Pyrolysis-Gas Chromatography/ Mass Spectrometry Analysis of Di- and Triterpenoids

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Abstract

The objective of this work was to study a specific class of extractives existing in lignocellulosic biomass and more precisely in wood materials, and their thermochemical behavior during pyrolysis. The focus was centered on the class of terpenes and terpenoids; specifically two model compounds, abietic acid and betulinol, were chosen to represent the subclasses of di- and triterpenoids, respectively.

The model compounds were investigated via pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and the main objective was to study their product profiles and characteristic fragmentations, as well as the influence of specific variables (pyrolysis temperature and time) on pyrolysis products. Pyrolysis experiments were performed at three different temperatures (700, 600, and 500°C) with two different pyrolysis times (20 and 5 seconds). The MS spectra indicated that the fragments obtained from abietic acid and betulinol, under the chosen conditions, were mainly aromatics in nature, especially at the higher temperature, whereas at the lower temperature different fragmentation products of the original molecule were also present. Among the pyrolytic products, benzene, indene, naphthalene, and their derivatives, mainly methylated, were dominant and common to both model compounds. Phenanthrene derivatives were only found during pyrolysis of abietic acid, due to the stability of the phenanthrene carbon skeleton, which is a characteristic of tricyclic resin acids. A general trend could be seen at the higher pyrolysis temperature and longer time enhancing the formation of the detected compounds. Overall, pyrolysis temperature was shown to be a more influential parameter than pyrolysis time.

The relevance of this type of research relies on the fact that investigations on model compounds can improve the understanding of the whole biomass behavior under different pyrolytic conditions**.** In addition to that, studies on the thermochemical behavior of lignocellulosic materials have a key role in evaluating the feasibility of producing certain fuels and chemicals from this renewable and abundant resource. This can offer an attractive opportunity for industry in the manufacture of various wood-based chemicals, fuels, and similar products, as an alternative to those derived from fossil resources.

Preface

First of all, I would like to thank Professor Raimo Alén for welcoming me in his research group, for his flexibility, positive encouragements, and helpful advises. Another person that immensely contributed to the realization of this work is Maryam Ghalibaf, who helped me from the very beginning. Thanks a lot for showing me the ropes, for being so helpful and motivating, and for the time we shared in the lab. Thanks also to all the people that I met at the Laboratory of Applied Chemistry of the University of Jyäskylä, who directly or indirectly contributed to this work.

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A great part of this achievement goes to my family, because I am what I am thanks to their examples and their unconditional support. Mamma, Papà, Vale, e Chicco, grazie per essermi stati così vicini anche nella lontananza, vi voglio bene un bel pò! The last but most important and heartfelt thanks go to Miguel, for constantly reminding me to not be so harsh on myself (perfection doesn't exist!), for inspiring me to always be the best version of myself, and for always making me smile. Thanks for keeping up with me even in the worst times: you are my hero!

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A1	Aromatics with one benzene ring, benzene and its derivatives
A2	Aromatics with two benzene rings, naphthalene and its derivatives
A3	Aromatics with three benzene rings, phenanthrene/anthracene and their derivatives.
CAS	Chemical abstract service
CTO	Crude tall oil
DP	Degree of polymerization
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
EI	Electron ionization
EPR	Electron paramagnetic resonance
FBR	Fluidized-bed reactor
GC	Gas chromatography
GHG	Greenhouse gas
HPLC	High-performance liquid chromatography
I	Indane/Indene and their derivatives
IR	Infrared
LCC	Lignin-carbohydrate-complex
LM	Light microscopy
LPC	Lignin-polysaccharide-complex
MS	Mass spectrometry
$\mathbf{M_n}$	Number average molar mass
$\mathbf{M_w}$	Weight average molar mass
m/z	Mass to charge ratio
NIR	Near-infrared
NMR	Nuclear magnetic resonance
NSC	Non-structural component
Py-GC/MS	Pyrolysis-gas chromatography/mass spectrometry
RT	Retention time
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis

TOR	Tall oil resin
X	Non-aromatics, alkanes/alkenes and cycloalkanes/cycloalkenes

1 Introduction

The need to shift from a fossil-based society towards a renewable and sustainable one is arising today due to several factors.[1,2] Frightening environmental effects, such as global warming, climate change, atmospheric pollution, and littering problems have played a major role in growing awareness. At the same time, the dwindling of fossil resources and consequent increasing of oil prices represent an important issue to be considered in a continuously growing and developing society.[1-3]

A main part of the present fossil resources are today used for transportation and energy production.[4] This is the reason why energy issues have been already largely debated with various alternative solutions. Great efforts have been put on investigating renewable resources for energy production in order to overcome the uncertainty of fossil resource availability. Various renewable energy sources alternative to fossil already today in commercial state are sun, wind, biomass, geothermal, and hydropower resources. Among them, biomass is the only sustainable source of carbon, since the energy it contains is stored in its chemical bonds. It derives that biomass is the only alternative to fossil resources for the production of chemicals, materials, polymers, and fuels.

