hazardous waste: 5,5% or 1,705 million tons.

Asbestos waste and treated wood waste constitute the main hazardous waste.

A report made in 2004 (IFEN, 2007) [39] estimates that the building sector would have generated 47,9 million tons of waste (double that of 1994), of which only 31,2 million tons were generated by the demolition. In total, demolition waste had the following distribution:

- Inert waste: 93,6% or 29,2 million tons;

- Non-hazardous waste: 5,8% or 5,8 million tons;

- Hazardous waste: 0,6% or 0,2 million tons;

To summarize: the table below shows the statistics values of the reports considered in relation to the total waste dismantling and demolition of the construction sector.

Material	1994 [millions of tons]	1999 [million of tons]	2004 [million of tons]
Inert waste	-	20,15	-
Non-hazardous waste	-	8,804	-
Hazardous waste	-	0,31	-
Total	24	31	47,9

Table 15) Construction, dismantling and demolition waste amounts, values from ADEME [38] report and IFEEN [39] reports.

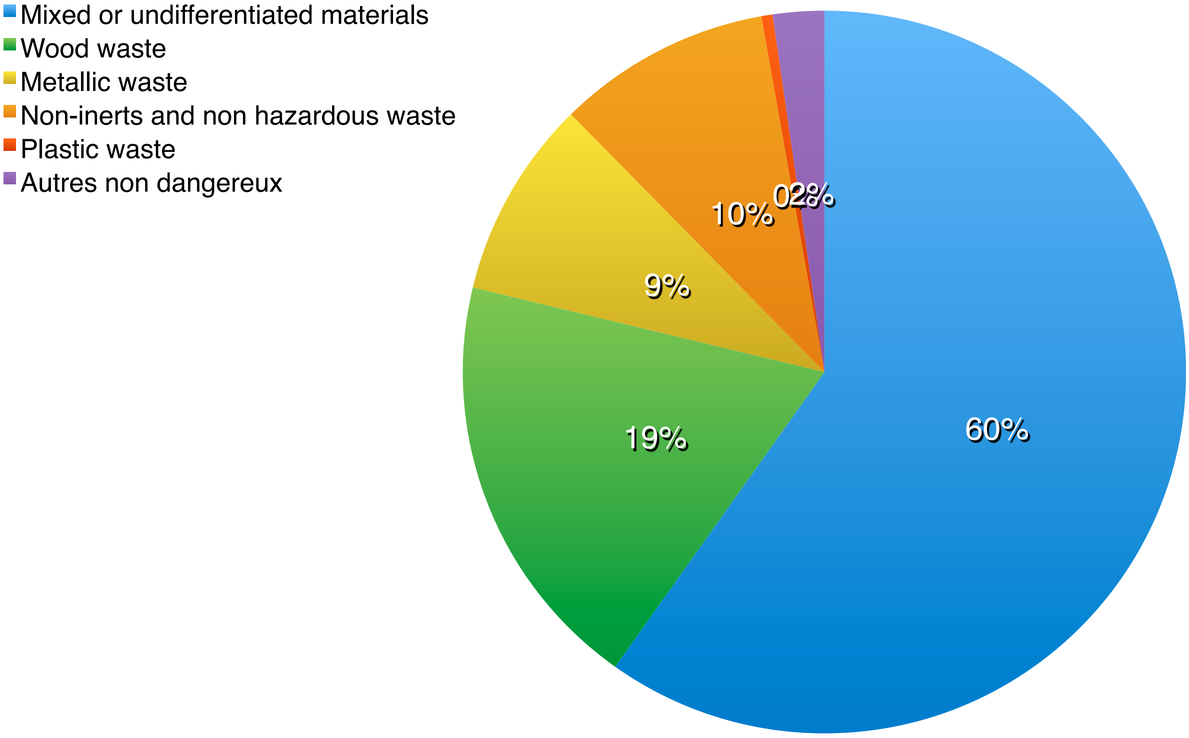
The growth trend for this category of waste is evident; anyway an assessment of the flow of hazardous and non-hazardous waste is insufficient.

On the 2004 data a distribution was made to establish the origin of materials.

The non-hazardous waste is mainly mixed or undifferentiated material (60% of non-hazardous waste from demolition). The rest is wood waste (19%), metal waste (8,9%), non-hazardous and non-inert waste such as plaster (9,6%), waste plastics (0,5%) and various other non-hazardous waste (2,3%).

The 2004 data therefore assesses a deposit of 340 thousand tons of class A and B wood, produced by the demolition and the dismantling of buildings only.

The data shown can be improved because, according to the IFEEN report, even if 71% of waste from demolition of buildings and public works was recycled or incinerated in 2004 (with energetic recovery), there would still be 488 thousand tons of wood from demolition and public works landfilled and not incinerated.



Graphic 1) Distribution of the building sector waste in the different categories.

In 2008, an ADEME information note [40] gave an estimation of the changes from the 2004 data, this briefing note highlights the characteristics of the waste of the building, where the mass of wood waste is 3,6 million tons.

This is the most consistent datum, therefore we refer to it on the final count.

- 10.4 Floated wood, wood from recycling centres and others

The availability of raw wood materials such as driftwood and wood from wood waste containers in recycling centres is difficult to quantify.

Regarding the driftwood, there are no studies on the availability at the national level because the problem is treated differently in each region and this wood is normally treated as household refuse.

The wood coming from the recycling centres is difficult to quantify at the national level as well.

- 10.5 Conclusions on the availability of wood waste

The table below shows the amount of wood waste collected today, divided by origin.

	Packaging wood	Furniture wood	Building sector wood	Total
Availability [million tons]	0,328	0,945	3,6	4,873
Percentage	6,73%	19,39%	73,78%	-

Table 16) Availability of wood waste, divided by class.

The total availability of class A or B wood recoverable energy is 4,873 tons, including:

- The packaging wood is 6,73% with a deposit of 328 thousand tons;

- Wood furniture is the 19,39% with a deposit of 945 thousand tonnes;

- Wood construction of the building is the 73,87% with a deposit of 3,6 million tonnes.

Comparing this data with other reports, we can say that the availability evaluated is consistent with the Pollutec reports estimation. On the other hand, the CTBA report estimates a double availability for the wood waste.

	CTBA	Pollutec	
Availability	12 million tons	5 million tons	4,873 million tons

Table 17) Comparison between the estimation of class B wood availability

The table below shows the availability of class B wood in the future (medium term).

	Packaging wood	Furniture wood	Building sector wood	Total
Availability [million tons]	1,741	1,095	3,6	6,436
Percentage	27,05%	17,01%	55,93%	-

Table 18) Availability of wood waste, divided by class in the medium term future.

The total availability of class A and B wood exploitable and recoverable will be 6,436 million tons including:

- The packaging will constitute the 27,05%, with an availability of 1,741 million tons;

- Wood furniture will constitute the 17,01%, with an availability of 1,095 million tons;

- Building sector wood will constitute the 55.93%, with an availability of 3,6 million tons.

- 10.6 Class C wood

Class C wood is categorized as a hazardous waste, so it cannot be recovered for energy. This type of wood gets waterproofing, fireproofing, creosote and CCA treatments.

According to a publication of ADEME (ADEME, 2002) [33], the national deposit of hazardous waste was 11 million tons in 1998, according to a doctoral thesis UNAM (University Nantes Angers Le Mans) [35] the deposit of hazardous waste in 2004 was 9,1 million tons, including treated wood waste estimated as 27% of the total, or 2,457 million tons. This amount consists exclusively of waste from public works.

The two main class C wood categories are the railway sleepers and the utility poles.

The railway sleepers collected by RFF (Réseau Ferrée France) and SNCF (Société Nationale Chemin de Fer, French National Railway Company) are a problem in relation to the disposal and treatment.

The amount of railway sleepers collected per year by RFF is 66,000 tons. A cost of 6 € per sleeper for the elimination, it will cost 4,8 million € each year to remove 800 thousand units [36].

SNCF said through a personal communication that the amount of railway sleepers gradually replaced is currently estimated at 1 million tons collected on a 10-year work scale, while there are other sources that the flux of railway sleepers is 150 000 tons/year. [36]

Regarding the utility poles, the companies involved are France Telecom and ErDF (Energie de France, Energy of France).

France Telecom estimates between 1,5 and 2 million € to remove 300 thousand poles annually, which corresponds to 12 thousand tons of wood. [35]

ErDF estimates a removal cost of 1 million € per year, but it doesn’t give any information about the mass of wood removed. Taking into account the same treatment cost estimated by France Telecom (between 5 and 6.67 €/poles) the removed poles are between 150,000 and 200,000 units, which corresponds to between 6 and 8 thousand tons. [36]

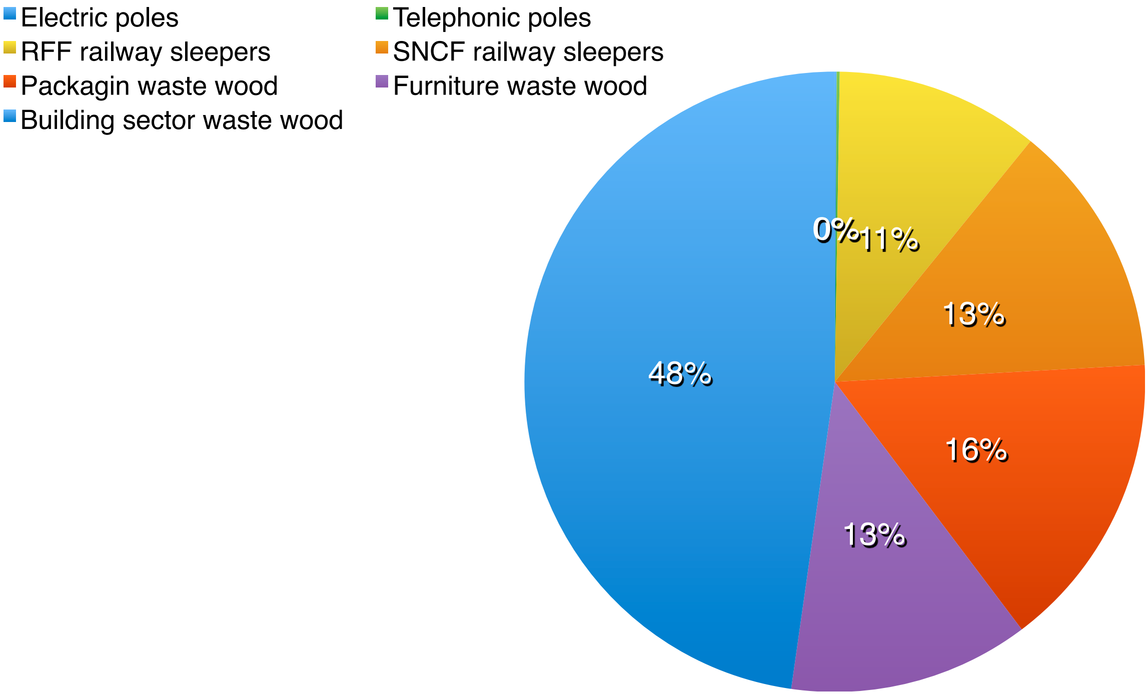
Therefore, the total availability of utility poles is between 18 and 20 thousand tons.

The amount of class C wood waste is considered about 1,82 million tons with a growth of 240 thousand tons per year. [36]

	Electric Poles (ErDF)	Telephonic Poles (Télécom France)	Railway sleepers (RFF)	Railway sleepers (SNCF)
Already removed [ton]	7000	12000	800000	10000000
Annual flux [ton]	-	-	66000	1000000

Table 19) Availability of class C wood.

- 10.7 Summary of the national availability of wood waste



Graphic 2) Distribution in categories of the wood waste.

The total mass of wood waste is 7,57 million tons including:

- between 4,87 and 6,44 million tons of class A or B wood waste, recoverable in energy, that is to say the 75,9% of wood waste;

- 1,82 million tons of class C wood categorized as hazardous waste and currently unusable, that is to say the 24,1% of the wood waste.

- 10.8 Rhône-Alps region

Several studies at regional level are made because of the easier data collection at this scale. The wood sector companies conduct surveys on the territory, especially in the recycling centres. The aim of these businesses is the development of the production of Refuse-Derived Fuels (RDF), especially for cement production and wood panel construction.

The table below shows the collection in the wood waste containers of the Rhône-Alps region, the investigation was conducted by Eco-Mobilier. [37]

	Population [hab]	Theoretical Availability [ton]	Collected waste [ton]	Wood collected [ton]
Ain	79424	774	121	81
	127795	1246	194	130
Allier	167969	1638	255	171
Ardèche	163408	1593	249	167
Cote-d’Or	134482	1311	205	137
Doubs	236783	2309	360	241
	7251	71	11	7
Drome	299396	2919	455	305
Isère	434324	4235	661	443
	673840	6570	1025	687
Jura	119506	1165	182	122
Loire	552671	5389	841	563
Haute-Loire	76987	751	117	78
Puy de Dome	524762	5116	798	535
Rhone	1281971	12499	1950	1306
	156399	1525	238	159
	181231	1767	276	185
Haute-Saone	248947	2427	874	585
Saone-et-Loire	319996	3120	487	326
Total			9297	6229

Table 20) Collection of the waste in the wood waste conainers of the Rhône-Alps region.

- 10.9 Rhône department

Another study was done by SITA Suez on the Rhône department, the report is based on eight EPCI (Etablissement Public de Coopération Intercommunale, Public Establishment for Intermunicipal Cooperation):

- Urban Community of Lyon (1,253,179 inhabitants, 57 municipalities);

- Community of the Heyrieux municipalities;

- Community of the Miribel municipalities (21 874 inhabitants, 6 towns);

- Community of the Pays de l'Arbresle municipalities (34 435 inhabitants, 18 towns);!

- Urban Community of Villefranche sur Saône (49 588 inhabitants, 4 towns);

- Urban Community of the Pays Viennois (67 264 inhabitants, 18 towns);

- Community of the Porte Dauphinoise de Lyon municipalities.

The area does not include all the Rhône department, but the mass of waste produced in the listed zones is comparable to the department's one, that is because, apart for Lyon, the region is largely rural.

The total amount of wood waste of the communities is estimated at 39 thousand tons in the region, it is divided into:

- 2,1 thousand tons collected in wood waste containers;

- 2,2 thousand potentially collectable via a sort action in the bulky waste containers, this wood is mainly of class B;

- 15,8 thousand tons potentially collectable: wood waste included in the complex waste (sofas, mattresses, etc..). This wood is essentially of class B;

The total amount of wood waste produced by professionals is estimated at 144 thousand tons in the region, it is divided into:

- 106 thousand tons collected in the wood waste conainers;

- 35 thousand potentially collectable from a sort action on the non hazardous industrial waste, whose recovery rate is 15%;

To conclude: the potential availability of wood in the studied area can be estimated to 183 thousand tons per year including:

- 127 thousand tons which currently available, which:

    -84,000 tons of class B;

    - 43,000 tonnes of class A;

    - 53 thousand tons more or less easily collectable by implementing the sorting process, including:

    - 20 thousand tons of class B;

    - 33 thousand tonnes of class A;

11. Collection

The waste can be categorized in two types, according to the collection path:

11.1 Non-Hazardous industrial waste

The non-hazardous industrial waste consists in all the non-inert and non-hazardous waste generated by industries, manufacturers, traders, craftsmen and service providers; many materials can be listed as non-hazardous industrial waste, such as: scrap, non-ferrous metal, paper and cardboard, glass, textile, wood, plastic, etc.

According to an ADEME report (ADEME, 2004) [42] the amount of wood in the non-hazardous industrial waste is around 29%. This wood is collected in the majority by specialized enterprises, which generally use it to produce Refuse-Derived Fuels (RDF) and grind it in order to produce panels.

Some recycling centre accepts the non-hazardous industrial waste from the small enterprises, generally collecting it the wood waste containers.

- 11.2 Municipal solid waste

Municipal Solid Waste (MSW) is the waste collected by the public service of waste collection. It includes the residual fraction of household waste, bulky waste collected door to door, recycling waste and the waste outgoing from the sorting and the composting.
The wood waste is not a large part of the MSW, but it is classified as recyclable waste. Some examples are: packaging, wood floated, pruning wood, etc…
The MSW is mostly collected in recycling centres.

The collection is made by two kinds of organization:

- 11.3 The enterprises

The aim of the collection for the specialized enterprises is to collect wood waste for recycling inorder to produce the panels or to recovery it in energy as Refuse-Derived Fuel (RDF). For example: in the furniture sector, Valdelia and Eco-Mobilier collect household and industrial waste in order to respect the recycling criteria imposed by the recycling law.

- 11.4 The recycling centres

The recycling centres collect waste such as municipal solid waste or non-hazardous industrial waste. They separate the waste sorting it in two containers:

- the wood waste container which normally accepts raw wood, doors, plywood, window frames, pallets and wooden furniture. The wood with many addictives is considered hazardous waste and it is rejected;

- the bulky waste container, in which it is possible to find different materials, fro this reason we need to sort the waste to recycle the wood containde in it.

A national level accurate characterization of the bulky waste is now unavailable. Several characterizations at the local level are available and the reported data are highly variable, there is a strong distinction between the urban and rural case.

The improving of the recovery technologies and the growing interest of environmental issues allowed the birth of the professional companies, specialized in the collection and the recycling of wooden furniture, such as Valdelia and Eco-Mobilier.

Unsorted and non-recoverable waste is sent to landfills.

• 12 Experimental analyses

The aim of the experimental anlyis was to find some differences between the natural wood and the wood with a few addictives. This aim was reached with three kind of analysis, the calorimetric analysis, the Termogravimetric Analysis (TGA) and the Differential Scanning Calorimetry (DSC). These analysis were chosen because they can give important informations with a realtive easy condition of work. Especially the TGA is a very common analysis and, with a temperature control, it can give informations about the thermal decomposition of the analyzed sample indicating the temperature where this thermal decomposition takes place.

Comparing the different TGA of the samples we can find the differences in their thermal decompositions and then get some conclusions about their different behaviors under a regime of temperature.

In an another part of this study it was applied a simulation model, with the aim of evaluating the consistence of the anlysis and the simulations. In this part some other analyses were made, changing the operation conditions, in order to test the model and the simulation.

• 13 Materials and methods of analysis

Several analyses were made to understand the differences on the different wood typologies.

Three kinds of analysis were made:

• 13.1 Calorimetric analysis (bomb calorimeters)

Calorimetric analysis allow us to measure the amount of energy contained in a mass unit of fuel, it can be reported as HHV or LHV.