The large majority of products used in our daily life, such as colorants, plastics, coatings, detergents, synthetic fibers, and medicines still heavily rely on fossil resources, mainly crude oil and natural gas.[1] The increasing population number, approaching 8 billion people[5] and the progressive industrialization of third world countries will lead to a proportional increase in resources demand, with problem in resource management and availability. The growing concern inevitably related to these issues has led our society towards the need of green and sustainable products. Therefore, more and more efforts have been put into researching eco-friendly materials based on natural resources.[1,6]

In modern times, the exploitation of renewable resources led to prepare useful products and plastics that have been prominent from the end of 19th century, with the production of natural rubber for tires, cellulose acetate and nitrate, plant-based dyes, oil and varnishes, and naval store products.[7,8] Nevertheless, a major shift of industrial chemistry raw material took place later, first towards coal and then petrol.

What we are seeking now is going back from fossil towards renewable and sustainable raw materials.[9] This change will allow decreasing gradually the dependence on fossil resources as well as obtaining beneficial environmental effects. In order to do that, one of the most promising alternatives to be utilized as a source of sustainable organic carbon is biomass.[9]

Among the different biomass feedstocks, lignocellulosic raw material has attracted significant attention as a mean to replace fossil resources.[6,10] This is due to its abundance, large availability, as well as environmental and ethical benefits, as it contributes to mitigate emissions and it does not compete with food production. A particularly abundant lignocellulosic material available on earth is wood. Many studies have been performed on different possible exploitation of wood main structural components, which are carbohydrates (cellulose and hemicelluloses) and lignin. However, wood non-structural components, for example, extractives, also can play an important role due to their large chemical variety.

This work concentrated in depth on a specific class of compounds within extractives, named terpenes and terpenoids. These terpenoid feedstocks could be interesting substances since they have the capability to be used as raw materials for potentially high-value products. To achieve this, one commercial possibility is offered by pyrolysis, by which it is possible to produce fuels and chemical for many purposes. The mechanisms behind pyrolysis can be investigated by analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Therefore, in this thesis, the main aim was to study the thermochemical behavior of two significant terpenoids (abietic acid and betulinol) via Py-GC/MS.

2 Biomass

2.1 General approach

Biomass is defined as any organic, thus decomposable, matter derived from plants or animals and available on a renewable basis.[11] It includes agricultural food and feed crops, herbaceous and woody energy crops, wood and agricultural wastes and residues, municipal organic wastes, aquatic plants, as well as manure.

Biomass has two remarkable characteristics:[12] firstly, it is a renewable and potentially inexhaustible organic resource, and the most abundantly distributed, in many part of the world, in different forms. Secondly, biomass fixes carbon dioxide (CO_2) in the atmosphere, through photosynthesis process. This is a great environmental advantage of biomass over fossil resources, since its utilization can lead to theoretical zero carbon emissions. This is possible because the CO_2 released in the atmosphere during utilization is theoretically equal to the CO_2 intake during biomass cultivation and growth. Simply speaking, biomass is obtained from CO_2 available in the atmosphere, water, and sunlight through the photosynthesis process, with shorter renovation cycle then fossil resources.[12] The truth is that biomass is really a carbon neutral feedstock and renewable resource only in the case in which is harvested sustainably, which means that its rate of growth is higher than its consumption.

The real value of biomass stands on the fact that its energy is stored in the form of chemical bonds, and therefore, it is the only renewable source of carbon.[13] Ultimately, fossil resources are simply obtained from biomass decomposition, under different conditions of high pressure and temperature, which led to the formation of coal, oil, and natural gas.[14] Therefore, biomass is the perfect equivalent of petroleum for sustainable production of chemicals and fuels. Nevertheless, some of its characteristics, such as high heterogeneity and chemical complexity, are still hindering the exploitation to its full potential.[15] Biomass heterogeneity is a consequence of different factors, such as availability of different species, production conditions, and different practices in harvesting, collection, and storage. Understanding the variability of the biomass attributes, like moisture, ash, and sugars content is of crucial importance for the optimization of processes and products.[15] Biomass compositional variety, on one hand, allows obtaining a wider range of products than fossil materials but, on the other hand,

it requires a larger number of technologies, some of which did not reach commercial level yet.[9] Furthermore, biomass is not available uniformly throughout the year, so there is need to adapt the present system to seasonal operations, whilst simultaneously improving storage systems to ensure continuous productivity.

Biomass has an enormous potential both for energy and for a variety of applications, provided that appropriate agricultural policies are implemented based on sustainability principles.[16] If biomass is used as feedstock for the chemical industry, a much lower amount is required than for energy production. From a mere economic point of view, biomass for chemicals is more desirable, but many factors need to be taken into account, such as resource availability, sustainable harvesting, market demands, economical, and ethical considerations.[16]

In this context, biorefinery is regarded as a promising emerging technology for the development of a sustainable biomass value chain.[9,10,17,18] Biorefinery is defined as a sustainable processing of biomass into a spectrum of marketable products and energy.[9] Essentially, biorefinery is able to use different types of biomass feedstocks and process them with different technologies into heat, power, and various products. This concept is analogous to the traditional petroleum refinery systems. Nonetheless, the huge exploitation of natural resources and large waste production are replaced by an integrated system where every component is used. A wide range of goods, like biofuels and biochemical, are produced breaking down the raw material in its building blocks. The main objective is to optimize the valorization of each biomass component with minimal waste. In this way, the residue of one plant can become the input for another bio-based process.[9]

2.2 Lignocellulosic biomasses

Among the different biomass types, lignocellulosic raw material stands out as particular suitable option to replace fossil resources.[6,10] The term “lignocellulosic” refers to the chemical composition of the material, which comprises lignin and cellulose that form the hard structure of the plant matter, and hemicelluloses binding them.[14]

Lignocellulosics show the same positive advantages of worldwide availability and quality to mitigate GHG (greenhouse gas) emissions typical of biomass feedstocks. In addition to those, lignocellulosic biomass has an advantage over other supplies of non-

competing with food production, since it represents the non-edible part of the plant. It can be grown on soil not suitable for agricultural cultivation and it can yield more than other edible biomasses, since the whole crop is available as feedstock. Technology for production of biofuels and bio-based chemicals from lignocellulosic material is continuously advancing in order to be able to fulfill the energy demand and chemical needs.

In particular, within lignocellulosic resources, wood represents a significantly abundant raw material with enormous potential, together with forestry and agro-industrial lignocellulosic wastes, which are widely spread around the world. The emphasis is nowadays concentrated on ways of getting higher value from these biomass wastes, since they offer a way to create value for the society without additional land use for its production.[9] One way to achieve this is via thermochemical conversion to produce fuels and chemicals, which is possible through pyrolysis.[19] The main types of lignocellulosic biomass currently used for pyrolysis are forestry residues, crop residues, sewage sludge, paper, cardboard, and organic municipal waste.[14]

Broadly, lignocellulosic biomasses can be divided into two categories: woody and non-woody feedstocks.[20] Agricultural residues and herbaceous crops, such as rice straw, sugarcane bagasse, corn stover, elephant, and reed grass fall into the category of non-woody biomasses, while short rotation woody crops, forestry residues, and lignocellulosic wastes are examples of woody biomasses.

Referring specifically to wood, the primary distinction possible among different wood types is between coniferous woods, commercially called “softwoods” (e.g., spruce and pine) and deciduous woods, called “hardwoods” (e.g., birch and poplar).[20] Softwoods are also referred to as conifers since they have seeds, which are produced in cones and not covered, while hardwood trees produce covered seeds within flowers. Another classification is based on the retention of leaves on the tree:[20] conifers retain new leaves for several years (ever green) while deciduous trees shred their broad leaves each fall at the end of the tree’s growing season.

All lignocellulosic biomasses share the same chemical components:[2,21,22] carbohydrates (cellulose and hemicelluloses) lignin, extractives, and inorganics (**Table 1**). Many studies have shown differences in chemical composition and structure for different

woody and non-woody feedstocks as well as between different species within the same group. In general, woody feedstocks present higher lignin content and lower extractives content when compared to those in herbaceous biomasses.