- The HHV (Higher Heating Value) represents the heating energy coming from the burning of the fuel by recovering the evaporation latent heat of the water in it.

In the SI (International System of Unit) it is measured as [J/g], but the most used unit is [MJ/kg] and it can be also written in [kcal/kg] or [kWh/ton].

This remains a theoretical value of the energy because the latent heat of the steam is not used in the real applications, in which is rejected with the outgoing gasses.

- LHV (Lower Heating Value) represents the heating energy coming from the burning of the fuel without recovering the evaporation latent heat of the water in it.

This value gives an indication of how much energy is theoretically recoverable by the user in a real application. The lower heating value is influenced by moisture, in fact the higher is the moisture content, the lower is the LHV.

In the SI (International System of Unit) it is measured as [J/g], but the most used unit is [MJ/kg] and it can be also written in [kcal/kg] or [kWh/ton].

To assess LHV and HHV, the sample is put in a bomb calorimeter in presence of oxygen. The HHV is determined at constant volume from the observed observed temperature rise, taking into consideration the secondary chemical reactions and possibly heat losses.

The LHV is then calculated from a measured basic wood decay. The calibration is performed with benzoic acid, whose HHV is known (26,453 kJ/g).

The wood sample is ground and pelletized under a 10 tons pressure. It is placed in a cup which is itself placed in a bomb calorimeter. The combustion is electrically initiated by a nickel chromium wire connected to a cotton thread. Each test is repeated three times.

- 13.2 Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) has the purpose of measuring the mass of the sample as function of temperature or time, under a temperature regime.

Such analysis requires a good accuracy for the three measures: mass, temperature and temperature variation. The thermogravimetric analysis aimed at monitoring the mass of the sample, but not in absolute terms, in fact it calculates the mass difference and the mass evolution under the temperature regime.

Most of the weighing scales dedicated to the TGA are now equipped with a beam or parallelograms mechanism operating from a zero-setted method. The position of the movable part is kept constant and the electromagnetic force required to balance it gives informations about the mass difference.

- 13.3 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a thermal analysis technique that measure the differences in heat exchange, as function of the temperature or the time, between a test sample and a reference sample, for example air.

There are two types of DSC calorimeters: heat flux DSC and power compensation DSC.

In the heat flux DSC calorimeters, the samples and the inert reference are arranged symmetrically in a furnace. The detectors are placed under the carriers supporting the sample and the reference is constituted of thermocouples (basical DSC) or a flow meter (several thermocouples in series), which allows to increase the sensitivity. They are connected in opposition such that, in the absence of physical-chemical transformation in the sample, the voltage sensor is zero.

In power compensation DSC calorimeters, the samples and the reference sample are equipped with heating elements to maintain equal the temperature of the sample and the one of the reference. The calorimeter's signal recorded is the difference of the thermal power delivered to the sample and the one delivered to the reference to ensure equal.

- 13.4 Equipment for the analysis

Fig. 8) SETRAM Labsys TG/DSC 1600.

The used device is a Labsys TG/DSC 1600 SETARAM whose working range extends from the room temperature up to 1600 °C. It is formed by a structure which integrates the controller and which can associate the beam balance module with the DSC sensor (heat flux DSC) in a metal resistor furnace. A permanent circulation of water in the furnace enables the regulation of the temperature and the cooling during the test. The device operates with a scavenging gas flux, directed upward by the two shells that surround the measuring rod.

All the experiments were conducted with a cane TG-DSC room temperature/1600 °C. Furthermore we have chosen an alumina crucible with a capacity of 100 μL.

- 13.5 Experimental conditions

For the selection of the experimental conditions several publications were studied, that is because the influence of experimental parameters is very important.

For each sample two analyses were carried out under air and under nitrogen, the values shown further are average values

- Scavenging gas

The scavenging gases used are two, air and nitrogen. They were used to enable either an oxidizing atmosphere (with air) to assess the phenomena of combustion, or a reducing atmosphere (with nitrogen) to assess the phenomena of pyrolysis. The scavenging gas is supplied at 30 mL/min. For comparable sample sizes the flow values vary between 20 and 120 mL/min [43]. A rate too low limits the supply of oxygen and can be a limiting factor for the combustion.

- Heating rate

The heating rate chosen for the first part of the analyses is 10 °C/min, this is the rate generally used to study the wood [44]. Low rate and therefore a slower reaction kinetics generally allows a better observation of related phenomena although the sensitivity (peak height) is diminished. Increasing the speed causes a shift in the maxima peak to higher temperatures [45].

The heating rate of the further analyses are 20 °C/min and 40 °C/min, these values are pretty high for a TGA on the wood (especially 40 °C/min), but they was used in order to test the model's simulation in unusual heating rate conditions.

- Process

The process is divided in three phases:

- a stabilizing phase of 300 seconds (5 min) that starts at the room temperature and ends at 20 °C;
- a heating phase, where the temperature rises up to 850 °C. The heating rate is 10°C/min, so this phase lasts 83 minutes (heating rate 10 °C/min); the ending temperature for the further analyses is 1400°C, in order to see a complete thermal degradation of the biomass
- a cooling phase with the decrase of the temperature from 850 °C down to 20 °C. The heating rate is -10 °C/min, so this phase lasts 83 minutes (heating rate 10 °C/min);

- Mass and crucible

The mass of the analyzed samples was about 10 mg (± 0,3 mg) and the crucible is made of alumina (Al_2O_3).

Cane	Crucible	Scavenging gas	Heating rate	Temperature range	Mass of the samples	Scavenging gas flux
DSC 1600°C	Alumina	Air or Nitrogen	10 °C/min	20°C - 850°C	10± 0,3 mg	30 mL/min

Table 21) Experimental Conditions of analysis.

- 13.6 Materials

The analyzed samples are:

1) mixture of class B wood taken from the enterprise LIGNATECH, specialized in recycling wood which normally use to produce RDF (reference name: Class B wood);

2) pellets of natural oak wood used by the enterprise COGEBIO as fuel for a gasification process (reference name: COGEBIO wood)

3) sample of a wooden cage, representing the packaging wood (reference name: Cage wood);

4) chipboard wood (reference name: Chipboard wood).

In the case of chipboard wood the first analysis were conducted on the whole piece, that is to say the mixing of the surface (mainly made of melamine) and the interior (chipboard).

To better assess the effect of the melamine on the wood, we added the following two samples

5) the surface of the chipboard wood, to better understand the behavior o the melamine surface under a temperature regime (reference name: Chipboard surface);

6) the interior of the chipboard wood, to better compare the difference made by the melamine surface and the resin in the inside of the chipboard wood (reference name: Chipboard interior);

An elemental analysis was conducted on the first two samples, in order to have the elemental composition of the sample representative for class B wood (Class B wood) and natural biomass (COGEBIO Wood).

Sample	C	H	O (by difference)	N	S	Cl	Ash	Moisture (after the drying phase)
Class B wood	49,3	5,7	40,9	1,74	0,056	0,075	2,2	0,5
COGEBIO Wood	47	5,8	41,9	1,44	0,061	0,065	1,5	0,3

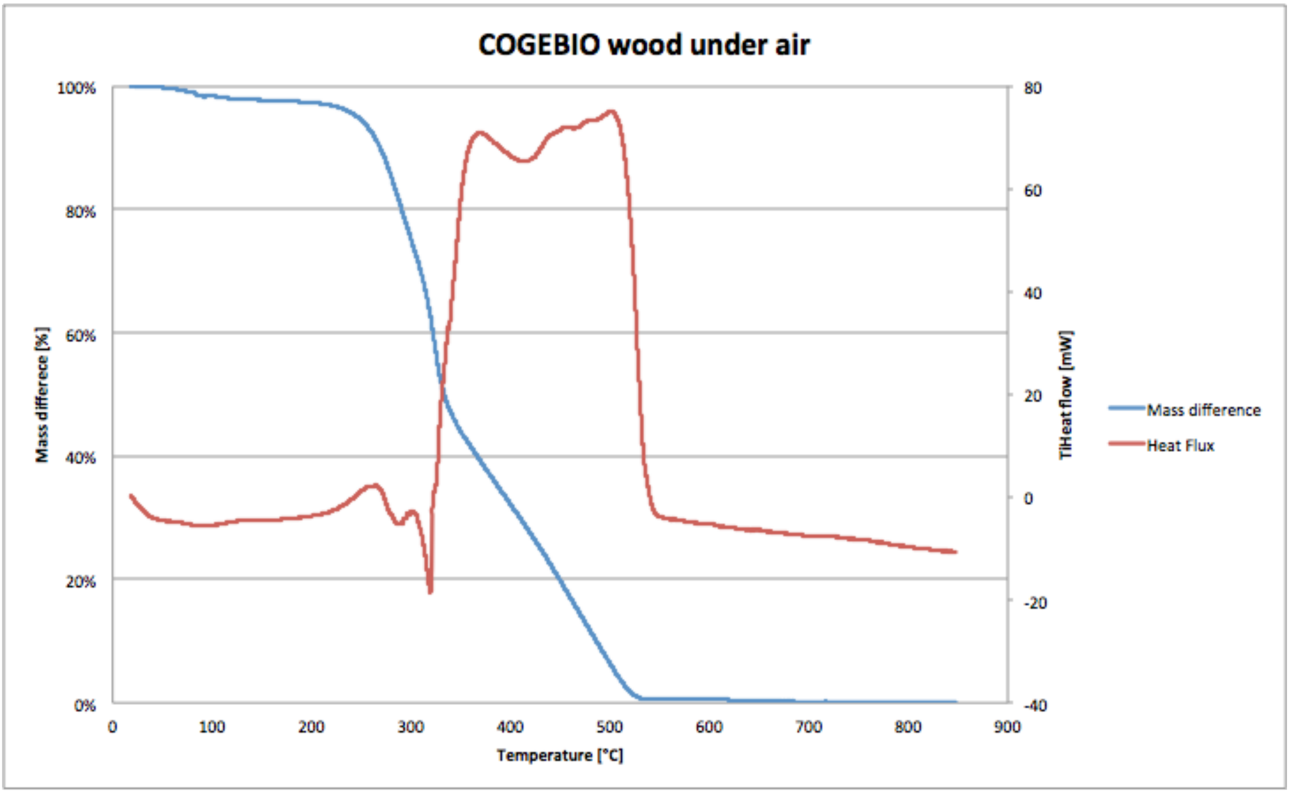
Table 22) Elemental analysis of the samples of Class B Wood and COGEBIO Wood. All the values are in percentage.

14. Results an discussion of the analysis

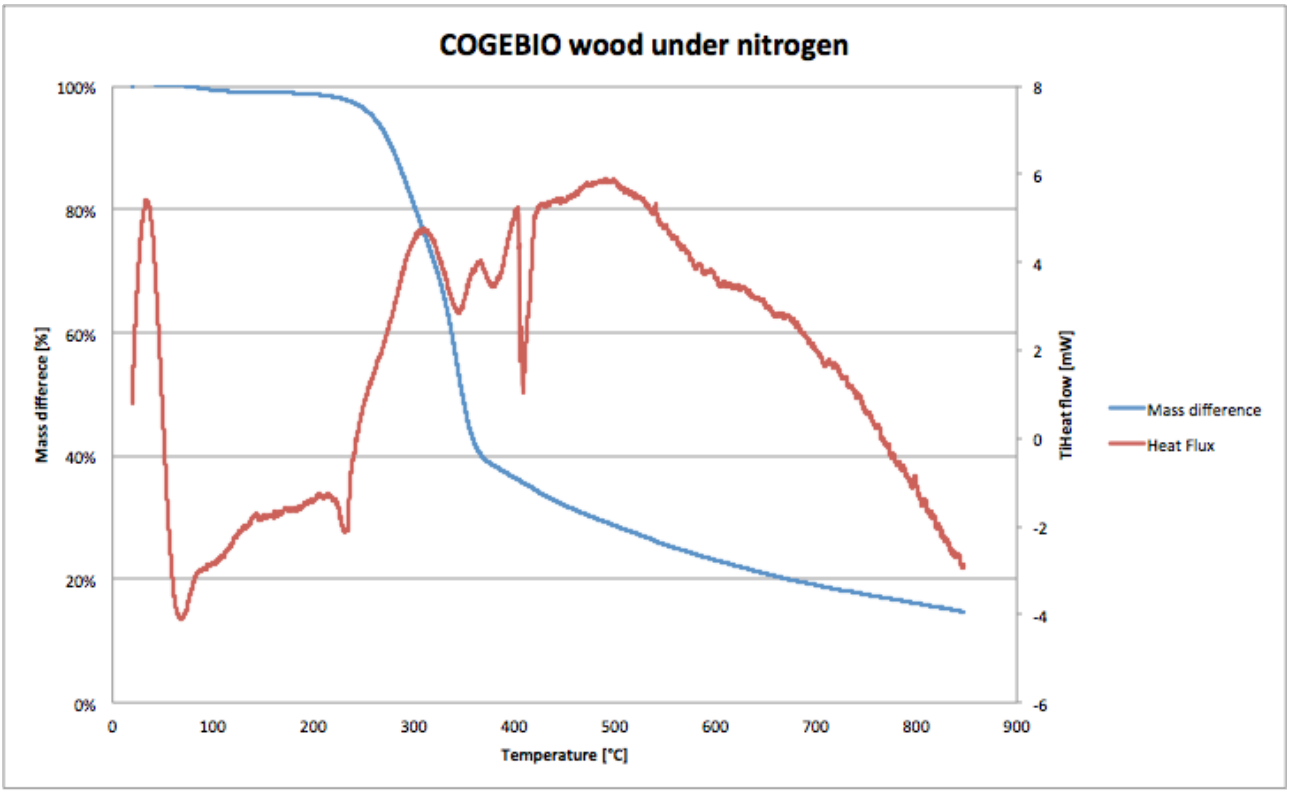
14.1 General features

The thermal analysis of wood has the advantages of being fast and to require a little technical expertise. In addition it is slow enough to allow the collection of informations about the state of degradation of the organic matter.

The analyses were conducted with samples of dry wood, the graphs above shows the COGEBIO wood taken as refernce to evaluate the general feautures.



Graphic 3) COGEBIO wood under air.



Graphic 4) COGEBIO wood under nitrogen.

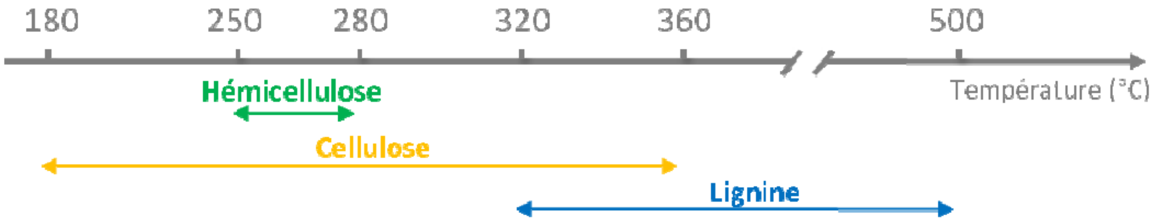


Fig. 9) Temperature ranges for the thermal degradation of the wood biological components.

Several studies have been done on wood [46], [47], and they all notice the same informations about the decomposition ranges of cellulose, lignin and low molecular weight substances such as hemicellulose.

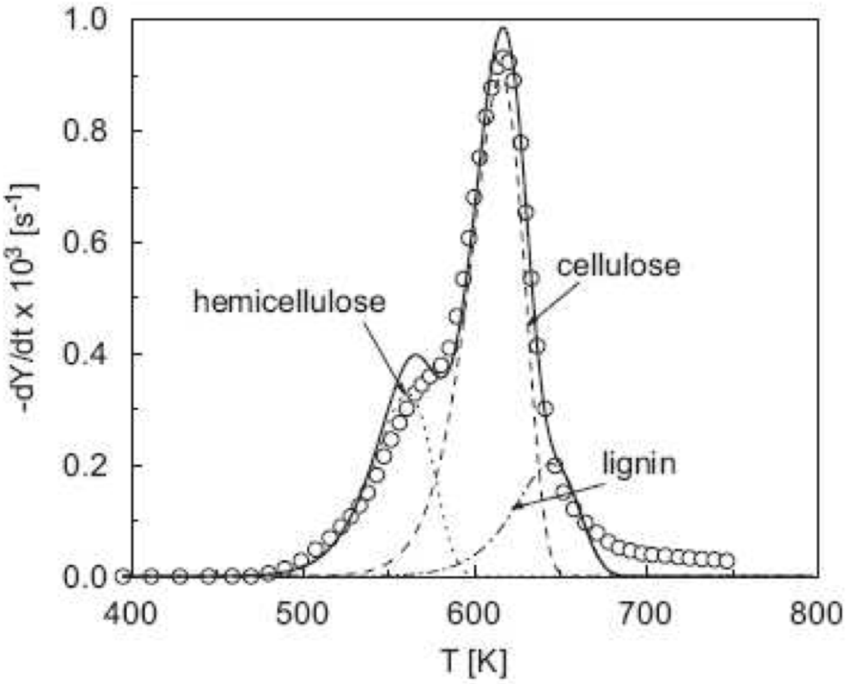
Considering the three main compounds of wood (hemicellulose, cellulose and lignin), each has its own properties in the domain of the thermal degradation, according to the composition of the polymer concerned. Thus, we can observe three independent and parallel degradation reactions during the thermal degradation of the wood. The decomposition temperature ranges for the hemicellulose, cellulose and lignin are partially superimposed.

Three phases of decomposition are present in the case of analysis under air:

1) Between 100 and 180 ° C there is a part of the mass loss in the dehydration of hydrated salts produced during the decomposition of wood. [48] The degradation of primary wood begins at about 230 °C [49]. It follows different stages, whose temperature ranges differ significantly depending on the species, wood degradation conditions, etc.

2) The second stage of decomposition observed between 200 and 360 ° C corresponds in part to the degradation of all the three macromolecules constituent the wood: hemicellulose, cellulose and lignin. It is known that the dTG (derivative of the termogravimetric analysis) shape is the sum of a component associated with hemicellulose, another to the cellulose and the last to the lignin [49] (Graphic 5).

3) The third stage of decomposition observed between 360 and 500 °C mainly corresponds to the degradation of lignin and cellulose, [47] [48].

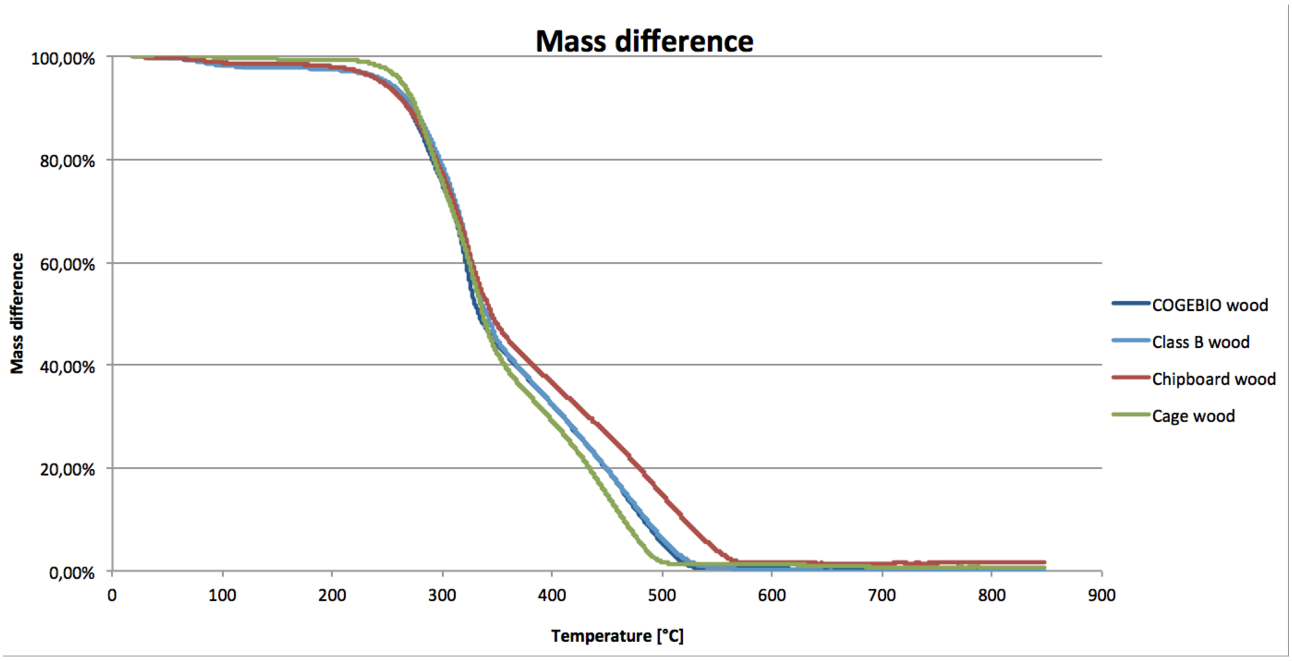


Graphic 5) Deconvolution of the dTG of a thermogravimetric analysis of the wood under air.

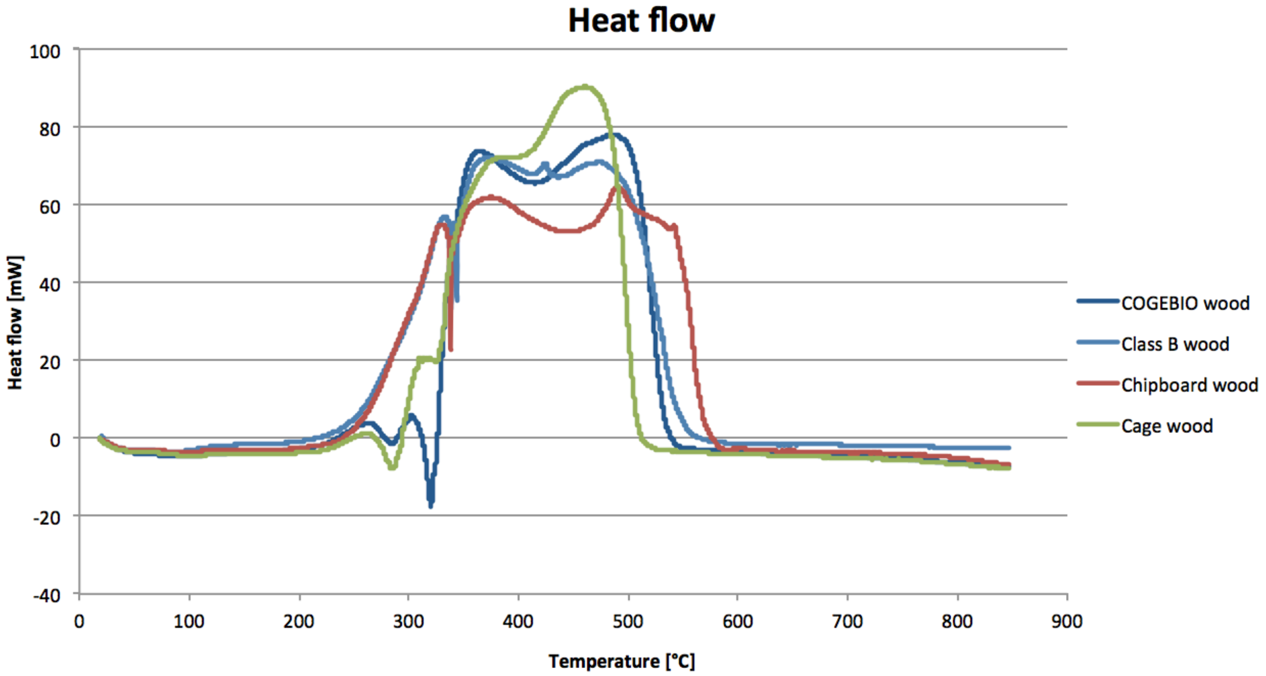
Concerning the pyrolysis, it is remarkable that the mass loss is not 100% as in the case of combustion, but is approximately 80%, it means that some of the components of the wood are not degradated. Indeed, the heat flow is less intense and the dTG shows that there is no mass loss between 350 °C and 500 °C. According to these results it is possible that the lignin is not fully degraded in the case of pyrolysis.

- 14.2 Comparison of the different wood typologies

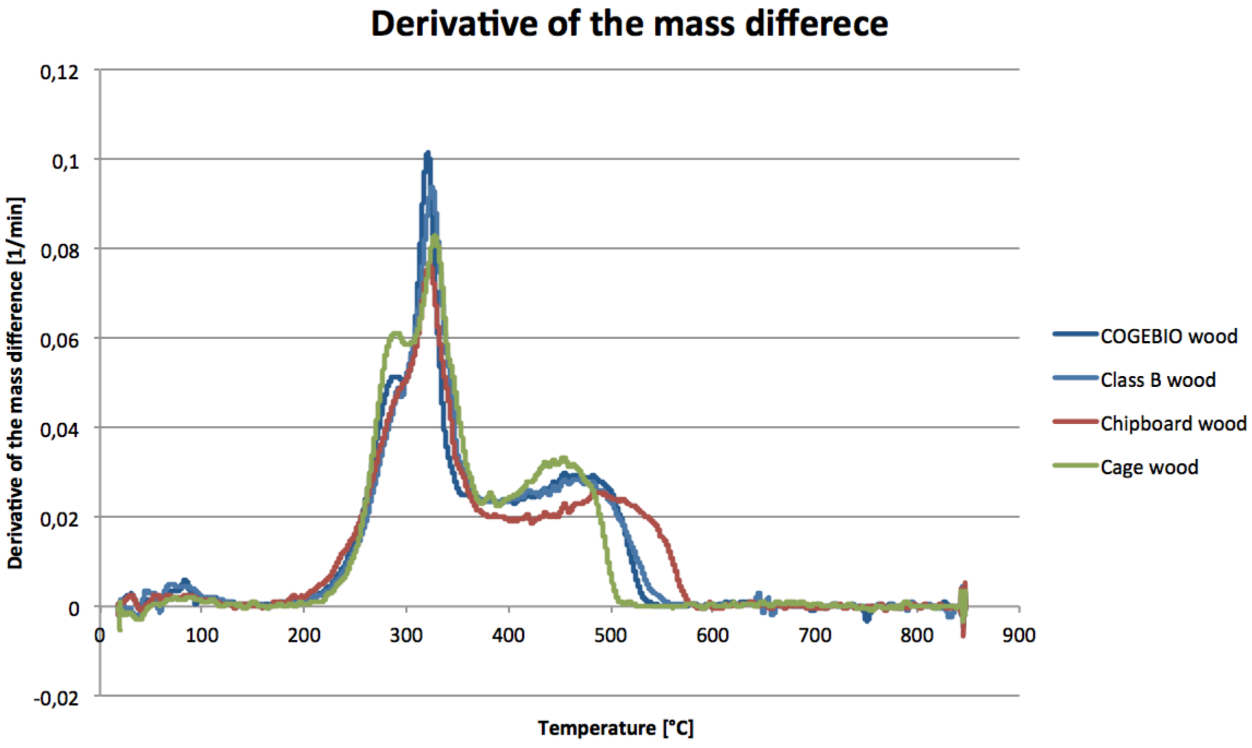
Firstly the analyses were conducted on the characteristics of different wood raw materials, that is to say the COGEBIO wood as reference for natural wood, cage wood as reference for packing wood, chipboard as reference for furniture wood and class B wood as reference of wood waste in general.



Graphic 6) Mass difference of the analyses under air.



Graphic 7) Heat flow of the analyses under air



Graphic 8) Derivative of the mass difference of the analyses under air.

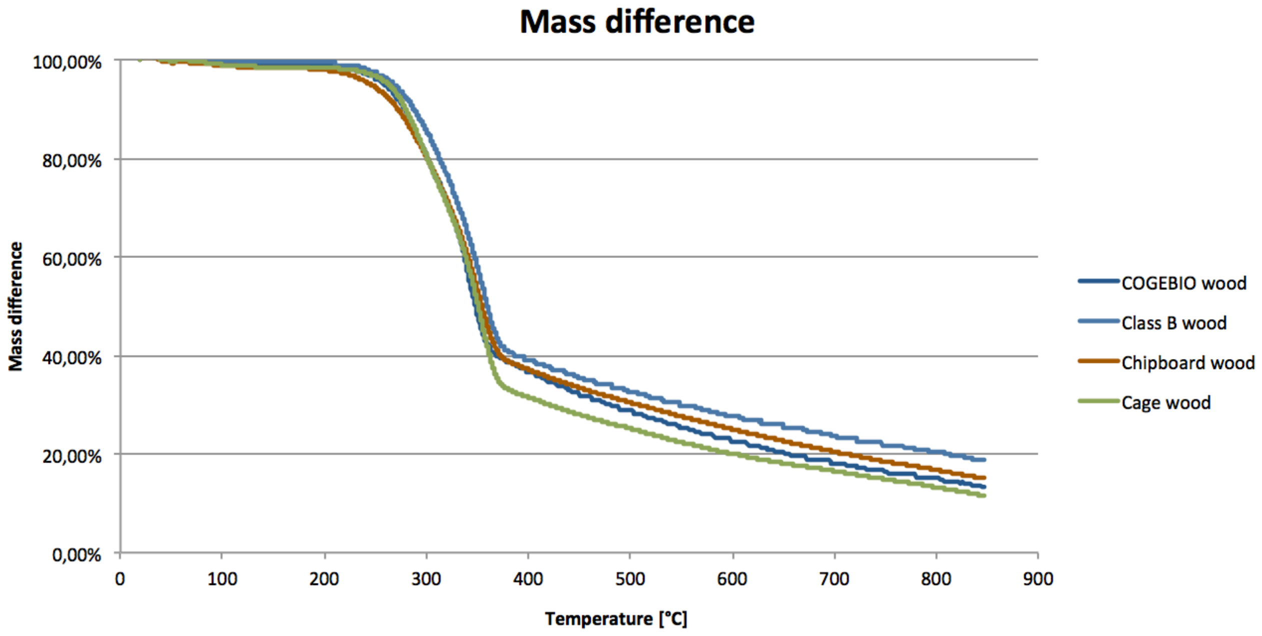
In the graphics above we can see four effects:

1) there is a a very different behavior between 400 °C and 600 °C, this range corresponds to the range of the decomposition of lignin, but also may be associated with the presence of long chain polymers hardly degradable, this is the case of the melamine contained in the chipboard wood;

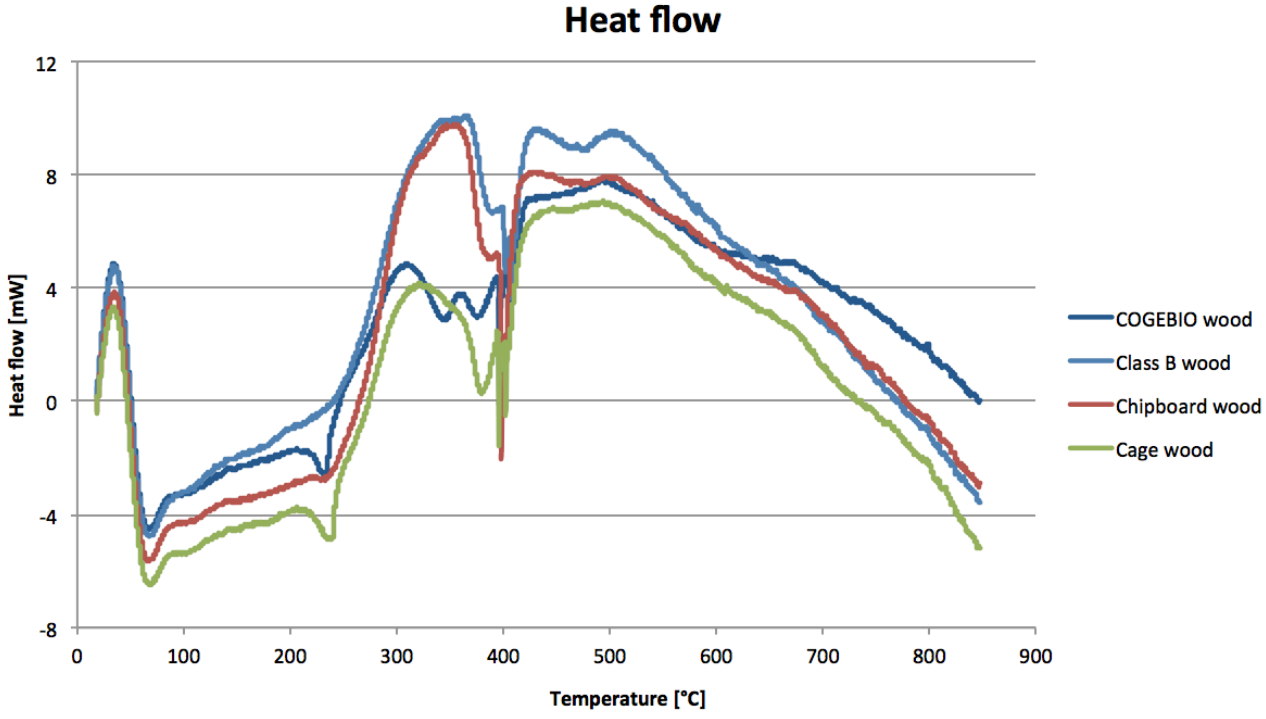
2) for the chipboard wood, as for the class B wood there is a peak in the heat flow at about 360 °C, this effect may be associated with the presence of readily degradable components. These components can be brought at the wood by the treatments;

3) the chipboard wood has a lower heat flow peak compared to other woods, this effect is always related to the presence of long chain polymers, degradable only at higher temperatures;

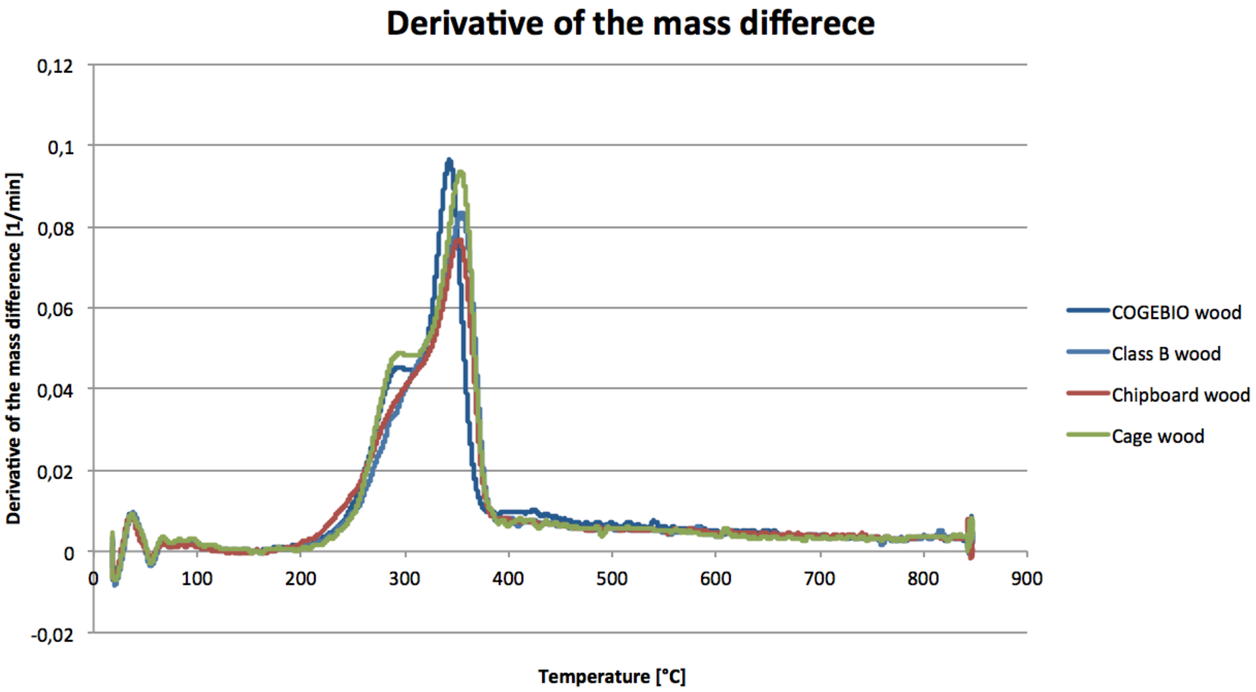
4) Cage wood has a faster degradation of its components, this effect is related to the nature of the wood, less mature and with a less content in lignin.



Graphic 9) Mass difference of the analyses under nitrogen.



Graphic 10) Heat flow of the analyses under nitrogen.



Graphic 11) Derivative of the mass difference of the analyses under nitrogen.