Table 1. Comparison of chemical composition of woody and non-woody feedstocks, as % of feedstock dry solids[20]

Component	Wood feedstock	Non-wood feedstock
Carbohydrates	65-80	50-80
Cellulose	40-45	30-45
Hemicelluloses	25-35	20-35
Lignin	20-30	10-25
Extractives	2-5	5-15
Proteins	<0,5	5-10
Inorganics	0.1-1	0.5-10
SO_2	0.1	0.5-7

Wood has unique characteristics, which makes it a particularly desirable material for a broad range of uses.[23] This is why a deep knowledge of its structure and chemical composition is of vital importance in order to optimize the development of technologies and processes for its implementation.

3 Structure and chemical composition of wood

Wood is a complex and not uniform material from the point of view of its anatomical, physical, and chemical properties.[23-25] Differences are not only between softwoods and hardwoods but also within a same sample, resulting from the growth of wood tissue. This is made of different types of cells, which are chemically heterogeneous and have different functions, such as mechanical support, water transport, and metabolism.[23-25]

Characteristic patterns can be individuated in softwoods and hardwoods. For softwoods, 90-95% of wood cells are fibrous in form, thus being called "tracheids" (prosenchyma cells) while in hardwoods species many different types are present, such as fibers (55%), vessel elements or pores (30%), and parenchyma cells (15%).[20] At their maturity states, in both wood types the large majority of cells are dead and hollow, being essentially only cell wall and void.[20] These walls are made of an insoluble polymeric matrix of the three main macromolecular components: cellulose, hemicelluloses, and lignin. They are all linked together to give structural strength and flexibility (**Figure 1)**. The content of these components is not uniformly distributed in wood cell walls and varies largely within different parts of the tree (roots, stem, top, branches, foliage, and bark) and different tree types.[20,24]

In addition to the main structural components, wood accounts for a minor fraction of non-structural components outside the cell walls, such as extractives and water-soluble organics and inorganics.[20] Trace amount of nitrogenous-containing compounds, such as pectin and starch are also present. In trees from temperate zones, the macromolecular substances building up the cell walls account for about 95% of the wood material, while in tropical trees can have average value of 90%, which means that their content of low-molar-mass materials as extractives, inorganics, and organics is higher.[20]

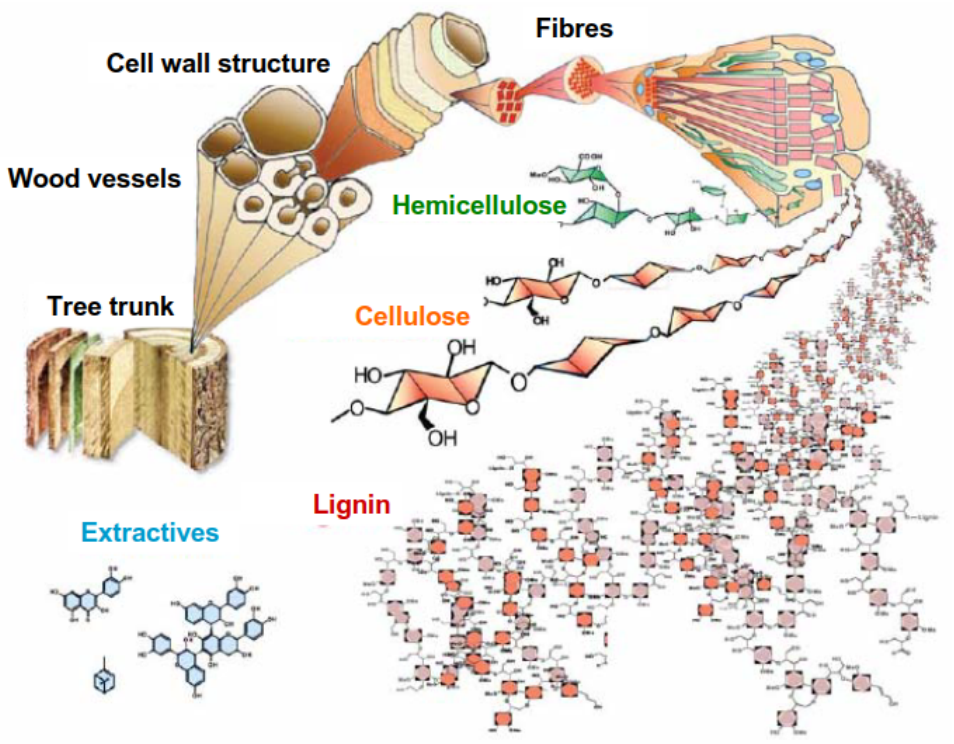

Figure 1. Chemical structure of wood.[13]

The moisture content of a living tree varies seasonally and diurnally, with average values of 40-50% of total wood mass.[23] Substantial differences in gross chemical composition, calculated on wood dry mass, are present between different wood types. **Table 2** shows a comparison between the two main wood types, softwood and hardwood, without considering the morphological distribution of the main groups.