The charts above show that:

1) even in the case of the pyrolysis the influence of the melamine brings to different behavior, with a less degradability of some components, currently the dTG curve of chipboard wood has a higher peak;

2) Class B wood and chipboard wood have a peak in the heat flow between 250°C and 400°C. This peak appears only in treated woods and not in natural woods like the COGEBIO one (that is natural biomass) or cage wood (that is not treated wood but it is considered a class B wood only because it is a packaging waste). Therefore we can assume that this peak is the result of the decomposition of short chain molecules that are present in the wood because of the treatments.

This initial analysis indicates that the class B wood is comparable to the natural biomass such as COGEBIO wood,

Anyway the chipboard has a very different behavior from the other, that is because of the effect of melamine surface and other long chain polymeric components including resins for bonding.

- 14.3 Melamine effect

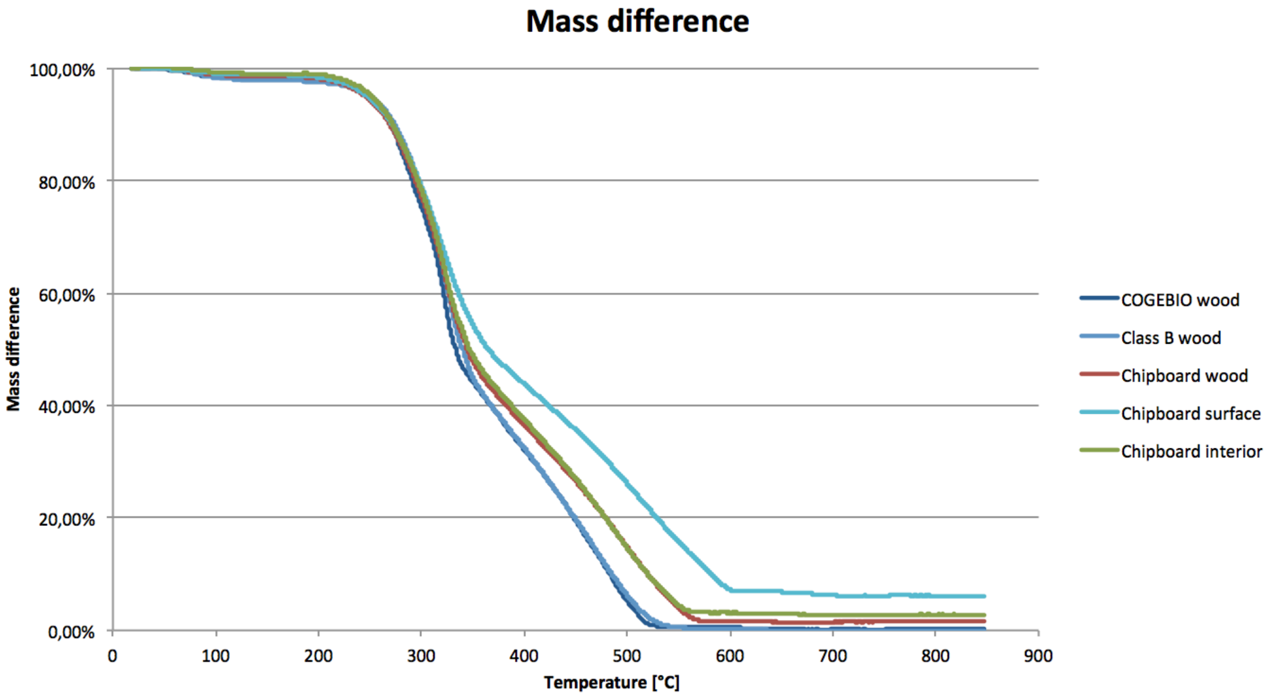
To better understand the effect of the melamine and the other long chain polymeric compounds such as resins for bonding, the chipboard wood sample was divided into three parts:

1) Chipboard surface: this is the protection part on the surface of the chipboard, usually full of melamine;

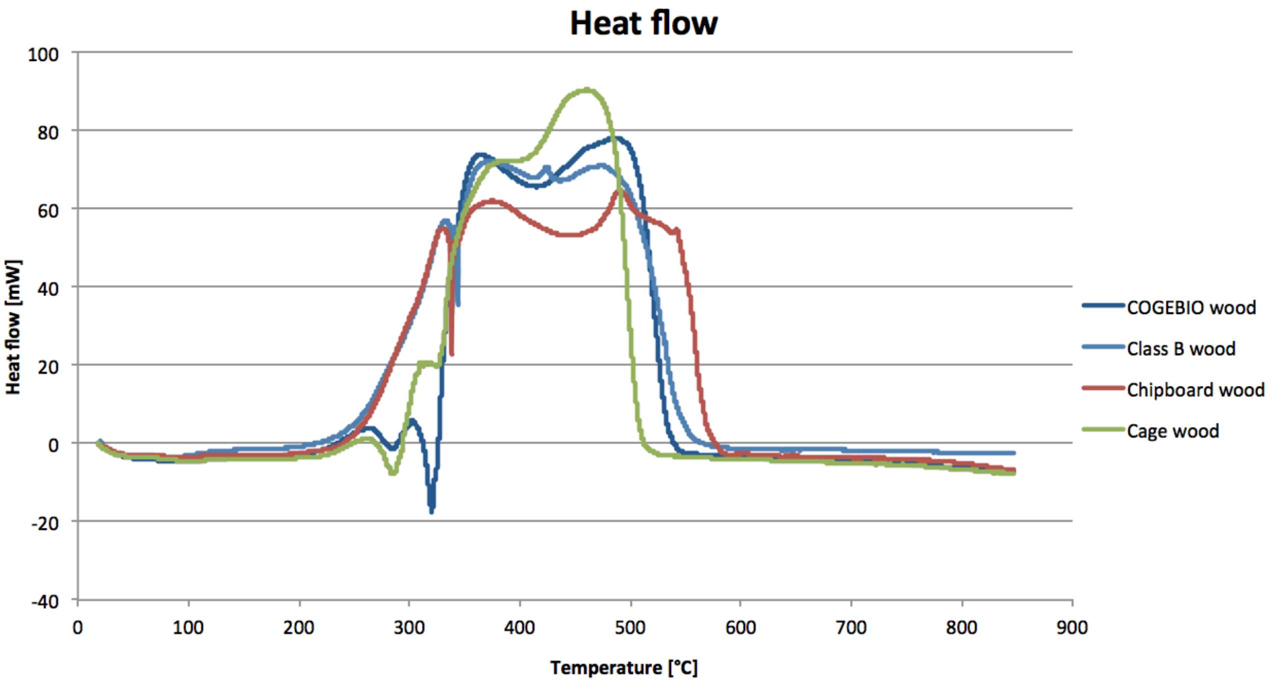
2) Chipboard interior: this is the inner part of the melamine wood, it does not contain melamine but it contains glues and resins from the family of aminoplasts;

3) Chipboard wood: this is the sample that was analyzed before, it is a ground piece of chipboard, therefore it is a mixture of surface and interior.

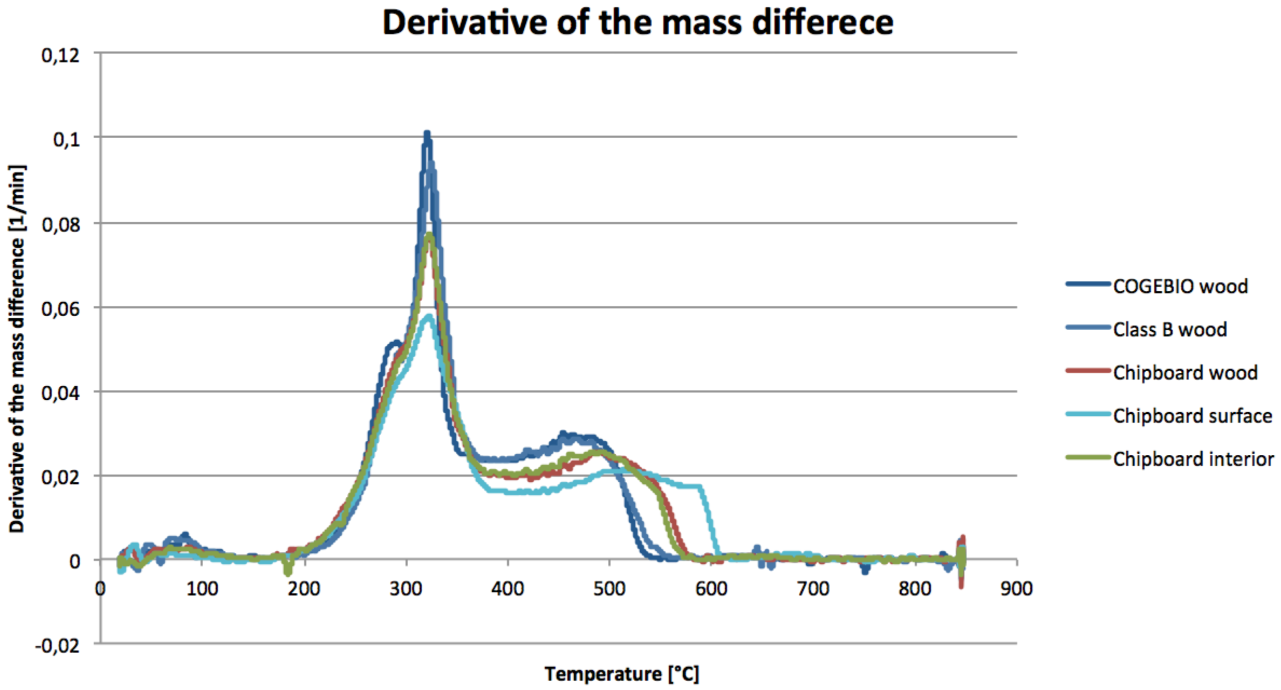
In the tables below the COGEBIO wood is used as a reference for natural wood or wood with few addictives such as packaging wood.



Graphic 12) Mass difference of the analyses under air.

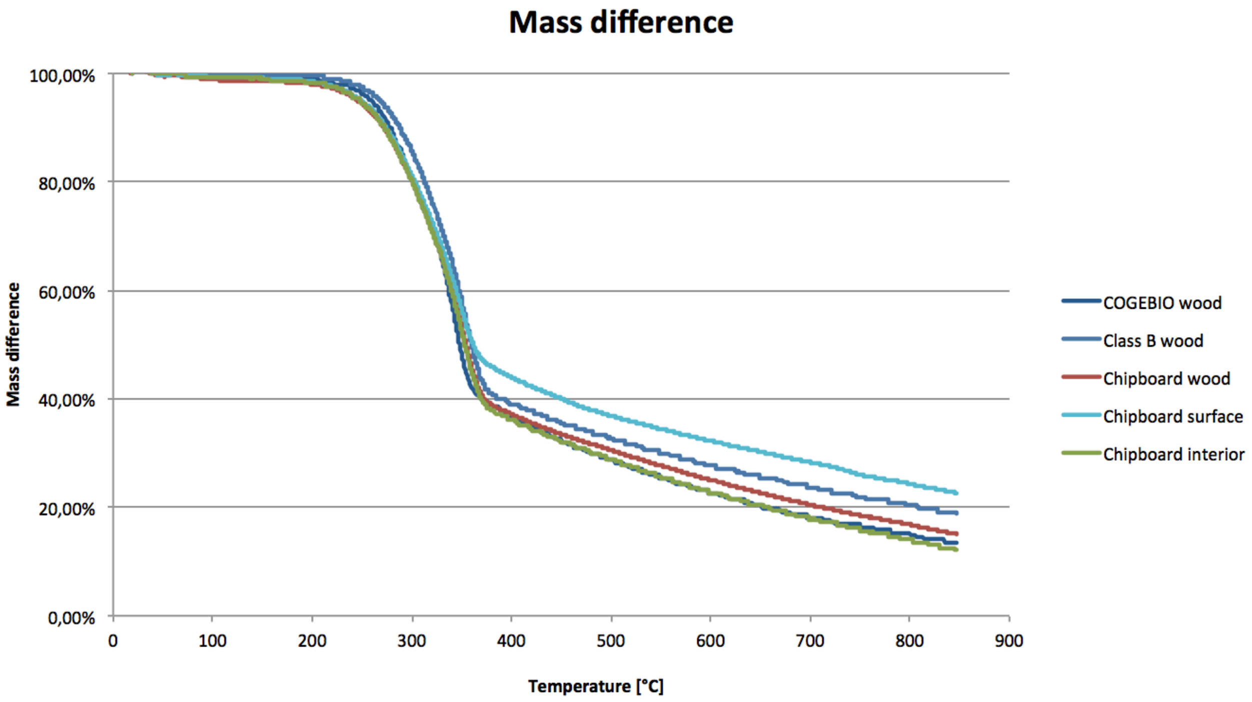


Graphic 13) Heat flow of the analyses under air.

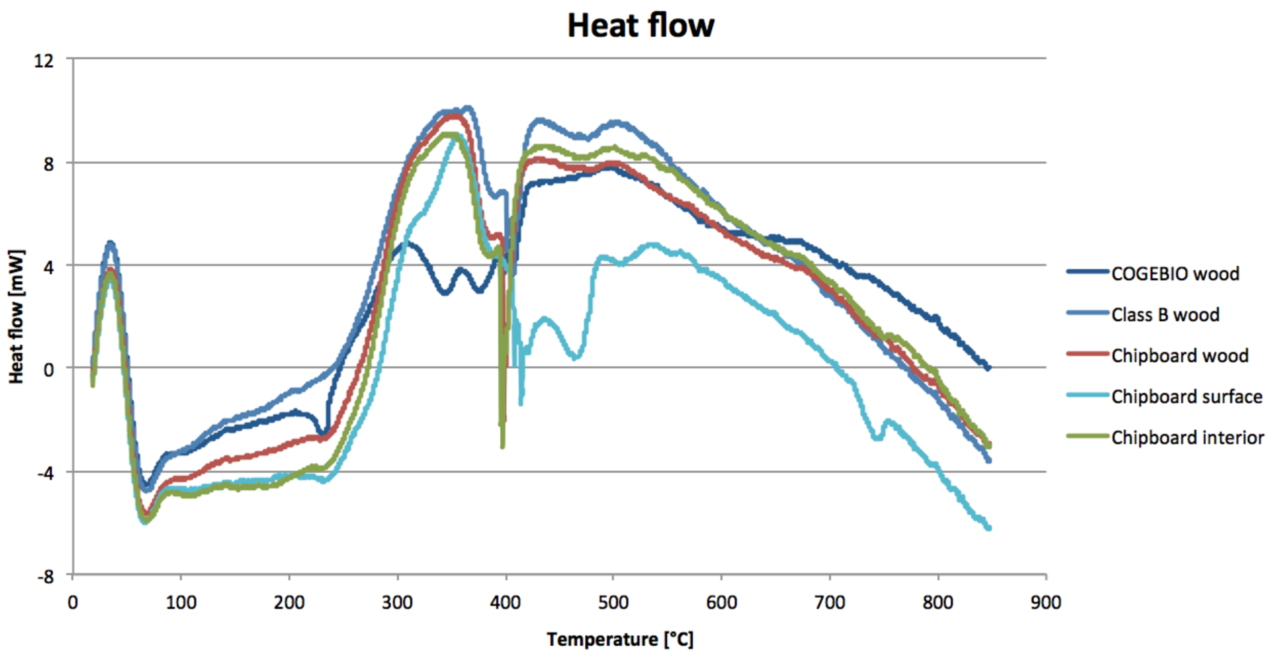


Graphic 14) Derivative of the mass difference of the analyses under air.

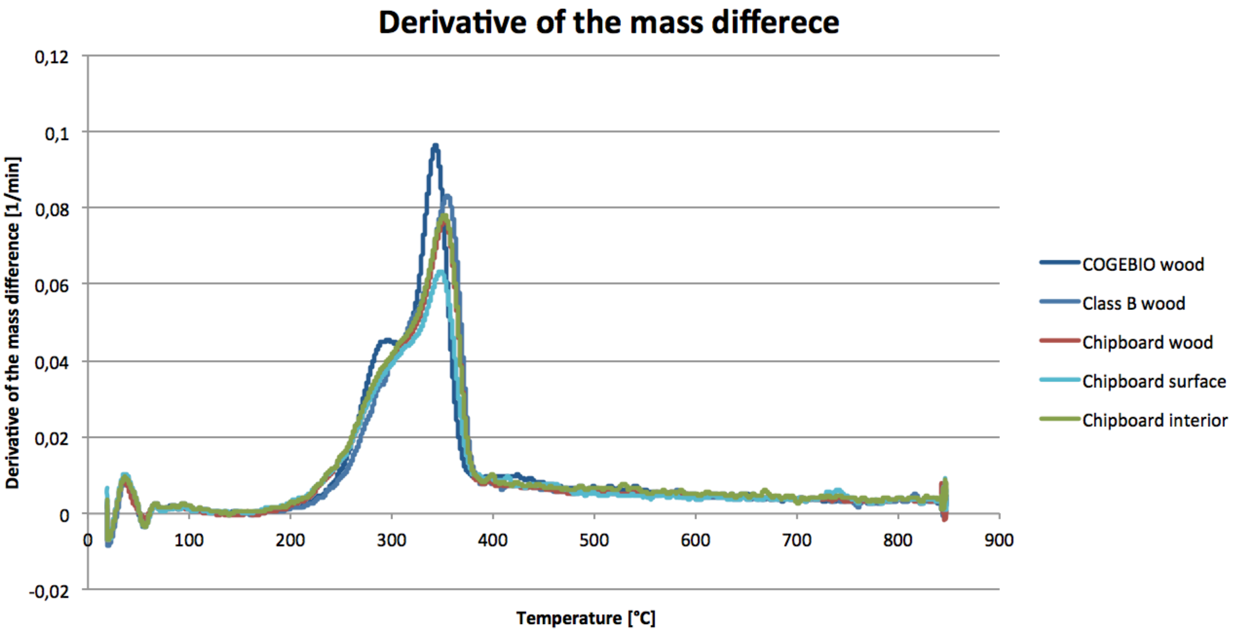
The supposed melamine and long chain aminoplasts effect is more remarkable, in fact the sample with more melamine ends his degradation over 600 °C, while the sample of chipboard wood and chipboard interior finish their degradation at 560 °C. Class B wood and COGEBIO wood finish their degradation at 530 °C, this proofs that, in the case of combustion, the class B wood is comparable to the natural biomass.



Graphic 15) Mass difference of the analyses under nitrogen.



Graphic 16) Heat flow of the analyses under nitrogen.



Graphic 17) Derivative of the mass difference of the analyses under nitrogen.

Even the analyses under nitrogen show that melamine is difficult to degrade, in fact the pyrolysis process at 850 °C can degrade only the 78% of the chipboard surface, the sample charged in melamine.

• 15. Introduction to the simulation

In the second part of this study the experimental analyses on the several wood samples will be compared with simulations made by a numerical tool developed at the Politecnico di Milano, D-SMOKE.

This program is able to perform the pyrolysis of biomass in a wide range of perative conditions, both in isothermal conditions and ensuring a programmed temperature.

The program simulates, step by step, the thermal degradation, decomposition and devolatilization of the biomass compounds and, moreover, it has a kinetic model for the gas phase.

The results of a simulation are the amounts of solid and gas phases compounds outgoing from the pyrolysis; in our case the interesting result, which may be compared to the previous analyses, is the evolution of the sum of the solid compounds mass, which is the thermogravimetric curve (TGA).
Obviously the precision of the input is very important for the development of a good simulation, for this reason the biomass must be well characterized in therms of his three major components: cellulose, hemicellulose and lignin [51].

• 16. Biomass characterization for the simulation

The term "biomass" generally refers to several materials, with different proprieties and composition. In our case we can reduce the field to the wood only, but still we have to consider that even the different typologies of wood have big differences in terms of composition, and in our case, analyzing woods with addictives, we have to consider the presence of chemical compounds which are not usual for a natural biomass.

One of the major difficulties is to find the biochemical composition of a normal, especially because of two reasons: the first is that accomplishing a biochemical analysis it is quite costly and onerous; the second reason is that only cellulose is a regular polymer having a precise chemical formula, but the hemichellulose and lignin chemical structures are not well-known, so we cannot be sure about their amounts in the sample of wood.

An easier way to characterize the wood is to do an elemental analysis which provides a characterization of the C/H/O ratios (which are determinant for the reactivity), and the contents of other elements, normally present in smaller extents (for instance, nitrogen and sulfur or humidity and ashes level).

Given that the model's input is the biomass composition in terms of cellulose, hemicellulose and lignin, the problem is to deduce this characterization starting from the elemental composition.

- 16.1 Model inputs

The kinetic model, in order to limit the number of components, takes as input the composition of the wood with three kind of components species:

- real species (molecules): these compounds are reported directly to their formula (H_2O, CO_2, CH_4, CH_2O,). One of these compound is the cellulose, its monomeric unit of glucose has been selected, and is identified in the kinetic scheme with the ID name of CELL;
- pseudo-components: these compounds are representative of several larger molecules which are present in a big amount of structural varieties, such as hemicellulose and lignin. The model simplify all of these in several kinds of pseudo-components, among these there are:
    - hemicellulose: HCE in the kinetic scheme. As the real polymer the hemicellulose is irregular and contains monomeric units of sugars having both five-membered and six-membered rings. As the distinctive feature of hemicellulose is represented by the five-membered ring monomers (glucose-type of units are already represented in cellulose), a monomeric unit having the chemical structure and composition of xylan was selected.
    - lignin: this is the most complex compound, that makes difficult its representation. Moving from the evidence that lignin is constituted of clusters of aromatic compounds, which are interconnected by propanoid chains, and have methoxy and hydroxyl substituents, a definition of three fictional reference species containing these distinctive elements was made. The three reference species for lignin are therefore LIGC (rich in carbon), LIGH (rich in hydrogen) and LIGO (rich in oxygen). The overall lignin polymer is represented by a linear combination of the three fictional monomeric units;

These three pseuo-components (HCE, LIGO, LIGH, LIGC), in addition to the cellulose (CELL), have a great importance for the characterization of the biomass as input of the simulation, the other compounds will be introduced in the physical model description;

- functional groups: linked to the solid residue, these spcies allow to describe the progressive decomposition and carbonization process with the final release of CO and H_2.

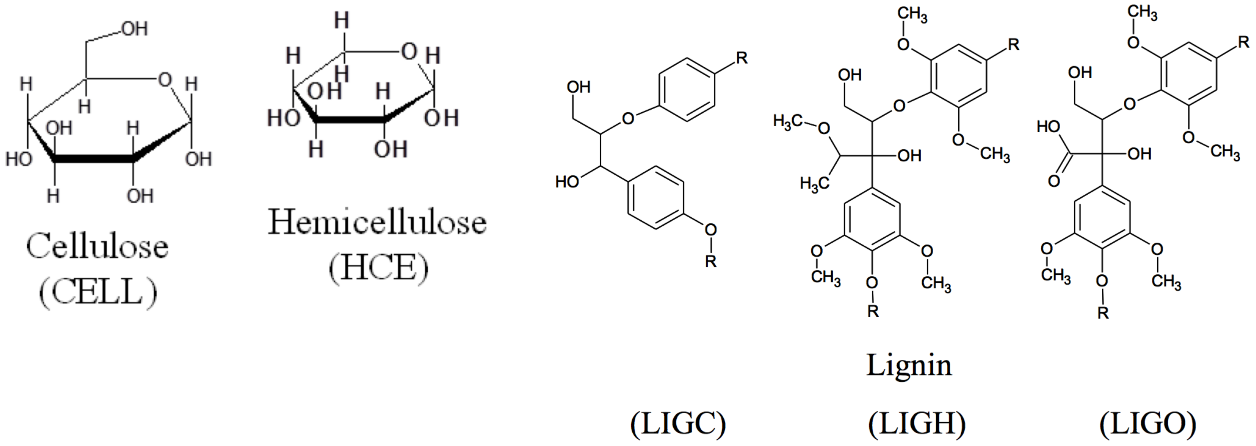
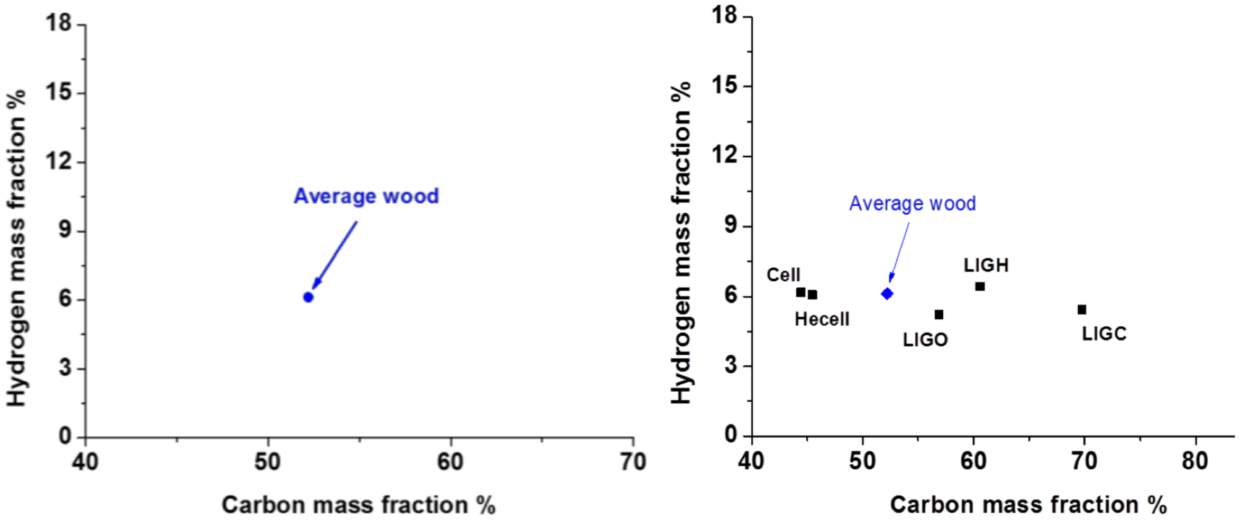

Cellulose (CELL)
Hemicellulose (HCE)
Lignin
(LIGC) (LIGH) (LIGO)

Fig. 10) Pseudo-components for cellulose, hemicellulose and lignin in the kinetic model.

- 16.2 Deduction of the biomass characterization

At this point we have the elemental analyses with the levels of C/H/O primarily, then nitrogen, sulfur, moisture and ash. The aim is to deduce the composition of the word in therms of CELL, HCE, LIGO, LIGH, LIGC for a dry-ash-free simulation (DAF) and eventually add the levels of ashes and moisture for a complete simulation.

Several studies have been made to accomplish this step [50] [51], essentially from the C/H/O contents it is possible to obtain the CELL, HCE, LIGO, LIGH, LIGC contents because everyone of these pseudo-components has fixed molecular composition. The main problem is that we have five unknowns and only three atomic balances (C, H and O), consequently the system is undetermined.



Graphic 18,19) Schematic representation of biomass as a multicomponent, multiphase and multiscale problem.

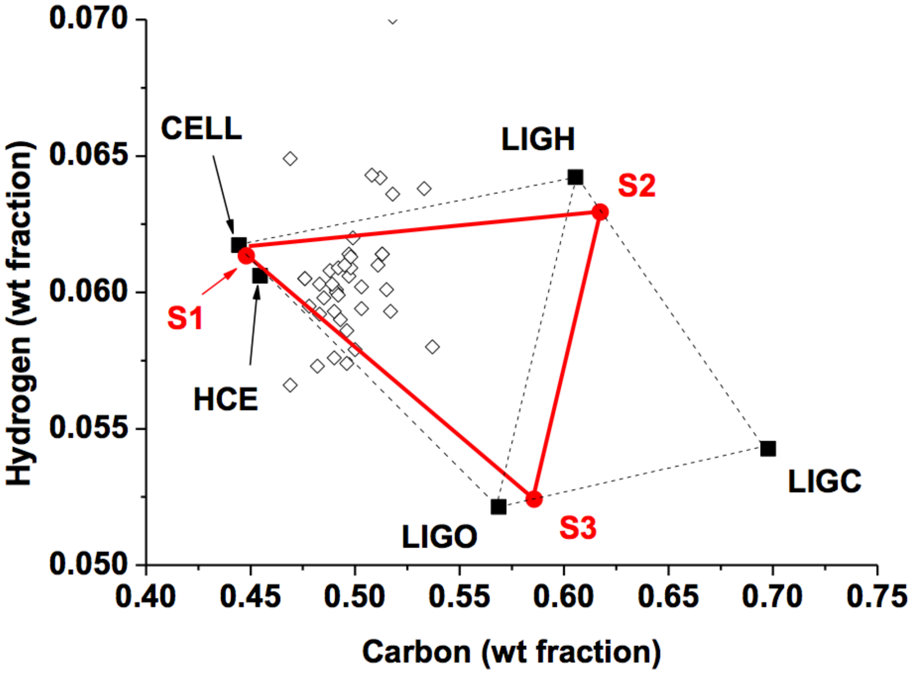
It is therefore necessary to define three new species (S1, S2 and S3) as an appropriate combination of the five reference species listed above.

S1, for example, is a pseudo-specie whose C/H/O ratio is a linear combination of the CELL and HCE ratios.

It is clear that the definition of these three values depends on the hypothesis that we assume, for exemple the further formulas, which are commonly used, consider that the ratio of the hemicellulose on the aggregate of hemicellulose and cellulose (S1) is 0,4, as for the other two ratios.

The definition of these hypoteses is guided by the effort of representing the highest number of biomass materials, in order to create a general method to characterize these biomasses and deduce their compositions in terms of pseudo-species.

The proposed characterization is extremely useful and valuable in most cases, especially dealing with woody biomass.



Graphic 20) Pseudo-components for biomass characterization in the C/H diagram (DAF basis). Empty symbols represent different biomasses taken from [52].

In every case, depending on the basic biomass, these hypotheses can be changed to find different values for S1, S2 and S3.

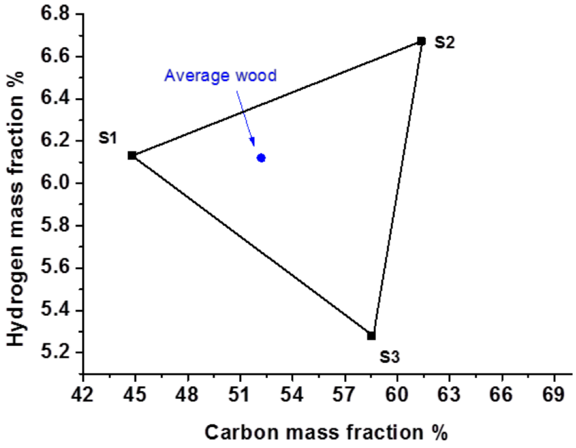
$$S1 = \frac{HECELL}{HECELL+CELL} = 0{,}4 \qquad \text{Eq. 1)}$$

$$S2 = \frac{LIGC}{LIGC+LIGH} = 0{,}2 \qquad \text{Eq. 2)}$$

$$S3 = \frac{LIGO}{LIGO+LIGH} = 0{,}2 \qquad \text{Eq. 3)}$$

At this point there are three atomic balances (C, H and O) and three unknowns (S1, S2 and S3). In the graphic above, in the C/H diagram, S1, S2 and S3 compose a triangle in which we can find the composition of the average wood. The model can simulate the pyrolysis with a good accuracy only if the corresponding biomass is present within the triangle.

If it is not in this traingle (for exemple because there is too much hydrogen) the model cannot characterize the biomass and consequently it cannot simulate its thermal beavior.



Graphic 21) Definition of the fictional reference species S1, S2, S3 and their collocation in the C/H diagram.

The next step is to write the three atomic balances in terms of S1, S2 and S3 and solve the system in which ω_i^j stands for the massive fraction of the element *i* in the species *j*, and α, β and γ are the mass fractions of S1, S2 and S3 respectively. The three elemental balances define a linear system of algebraic equations that can be easily solved to determine the three unknowns α, β and γ.

$$\begin{cases} \alpha\omega_C^{S1} + \beta\omega_C^{S2} + \gamma\omega_C^{S3} = \omega_C^{solid} \\ \alpha\omega_H^{S1} + \beta\omega_H^{S2} + \gamma\omega_H^{S3} = \omega_H^{solid} \\ \alpha\omega_O^{S1} + \beta\omega_O^{S2} + \gamma\omega_O^{S3} = \omega_O^{solid} \end{cases} \quad \text{Eq 4,5,6)}$$

Now, having α, β and γ, the system composed by the equations 1) 2) and 3) can be solved in order to find the values of HECELL, CELL, LIGO, LIGC and LIGH.

• 17. Kinetic and physical model

Once the biomass is characterized in terms of pseudo-components we have the inputs of the model. The combination of biomass characterization and kinetic model determines the chemistry of the biomass thermal degradation process.

As a general rule, the first step in the kinetic model involves the formation of a solid-liquid phase (also called metaplast) caused by de-polymerization processes. A competition among cracking reactions and vaporization is then established, which can either form permanent gases and char or high molecular weight tar species.

One of the most interesting feautures of this model is that the devolatilization of one biomass constituent is not dependent on the devolatilization of the others. This is a simplifing assumption, but it is generally accepted and it represents a step forward with respect of many one-step or multi-step models availables in literature.

The whole kinetic scheme comprises 38 species and 19 reactions, but we are going to represent only the most important.

• 17.1 Cellulose

The pyrolysis of cellulose is a molecular process that involves free radicals and occurs in the metaplastic phase.

It is widely accepted that the main reaction in the process of degradation of cellulose is a depolymerization chain reaction that produces levoglucosan (LVG). The kinetically limiting stage is the subsequent vaporization of cellulose tar, whose boiling point is about 260°C.

At temperatures above 230°C, the pyrolysis of cellulose also follows a radical process where the major products are hydroxyacetaldehyde (HAA), glyoxal ($C_2H_2O_2$), CH_3OH, CH_2O, CO and CO_2.

Figure 11 shows a schematic representation of cellulose devolatilization scheme.

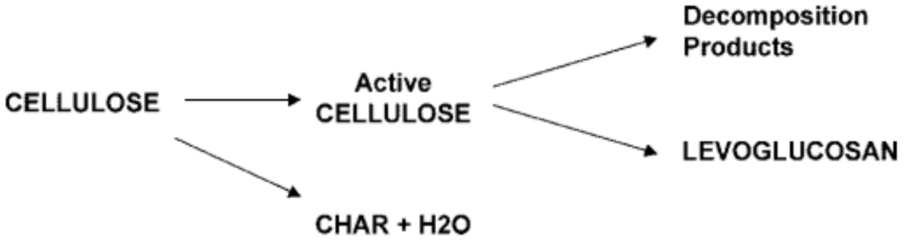


Fig. 11) Major reaction pathways in the decomposition of cellulose.

- 17. 2 Hemicellulose

The behavior of hemicellulose in pyrolysis is different from the one of cellulose: its thermal degradation starts at lower temperatures and shows a greater tendency to form a carbon residue (char).

Hemicellulose depolymerizes to form the activated monomers HCE1 HCE2, which represent the reaction intermediates in the solid matrix subjected to successive stages of vaporization and degradation. HCE1 undergoes vaporization, with the formation of the volatile tar XYLAN. It may also undergo high temperature decomposition to form char and light gases. HCE2 only undergoes high temperature decomposition.

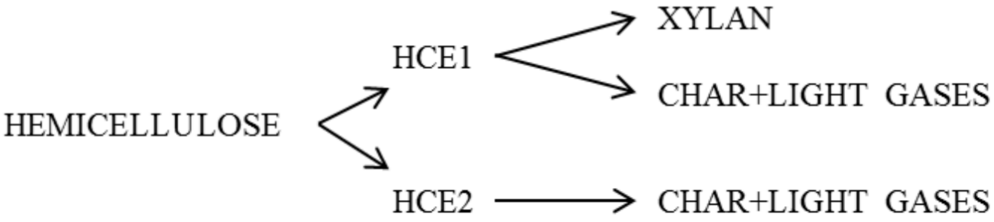


Fig. 12) Major reaction pathways in the decomposition of hemicellulose.

- 17.3 Lignin

The structure of lignin is of considerable complexity, and this makes it more difficult to describe the pyrolysis process.

The simplified kinetic scheme of the decomposition of lignin considers the evolution of the different components, as shown in the schematic in Figure 13. LIGH and LIGO decompose releasing gases (rich in oxygen in the case of LIGO and hydrogen in the case of LIG-H) and forming the same pseudocomponent (LIGOH).

During the early stages of pyrolysis, LIGC gives rise to the pseudospecies LIGCC, with the consequent formation of gases and char. Both LIGOH and LIGCC decompose to form a different pseudospecies (LIG), developing gas, tar and other compounds forming the char. Finally, LIG always evolves to char, forming gas and tar.

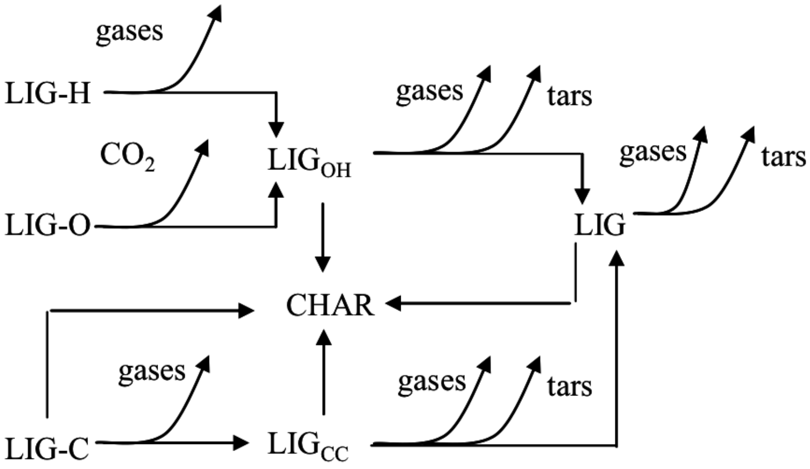


Fig 13) Schematic representation of the reaction mechanism for lignin.

- 17.4 General scheme

Table 23 summarizes all the presented reactions, including the information on the enthalpy associated to the reaction. All the kinetic rate constants are expressed in [kcal/kg].

Reactions	Heat of reaction [kcal/kg]
CELL → CELLA	107
CELLA →0,95 HAA + 0,25GLYOX + 0,2 C_2H_4O + 0,25 HMFU + 0,2 C_3H_6O + 0,16 CO_2 + 0,23 CO + 0,9 H_20 + 0,1 CH_4 + 0,61 Char	215
CELLA → LVG	175
CELL → $5H_20$ + 6 Char	-260
HCE → 0,4 HCE1 + 0,6 HCE2	131
HCE1 → 0,75 CH_2S + 0,8 CO_2 +1,4 CO + 0,5 CH_2O + 0,25 CH_3OH + 0,125 C_2H_5OH + 0,125 H_20 + 0,626 CH_4 + 0,25 C_2H_4 + 0,675 Char	107
HCE1 → XYLAN	169

HCE2 → 0,2 CO_2 + 0,5 CH_4 + 0,25 C_2H_4 + 0,8 CO_2S + 0,8 COH_2S + 0,7 CH_2O + 0,25 CH_3OH + 0,125 C_2H_5OH + 0,125 H_20 + Char	62
LIGC → 0,35 LIGCC + 0,1 COUMARYL + 0,08 FENOL + 0,41 C_2H_4 + H_2O + 0,495 CH_4 + 0,32 CO + COH_2S + 5,735 Char	144
LIGH → LIGOH + C_3H_6O	125
LIGO → LIGOH + CO_2	122
LIGCC → 0,3 COUMARYL + 0,2 FENOL + 0,35 $C_3H_4O_2$ + 0,7 H_20 + 0,65 CH_4+ 0,6 C_2H_4 + COH_2S + 0,8 COS + 6,4 Char	69
LIGOH → LIG + H_20 + CH_3OH + 0,45 CH_4 + 0,2 C_2H_4 + 1,4 COS + 0,6 COH_2S + 0,1 CH_2S + 4,1 Char	24
LIG → FE2MACR	138
LIG → H_2O + 0,5 CO + 0,2 CH_2O + 0,4 CH_3OH + 0,2 C_2H_4O + 0,2 C_3H_6O + 0,6 CH_4 + 0,65 C_2H_4 + COS + 0,5 COH_2S + 5,5 Char	-50

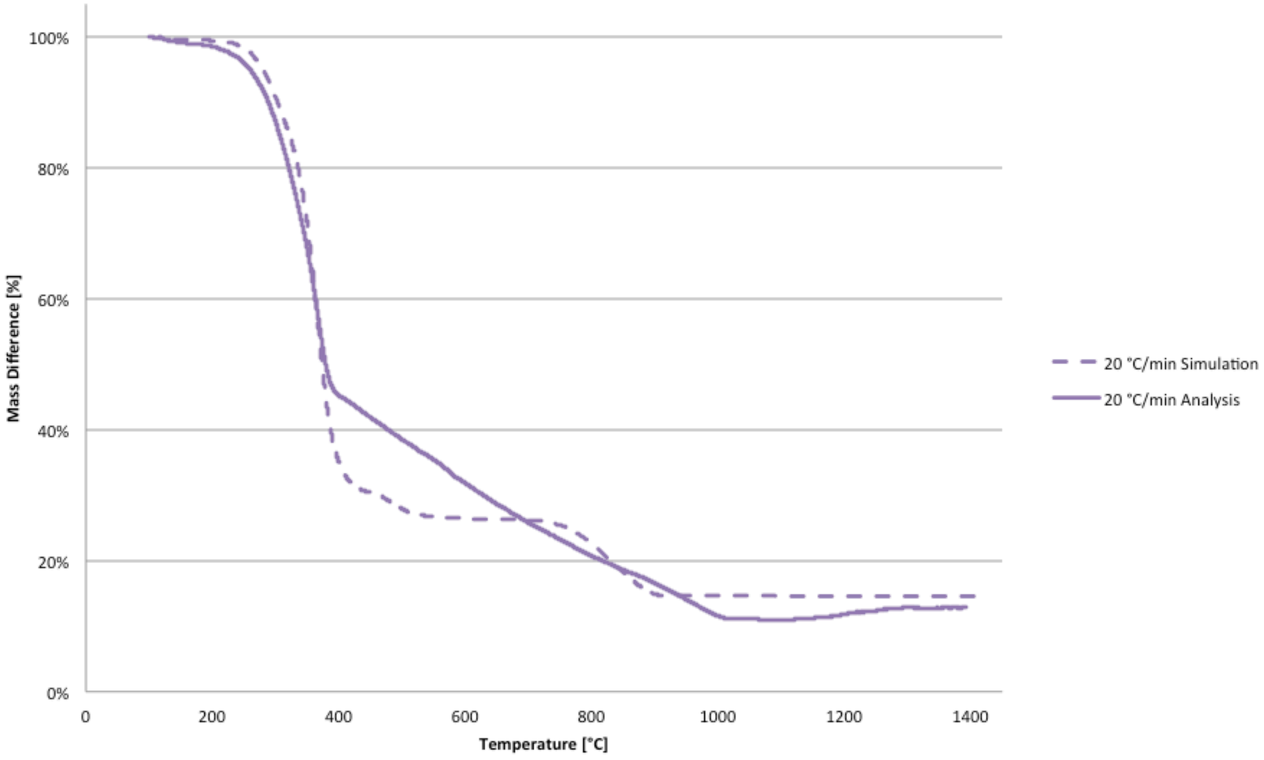
Table 23) Major reaction pathways in biomass decomposition and their correspondent heat of reaction [51].

• 18. Simulations and comparisons

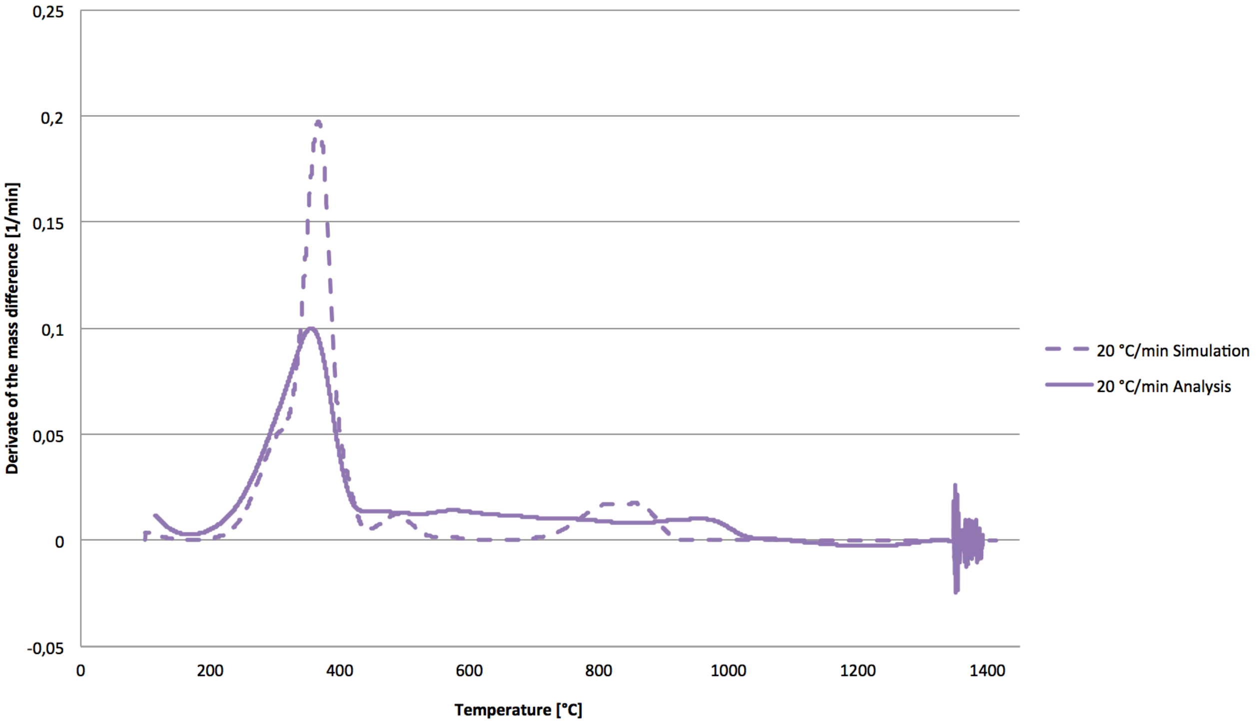
The simulations are based on one only wood sample, in order to have a general vision, we have chosen the sample of Class B wood.
The elemental analysis of this wood is given in the table 22, the experimental conditions are the same of the first analysis. Moreover two more analyses were made changing the methods, with a different heating rate (20 °C/min and 40°C/min) to test the model in different analytic conditions.

• 18. 1 Description

To better understand the general feautures, the graphics 21 and 22 show only the comparison of simulation and analysis at 20°C/min.



Graphic 21) TGA comparison of simulation and analysis at 20 °C/min.



Graphic 22) dTG comparison of simulation and analysis at 20 °C/min.

As we can see from the graphic:

- The first part of the simulated TGA (from 20°C to 380 °C) fits very well to the analytic one. We can notice just a little difference at the very beggining of the curve.

- The second part of the simulated TGA (from 380 °C to 910 °C) does not fit very well with the analytic one. In the range of temperture of this second part there is the degradation of cellulose and lignins. We can see that the analytic TGA curve changes its slope at about 380 °C and it follows a constant degradation up to 1000 °C, but the simulated curve changes slope at about 390 °C and proceed with two steps: the first one ends at 500 °C and the second one that goes from 710 up to 910 °C.

In fact we can clearly see that in the analytic dTG curves there is only one peak at 380 °C, but in the simulated curve we have three peaks, one at 390 °C, another at about 480 °C and the last one at 820 °C approximately.

Describing the dTG there is a remarkable difference, the main peak of the simulation is the double of the analytic one.

In this case the difference is clear, the simulation follows a step-by-step degradation and the anlyisis follows a continuous one.

- The final part of the simulated TGA (from 910 °C) is similar to the analytic one, in this part there is no degradation and both of the curves reach the same level (18% fot the simulation and 16% for the analysis).

- 18.2 Discussion

- The first part of the degradation is very well described by the model becase in this temperature range there is the degradation of hemcellulose (mainly), cellulose and extractives. The precision of the simulaion is given by the few approximations used to represent the hemicellulose and its decomposition. The difference at the very beggining is caused by the decomposition of some extractives (mostly the terpenes) not described by the model.

- In the second part there is an important difference which is caused by the approximations done by the model, mostly in describing the lignins.

In fact in this temperature range (380 °C - 1000 °C) the degradation of the hemicellulose it is ended (which is the reason of the slope change, clearly visible in the dTG graphics) and there are the degradations of cellulose, lignins and long chain polimers.

In real wood there are several kinds of lignin, this causes the continuous shape of the analytical curve. Moreover in real wood there also are several compounds which the model does not take in account, in this case especially, where it was analyzed a wood waste containing several compounds coming from its treatments.

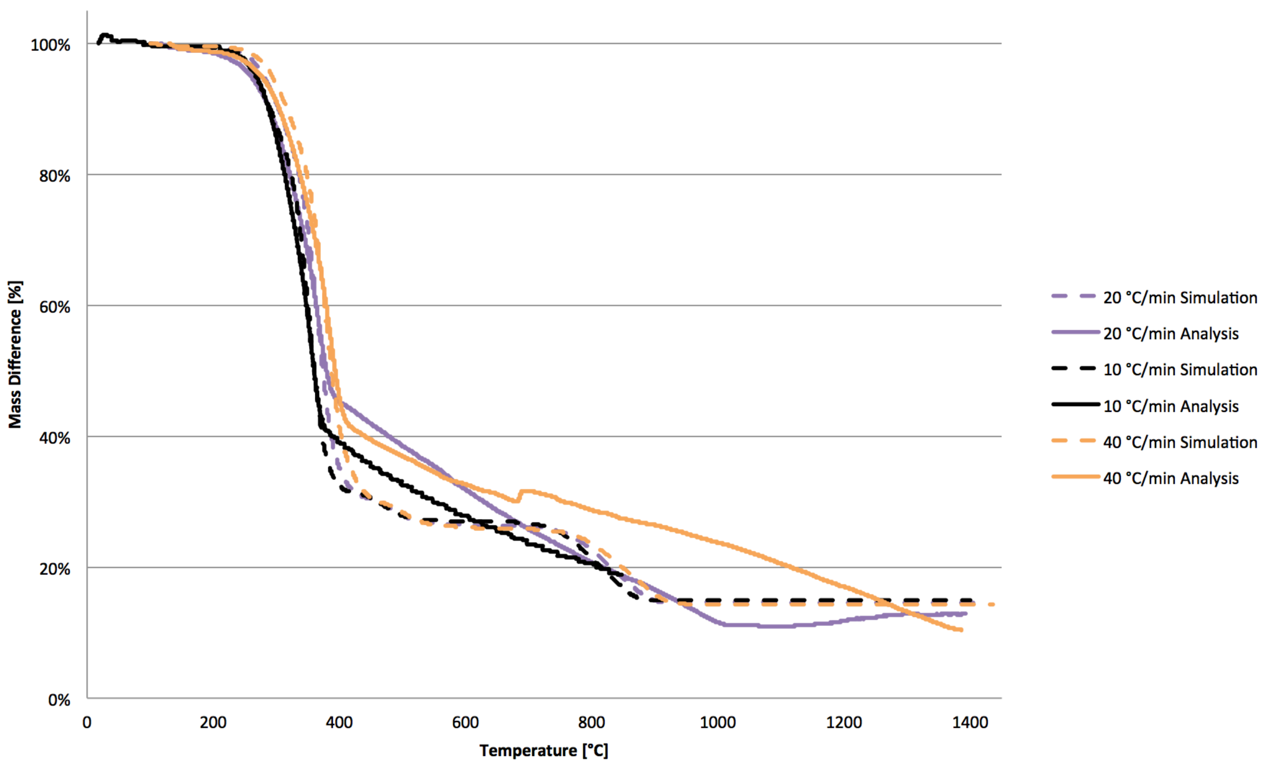
The model, instead, is very schematic, we can clearly see the three peaks that coincide with the end of the degradation of the three main compounds of the wood: one for the hemicellulose (390°C), the second for the cellulose (480 °C) and the third one for lignins (820 °C). It is clear that this last peak is larger to include the degradation of more than a compound, in fact the pseudospecies used by the model to represent the lignins are three.

Moreover we can assume that the main peak in the simulated dTG, so as the change of slope of the simulated TGA, is the double of the analytic one. That is because in the real case the change of slope begins before and more slowly by reason of the greater variety of compounds to degradate and the approximation of the model in describing the lignins dergadation.

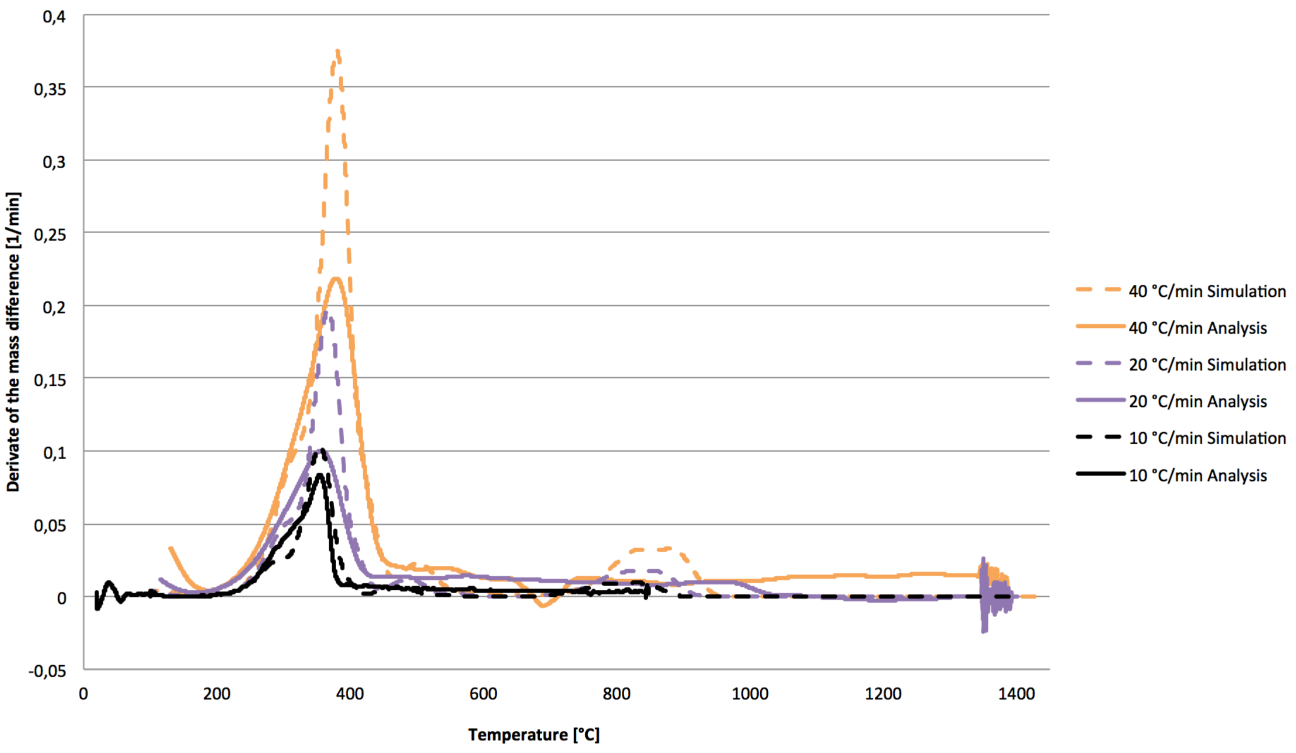
In the last part there are no more degradations, but it is remarkable that the remaining solid part content, mostly ashes, obtained by the model is very similar to the analytic one, this means that, despite the approximations, the model describe the global thermal degradation of the wood with a good accurancy.

• 18.3 Comparisons at different heating rates

The comparisons of the analysis to the simulation are extended to the cases of different heating rates. The general feautures described in the case of 20 °C/min are common for all the heating rates.



Graphic 23) TGA comparison of simulation and analysis at 10°C/min, 20°C/min and 40°C/min.



Graphic 24) dTG comparison of simulation and analysis at 10°C/min, 20°C/min and 40°C/min.

As shown by the graphics the simulations are very similar to the analysis up to the end of the first step, the general feautures are respected in every case, and the curves are similar with a little transfert, the higher is the heating rate, the higher is the temperature where the decomposition takes place. This effect is caused by the non-homogeneous heating of the sample, the slower is the temperature rate, the higher is the temperature homogeneity in the sample and then the reaction. With higher heating rates the sample temperature is not homogeneous and the degradation of the internal part takes place when the external part is at higher temperature.

Moreover the model was designed in order to evaluate the thermal degradation of the biomass in a purely theorical way. Only analyzing little masses, in the order of micrograms, the analysis is not influenced by the heat and mass transfert and then similar to the model's simulation. At the scale of milligrams the effect of mass and heat transfert influences the TGA results.

It is remarkable that with the growth of the temperature there is a loss of precision for the model in the second part (from 380°C to 910 °C), and for the analysis lead at 40 °C/min this loss of precision goes on up to the end of the analysis.

In fact at this temperature the analytic TGA does not have an asymptotic behavior as it it supposed to have. In every case at this heating rate exeperimental errors are not excluded.

The last remark on these graphics concerns the remaining part: the model, even in the case of high heating rates, gives an accurate evaluation of the remaining part of the pyrolysis thermal degradation; this means that, despite the approximations made, the model is able to simulate the reality with a good accurance.

• 19. Model development for comprising larger range of biomasses

As already shown in the graphic 20, we can only run simulations of the biomasses whose C, H and O ratio is positioned inside the characteristic triangle, but, in fact, there are several woody biomasses which are positioned outside of this triangle.

The development of the model is thus concerned to enlarge the triangle in order to comprise biomasses which, at the moment, do not fit the model.

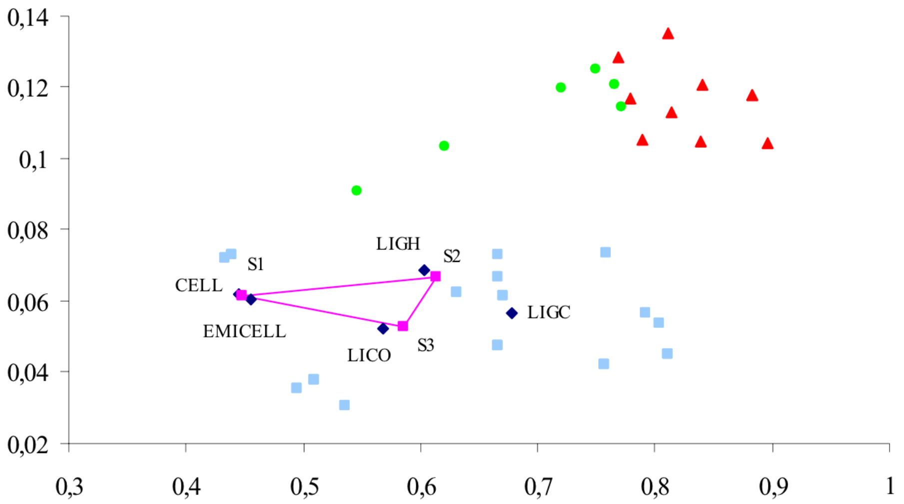
Among these biomasses there are several wood waste. According to the database of the biomasses developed by the CRECK research group at Politecnico di Milano, the richest component in hydrogen among the wood waste is the "mixed softwood residues", and the poorest is “demolition wood” waste. Among these extreme there are several wood waste biomasses with a high content of hydrogen that are not inside the characteristic triangle.

Biomass	**Reference**	**C**	**H**	**O**	**Inside the triangle?**
Mixed softwood residues	BIOBIB [53]	0,5478	0,0738	0,3784	No
Fiberboard	IEABCC [54]	0,5193	0,0679	0,4127	No
Laminated	BIOBIB	0,5242	0,0641	0,4117	No
Residues containing particle boards	BIOBIB	0,5227	0,0635	0,4138	No
Residues containing adhesives	BIOBIB	0,5084	0,0632	0,4283	No
Furniture waste	BIOBIB	0,5232	0,0630	0,4137	No
Telephone poles	BIOBIB	0,5786	0,0626	0,3588	No
Uncontaminated wood waste	BIOBIB	0,5058	0,0622	0,4320	No
Railway sleepers	BIOBIB	0,5518	0,0618	0,3864	Yes
Mixed	BIOBIB	0,5243	0,0611	0,4146	Yes
COGEBIO wood		0,5072	0,0599	0,4328	Yes
Class B wood		0,5140	0,0594	0,4264	Yes
Demolition wood	BIOBIB	0,4923	0,0585	0,4493	Yes

Table 24) Wood waste biomasses in the CRECK database, ordered by H content.

Some of the biomasses are positioned outside the bounds because of their high hydrogen content, which means that, in the biochemical composition, there are some hydrogen rich compounds.

The major components of the biochemical composition have altready been shown in chapter 9. Those components have mostly structural roles on plants in opposition to the extractive compounds, which are present in minor quantities but act mainly on biological roles such as defense, reproduction, energy absorption and storage, among others. Those three major compounds are already described in the model, therefore it is very likely that among the extractives there are some compunds that increase the level of hydrogen. The hydrogen richest compounds among the extractives are the terpenes.



Graphic 25) The basic characterization triangle in the C/H plot. In blue are shown the phenols, in green the fatty acids asd in red the terpenes.

- 19.1 Terpenes

The terpenes are the largest group of the plants-derived compounds, with more than 20.000 known structures, including essential oils and fragrances. They are hydrophobic and derivated from isoprenic units [$CH_2=C(CH_3)–CH=CH_2$], a hydrocarbon with five carbons, thus they are called isoprenoids.

The isoprenic units are bonded to form terpenoidic structures; according to the number of Isoprene units and consequently, the number of carbons, they are subgrouped into: monoterpenes (C_{10}), sesquiterpenes (C_{15}), diterpenes (C_{20}), triterpenes (C_{30}), tetraterpenes (C_{40}) or carotenois and polyterpenes (more than C_{50}).

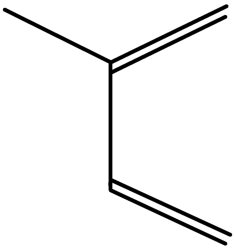


Fig 14) Isoprene chemical structure.

Terpene	Chemical Formula	C (% weight)	H (% weight)	O (% weight)
α-pinene	$C_{10}H_{16}$	0,882	0,118	0,000
Camphor	$C_{10}H_{16}O_1$	0,789	0,105	0,105
Nerol	$C_{10}H_{18}O_1$	0,779	0,117	0,104
Pitol	$C_{20}H_{40}O_1$	0,811	0,135	0,054

Limonene	$C_{10}H_{16}$	0,882	0,118	0,000
Menthol	$C_{10}H_{20}O_1$	0,769	0,128	0,103
A vitamin	$C_{20}H_{30}O_1$	0,839	0,105	0,056
β-carotene	$C_{40}H_{56}$	0,886	0,104	0,000
Betulin	$C_{30}H_{50}O_2$	0,814	0,113	0,072
Sitosterol	$C_{29}H_{50}O_1$	0,841	0,121	0,039

Table 25) Elemental analyses of some terpenes [55].

- 19.2 Introduction of new pseudo-species

In order to model the terpenes we created two pseudospecies for the solid phase and one for the gas phase:

- TERP1: this pseudo-specie represents what we call the light terpenes (carbon number less or equal to 15), the pseudo-specie chosen is an isoprene unit in solid phase at room temperature.

The thermal behavior of this specie follows the one of the monoterpenes, such as limonene or pinene; this two components are well studied but the study of their thermal decompositions is not easy because of their low boiling points.

Limonene, for example, is believed to decompose into trimethylbenzene, *m*-cymene and indane at 450-480 °C [56], but the boiling points of all of these compounds is around 175-180 °C (limonene's boiling point is at 175-176 °C), thus we assume that terpenes, similar to limonene in composition, structure and molecular weight, volatilize in a range of temperature between 120 and 210 °C. This range of temperature was chosen according to the fact that this pseudospecie must describe the behavior of several mono and sesquiterpenes.

-TERP2: this pseudo-specie represents what we call the heavy terpenes (more than 15 carbon), the pseudo-specie chosen is also an isoprene unit in solid phase.

The thermal behavior is based on carotenoids (tetraterpenes) such as β-carotene or compounds similar to the natural rubber (Polyisoprenes).

The β-carotene is a very well studied compound, whose high boiling point (654.7 °C [57]) allows following its degradation during a TGA. Its thermal degradation was studied in several ranges of temperatures. In the range between 200 and 350 °C, for exemple, it is believed to decompose into compounds with molecular weights of 138, 240, 346 and 444 and some isomers [6].

The natural rubber, a natural polymer produced by some trees, is mostly composed by polyisoprene, which can be produced in industrial scale. Since it is a polymer of isoprene units, it can also be considered a terpene. Due to its economical importance and applications, there are several pubblications which analyse both the natural and synthetic polymer thermal degradation,

which takes place between 330-470°C, with a peak of mass loss at 380°C with the formation of compounds such as limonene in gas phase [7].
According to these studies, we have set the main thermal degradation of TERP 2 in a range of temperatures that goes from 300°C to 480 °C.

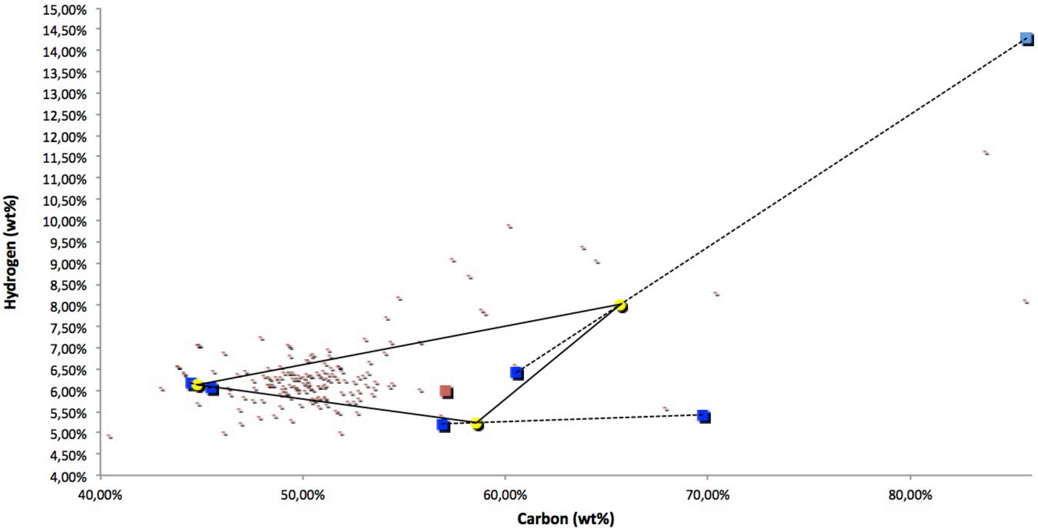
We assume that the content of light terpenes is bigger than the heavy terpenes. For this reason, we assume that only the 30wt% of the terpenes are heavy and 70wt% are light.

- TERP 3: this pseudo-specie models the light terpenes in gas phase. In other words it is the representation of a tar (vapor at high temperature and solid/liquid at room temperature), produced by devolatilisation of TERP1 and thermal degradation of TERP2.

The three pseudospecies have the same C/H ratio, therefore in the characterization triangle they will be all represented by the same point, which we are going to call TERP.

- 19.3 Recostruction of the terpenes TGA and comparison with the former model

After the introduction of the terpenes we can change the shape of the triangle.
In the former triangle the S_2 point was traced by on the interpolation line of LIGH and LIGC, in the new triangle this point will be traced on the interpolation line of LIGH and TERP, in this way we can move the S_2 point in a higher and hydrogen richer position.



Graphic 26) Characterization triangle of the model with terpenes.

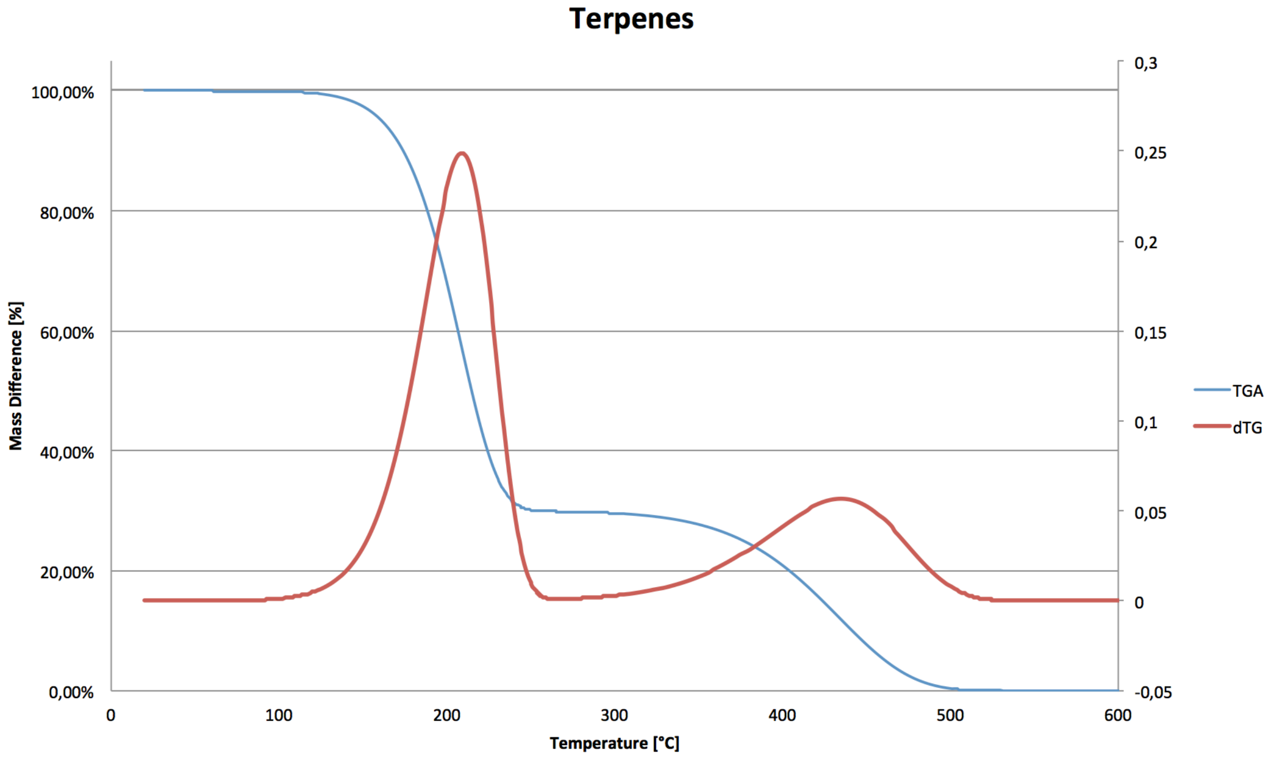
Comparing to the characterization triangle shown in graphic 20 many biomasses were comprised, even if there still is someone left out.

At this point we can simulate the thermal behavior by TGA.

As shown in the graphic 27 the terpenes have two steps of degradation:

The first step is the devolatilization of the light terpenes, this degradation takes place in a short range of temperature (120-210 °C).

The second step is the degradation and the isomerization of the heavy terpenes, this step has a larger range of temperature (200-480 °C) and, thus, is slower than the first one.



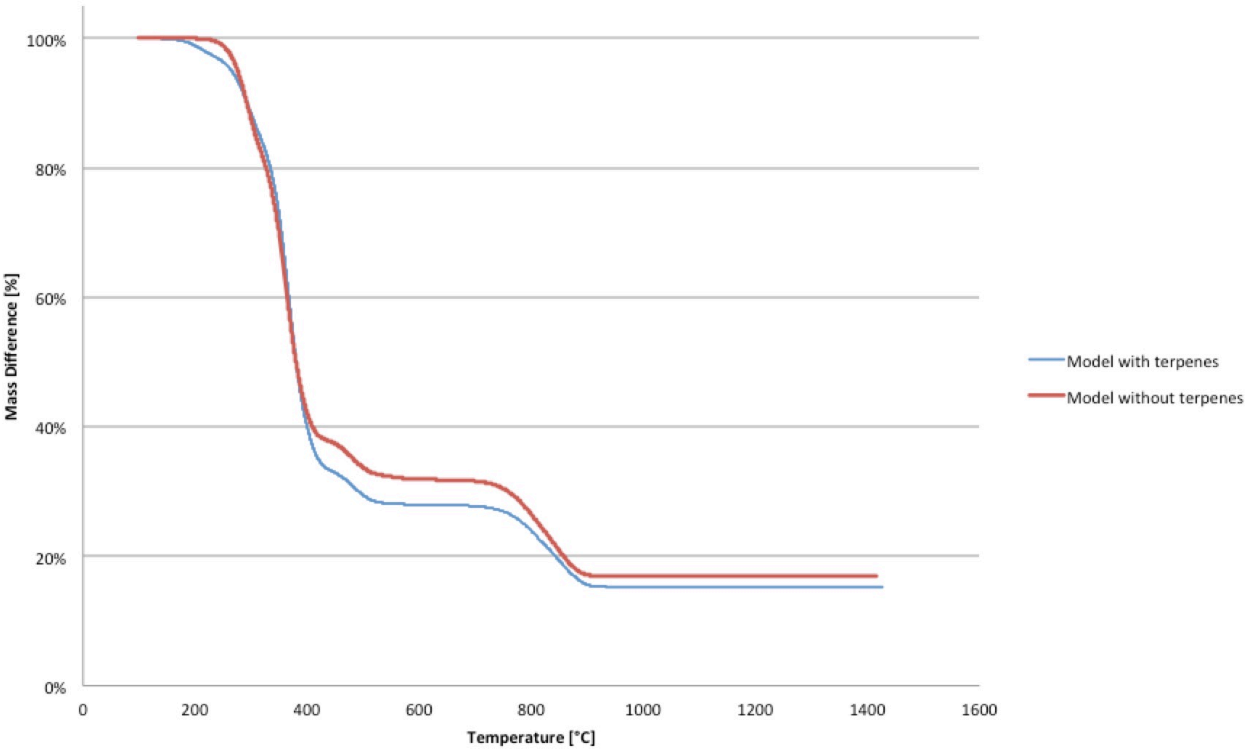
Graphic 27) Simulated TGA for the terpenes.

In the graphic 28 we can see the comparison between two simulations made on the Railway sleepers: the first one (in blue) is the newly developed model with the terpenes reactions and the second one (in red) is a simulation done with the former model.

This sample was use since it is the richer in hydrogen which is inside of both the characterization triangles, the railway sleeper sample. The table below shows the characterization of the former and new model

	CELL	HCE	LIGC	LIGH	LIGO	TERP1	TERP 2	ASH
Former Model	24,13	13,11	7,92	49,09	4,32	-	-	1,44
Model with terpenes	23,46	12,74	3,53	32,39	23,07	2,36	1,01	1,44

Table 26) Biochemical characterization for the former model and the model with terpenes, all the values are in percentage.



Graphic 28) Comparison of the model with terpenes and the one without terpenes on the Railway sleepers (elemental composition in table 25).

The two simulations are really similar, especially in the first part (before 380 °C) and the final one (more than 950 °C). Nevertheless there are some important differences, the first one concerns the devolatilization of TERP 1 at around 200 °C, the second one is the degradation of TERP 2 which, in the global behavior, originates an early degradation.
Despite this two dissimilarities the difference between the two simulation at 600°C decrease, this means that TERP 1 and TERP 2, in the new model, take the place of some lignin and ashes of the former model.

• 20. Perspectives

The advancement of this work can be done in several ways, concerning its several aims.
For the wood waste availability the evaluation can be specified analyzing the fluxed of pruning, flotted wood and MSW wood. This operation can be realized uniforming the french regional data, which are the most precise in terms of specifying the waste fluxes. An importan research field is the wood waste conainers in the recycling centers, these may contain a large availability of class B wood waste not recovered. This operation can be accomplished with field research to estimate the quantity of wood in the wood waste containers and the percentage of wood in the bulky waste containers.

For the wood waste characterization in this work were analyzed only a few wood materials, and the attention was focused on furniture wood containing resins and melamine, but there are several wood waste to consider. A possible way of development is to create a database, some are already available in literature, with an elemental analysis and a chemical analysis of the polluting compounds and the thermal behavior.

Since the aim is the gasification and the energetic recovery of the wood waste, the characterization of the polluting compounds in the combustive agent is very important, as it is the study of the spreading of these compounds on the effect of the incineration/gasification.

Because of this an important step is to characterize the polluting compounds, especially the heavy metals, in the ashes, in the tars and in the outgoing gases.

The thermal behavior of the waste biomasses can be precisely described by the model, as the previous comparisons show; but the model cannot simulate the biomasses out of the characterization triangle. The attempt of enlarging the triangle with the addition of the terpenes is a starting point, in fact, despite the better accuancy of the new model, there still are some biomasss outside the triangle.

A possible way of development of the model is enlarging the triangle, changing its bounds in order to comprise all the biomasses. This goal can be achieved adding another compunds and then a new pseudo-specie. The more likely to be added are the fatty acids, which have a similar hydrogen percentage of the terpenes but with a lower percentage of carbon. A pseudospecie representing fatty acids, interpolated with the LIGH pseudospecie, can define a segment in which spot a new vertex of the triangle.

• 21. Conclusions

In this work several points of view about wood waste are debated in order to primarly understand if the enrgetic recovery of the wood waste is a possible way of reclamation and energy production.

The analysis of the availability shows that the class A or B wood waste in France recoverable energy is 4,873 tons, including:

- The packaging wood is 6,73% with a deposit of 328 thousand tons;

- Wood furniture is the 19,39% with a deposit of 945 thousand tons;

- Wood construction of the building is the 73,87% with a deposit of 3,6 million tons.

In the medium term future (25-30 years), because of the application of the recycling law (law Grenelle II especially), the total amount will increase to 6,436 million tons, including:

- The packaging will increase its availability to1,741 million tons;

- Wood furniture will increase its availability to 1,095 million tons, but this value depends in how much recycling the enterprises will be able to reach;

- Building sector wood availability will remain around 3,6 million tons.

These values show that the energetic recovery is a possible way of reclamation, nevertheless, since the availability and the way of reclamation is strictly dependent to the regional level, the recovery can be done at his best only at this scale. Therefore small gasification plants are favourite, even because the ratio of the production unit dimension and the energy produced favours the gasification compared to the incineration.

The class C wood has a wide availability, about 1,82 million tons with a growth of 240 thousand tons per year, but it cannot be incinerated or recovered in energy because of his status of hazardous waste.

The characterization of these kind of wood is necessary, in order to recognize the polluting compounds which it may contain, especially heavy metals, coming from several tratments, as the conservative one with CCA.

The samples of wood waste analyzed show a different thermal degradation because of the treatment they recived. In particular there are some wood waste which are poorly treated, and therefore, very likely to the natural biomass, as packaging wood. Other kinds of wood have common dissimilarities, as the furniture wood which contains resins and melamine.

The TGA comparisons show that there is a strong effect of the melamine, changing the thermal degradation behavior. These compounds, being long chain polymers, change the thermal degradation behavior at high temperatures (500-600 °C) in the pyrolising process. Even thoug these compounds degradate at temperatures higher than 600 °C, leaving only a small percentage of residue.

Nevertheless these comparisons display that, in therms of thermal degradation, the class B wood is very likely to the natural biomass, and then it can be gasificated/incinerated without any differences.

The comparison between the analyses and the simulations shows that, despite the melamine and the other addictives effect, the model used represents very well the real thermal behavior, except for his theoretical and schematic nature, which brings the simulations to be imprecise in describing the degradation of the lignin and all the compound which degradate at the same temperature (320-600 °C).

Despite the good accurancy in describing the thermal behavior of the biomasses, the model can not characterize (and therefore simulate) several biomasses, because of their high hydrogen content.
The introduction of new pseudospecies, which represent the terpenes, helps the model to comprise several biomasses.

This development make the simulation more precise, but some efforts must be done in order to comprise more biomasses and improve the precision.

In general this work is a good base for the development of an energetic recovery sector for poorly treated wood waste, displaying that there is a good availability of this waste and, through the analitic comparisons, it is very likely to the natural biomass. The simulation and the model development are a good base for the improvement in the study of the thermal degradation beavior of the biomasses.

- **Bibliography**

[1] Décret n° 2013-814 of 11 september 2013 modifying the regulation of the classed installations

http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000027945250&dateTexte=&categorieLien=id

[2] Pollutec Report, FEDEREC et FCBA: Le bois de recyclage : de fortes potentialités.... mais pour quels usages ? Bilan et perspectives

The recycling wood: big potential … but for which use? Analyses and perspectives, 2012.

http://www.federec.org/sites/default/files/le_bois_du_recyclage_de_fortes_potentialites_mais_pour_quels_usages_-_louis_de_reboul_-_pollutec_2012.pdf

[3] HELSEN et al.: Review of disposal technologies for chromated copper arsenate (CCA) treated wood waste, with detailed analyses of thermochemical conversion processes , 2005.

http://www.sciencedirect.com/science/article/pii/S0269749104003380

[4] ALTAFINI et al.: Prediction of the working parameters of a wood waste gasifier through an equilibrium mode, 2002

http://www.sciencedirect.com/science/article/pii/S0196890403000256

[5] HELSEN et al: Total recycling of CCA treated wood waste by low-temperature pyrolysis, 1998

http://www.sciencedirect.com/science/article/pii/S0956053X98001482

[6] P.N. SHETH, B.V. BABU: Experimental studies on producer gas generation from wood waste in a downdraft biomass gasifier, 2009.

http://www.sciencedirect.com/science/article/pii/S0960852409000480

[7] European Parliament and Council directive 94/62/CE about packaging and packaging waste. http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000000888850

[8] European Parliament and Council directive 2006/12/CE of 5 april about waste

http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:114:0009:0021:fr:PDF

[9] Council directive of 15 july 1975 about waste (75/442/CEE)

http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:1975L0442:20031120:FR:PDF

[10] European Parliament and Council directive 2000/76/CE of 4 december 2000 about waste incineration

http://www.central2013.eu/fileadmin/user_upload/Downloads/Document_Centre/OP_Resources/Incineration_Directive_2000_76.pdf

[11] European Parliament and Council directive 2001/80/CE about the limitation of the emission of some polluting compound in the atmosphere, coming from big incineration plants

http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000000330993&dateTexte=

[12] Directive of 26 august 2013 modifyin the directive of 25 july 1997 about the general prescriptions appliables to the classed installations for the environment protection decleared to the rubrique n° 2910 (Combustion).

http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000027995864&dateTexte=&categorieLien=id

[13] Code général des impôts

General taxes code, annexe 4, CGIAN4. - Article 18 bis

http://www.legifrance.gouv.fr/affichCodeArticle.do;jsessionid=05BDE42DE4624C4A0D3E7461D41C8B87.tpdjo07v_3?idArticle=LEGIARTI000021660790&cidTexte=LEGITEXT000006069576&dateTexte=20100429

[14] Law n° 2009-967 of 3 august 2009 of programming relative to the start of the law “Grenelle de l'environnement (1) “

http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000020949548&categorieLien=id

[15] Law n° 2010-788 du 12 juillet 2010 portant engagement national pour l'environnement (1)

http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000022470434

[16] Law of 25 juy 1997 about the general prescriptions appliable to the classed installations for the environment protection decleared to the rubrique n° 2910 (Combustion).

http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000000202304&dateTexte=&categorieLien=id

[17] Law of 20 june 2002 about boiler rooms presents in a brand new plant or modified of a powe superior to 20 MWth

http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000000779198&dateTexte=&categorieLien=id

[18] Law of 30 july 2003 about boiler rooms presents in a brand new plant or modified of a powe superior to 20 MWth.

http://www.legifrance.gouv.fr/affichTexte.do;jsessionid=BD898FE9B1C2240ED70621E98C697CA5.tpdjo10v_3?cidTexte=LEGITEXT000005689673&dateTexte=20031106&categorieLien=cid

[19] Law of 7 january 2002 about the general prescriptions appliables to classed installation decleared on the rubrique n° 2170.

http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=LEGITEXT000005632261

[20] International Standards For Phytosanitary Measures No. 15 (ISPM 15)

http://fr.wikipedia.org/wiki/NIMP_15

[21] Wikipedia

http://fr.wikipedia.org/wiki/Panneau_de_grandes_particules_orient%C3%A9es

[22] NF EN 14080 August 2013 Wood structures – Laminated wood and restored timber - exigences,

Structures en bois - Bois lamellé collé et bois massif reconstitué - Exigences

http://www.boutique.afnor.org/norme/nf-en-14080/structures-en-bois-bois-lamelle-colle-et-bois-massif-reconstitue-exigences/article/673729/fa170492

[23] NF EN 335, Wikipedia

http://fr.wikipedia.org/wiki/NF_EN_335

[24] HADJISAVVAS D.: Origines et impacts de certains elements - traces mineraux sur la filière bois-energie,

Origins and impacts of certains compounds – mineral traces on the wood-energy sector, 2012. Confidential Report.

[25] DAMIEN A.: La biomasse énergie : définitions, ressources, usages,

The energy-biomass: deifnitions, ressources, uses 2008

[26] CTBA: Valorisation énergétique des déchets de bois faiblement adjuvantés,

Energetic recovery of wood waste with few addictives, 2003

[27] CSTB: caractérisation des déchets de bois de chantiers de bâtiments, recommandations de tri, pistes de valorisation,

Characterization of wood waste from construction site, sorting reccomendation, way of recovery, 2006

[28] VAN ALKEMADE M.M.C., LOO S., SULILATU W.F.: Exploratory investigation into the possibilities of processing ash produced in the combustion of reject wood,1999.

[29] http://www.nextenergies.com/bois-energie.html (visited on 23/05/2014).

[30] ADEME: La valorisaiton des Emballages en France,

The packaging recovery in France, 2013

http://www.sinoe.org/documents/download/idDoc/872

[31] ADEME: Emballages industriels, commerciaux et ménagères, 2011, collection repère

Industrial, commercial and residual packaging, 2011, répere collection

file:///Users/stefanobergami/Downloads/7907-synthese-eicm-donnees-2011.pdf

[32] ADEME: Déchets d'éléments d'ameublement (DEA), données 2010

Waste of furniture elements, data 2010

http://www2.ademe.fr/servlet/KBaseShow?m=3&cid=96&catid=25362

[33] RECORD, Etude RECORD n° 09-0139/1°: Déchet de demolition et déconstruction: gisements, caractérisation, filières de traitement et valorisation,

Demolition and deconstruction waste, availavbility, characterisation, treatment and recovery ways, 2011

[34] ANFOR: Note de synthèse de l'ADEME sur les mesures à l'émission d'installations de combsution de bois faiblement adjuvantés

Synthesis note of ADEME on the measures of emission of the incineration plants of the wood treated with few addictives, 2002

[35] SENGA KIESSE S. E.: Valorisation énergétique des déchets de bois traités par voies thermochimiques (pyrolyse et hydroliquéfaction),

Energetic recovery of the waste tood treated with thermochemicals (pyrolysis and liquefaction), 2013

[36] http://www.actu-environnement.com/ae/news/charte-elimination-bois-pollue-creosote-poteaux-traverses-10700.php4 (visited on 25/05/2014)

[37] SUEZ SITA: Etude de marché du secteur bois dans le Rhône

Study on the market of the wood sector in the Rhône region, 2009

[38] ADEME, FFB : Déchets de chantiers de bâtiment - Quantification nationale. Publication ADEME/FFB

Construction site waste – National Quantification. ADEME/FFB publication,june 1999, 19 p.

[39] IFEEN : Le recyclage des déchets du bâtiment et des travaux publics peut progresser. Le 4 pages de l'IFEEN, Déchets, n°116,

The recycle of bulding an public works waste can progress. The 4 passages of IFEEN, waste, n°116, febrary 2007

[40] ADEME (Laurent Chateau): Déchets du BTP, gisements, filières, perspectives d'évolution. Note d'information, document de travail,

Public works waste, availability, sectors, evolution perspectives. Information note, working document, april 2008, 44 p.

[41] Norme NF EN 14899 X 30-400, 2006,

http://www.installationsclassees.developpement-durable.gouv.fr/IMG/pdf/guide-SEVESO-publie.pdf

[42] ADEME, Evaluation de la production nationale des déchets des entreprises en 2004

(Etablissements industriels et commerciaux de 10 salariés et plus),

National production analysis of the Enterprises wast in 2004 (Industrual and commercial enterprises with 10 or mor employés) 2004,

http://www2.ademe.fr/servlet/list?catid=14696 (visited on 23/05/2014).

[43] PROVENZANO M.R., OUATMANE A., HAFIDI M., SENSI N.: Differential scanning calorimetric analysis of composted materials from different sources. Journal of Thermal Analysis and Calorimetry, Vol. 61, 7, 607-614, 2000

[44] TSUJIYAMA S.,MIYAMORI A.: Assignment of DSC thermogram of wood and its components. Thermochim Acta, 177-181, 2000.

[45] RIESEN R.: Adjustment of heating rate for maximum resolution in TG and TMA (MaxRes). Journal of Thermal Analysis, vol. 53, 365-374, 1998.

[46] SANDU I.C.A., BREBU M., LUCA C., SANDU I., VASILE C.: Thermogravimetric study on the ageing of lime wood supports of old paintings. Polymer Degradation and Stability, Vol. 80, 2002

[47] FRANCESCHI E., CASCONE I., NOLE D.: Thermal, XRD and spectrophotometric study on artificially degraded woods. Journal of Thermal Analysis and Calorimetry, Vol. 91, 2008.

[48] GENESTAR C., PONS C.: Analytical characterization of biodegraded wood from a 15th century spanish cloister. Microchim Acta (2008) 162: 333–339, 2008.

[49] DI BLASI C.: Modeling chemical and physical processes of wood and biomass pyrolysis. Progress in Energy and Combustion Science, 55, 2006.

[50] RANZI E., CUOCI A., FARAVELLI T., FRASSOLDATI A., MIGLIAVACCA G., PIERUCCI S., SOMMARIVA S.: Chemical Kinetics of Biomass Pyrolysis, 2008.

[51] RANZI E., CORBETTA M., MANENTI F., PIERUCCI S.: Kinetic modeling of the thermal degradation and combustion of biomass, 2014.

[52] RANZI E., CORBETTA M., MANENTI F., PIERUCCI S.: Kinetic modeling of the thermal degradation and combustion of biomass, 2014.

[53] BIOBIB - A Database for biofuels
http://www.vt.tuwien.ac.at/biobib/

[54] IEA Bioenergy Task 32
http://www.ieabcc.nl/

[55] STEFANELLI K.:Caratterizzazione chimica delle biomasse e modellazione cinetica del loro degrado in condizioni di pirolisi, 2007.

[56] PAKDEL H., MAGDALENA PANTEA D., ROY C.:Production of *dl*-limonene by vacuum pyrolysis of used tires, 2000.

[57] Wikipedia
http://en.wikipedia.org/wiki/Beta-Carotene

[58] ISHIWATARI M:Thermal reaction of β-carotene, Part 1 and 2.