Table 2. Average chemical composition of Scots pine and silver birch (%)[20]

Component	Softwoods	Hardwoods
Cellulose	40	40
Hemicelluloses	25-30	30-35
Lignin	25-30	20-25
Others (mainly extractives)	<5	<5

Specifically, Scots pine (*Pinus sylvestris*) and silver birch (*Betula pendula*) have been considered as representing, respectively, the category of softwoods and hardwoods, since they are the main species of indigenous conifers and broad-leaves tree, which are found in Finland.[26]

The following sections will present a summary of important chemical features of the main wood structural components as well as the non-structural ones, with particular

emphasis on extractives. Since extractives encompass a wide range of different types of chemical substances, a deeper attention is focused on a specific class of extractives, terpenes and terpenoids, as terpene feedstocks can be an interesting substrate to be used in chemical industry.

3.1 Carbohydrates

Cellulose and different types of hemicelluloses belong to a larger group of biomolecules called "carbohydrates" that play a central role in all form of life.[27] Carbohydrates are polyhydroxy compounds common in Nature in the form of relatively small molecules (sugars) or larger entities (polysaccharides). Sugars are formed in green plants as early products of photosynthesis from CO_2 and water, and are then converted into organic plant constituents through a variety of biosynthetic paths. Carbohydrates can be classified into mono-, oligo-, and polysaccharides. Monosaccharides are simple sugars and among them, D-glucose, D-mannose, D-galactose, D-xylose, and L-arabinose are the most common constituents of the wood cell walls. Oligosaccharides comprise different monosaccharide units linked together by glycosidic linkages with a number of units 2-9, while polysaccharides represent complex molecules where the units linked together exceed ten. Carbohydrates can present either an aldehyde (aldose) or ketone (ketose) functional group and the major types found in wood are aldopentoses and aldohexoses, with, respectively, five and six carbon atoms.[25] Carbohydrates differ from each other by rather small differences in structure, like the direction of one hydroxyl group that, however, can give important features from a biological and mechanical perspective.[27]

3.1.1 Cellulose

Cellulose is the major component of natural plant and the most abundant and important biopolymer on earth.[27] Its percentage in plant material varies depending on the origin. Although its chemical structure is rather simple, long unbranched chains of glucoses, cellulose displays various properties of great scientific and technical interest.[27] Utilization of cellulose for pulp and paper products, as well as for textiles has a long history. The same trend can be seen for cellulose derivatives, with cellulose nitrate as precursors of modern explosives, plastics, and photographic films already at the end of the 19th century.[28]

Cellulose is a linear high-molar-mass biopolymer composed exclusively of β-D-glycopyranose units with a $^4C_1$ conformation, joined together by (1→4)-glycosidic bonds (**Figure 2**). Two adjacent glucose units are linked through elimination of one molecule of water between their hydroxyl groups at the carbon atoms 1 and 4. Strictly speaking the repeating unit of cellulose is then the so-called "cellobiose residue".

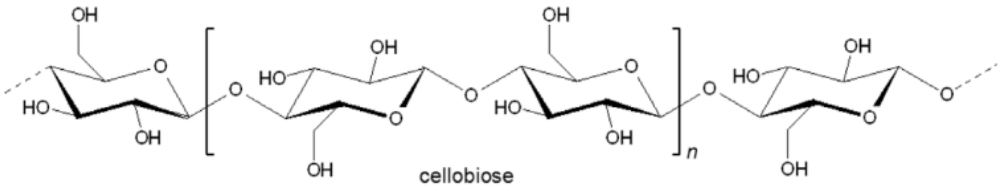

Figure 2. Partial molecular structure of a cellulose chain.[16]

In the $^4C_1$ conformation, all the substituents of the chain unit are oriented equatorially making the chain units very stable due to minimized interactions between the substituents.[23] Due to the presence of hydroxyl group as substituents, cellulose has strong tendency to form intra- and intermolecular hydrogen bonds. As a consequence of that, bundles of cellulose molecules tend to aggregate in microfibrils, in either ordered (crystalline) regions or less ordered (amorphous) ones. The microfibrils further aggregate into fibrils, which finally form cellulose fibers. The result is a tight fiber structure created by hydrogen bonds, which gives the typical fiber strength and insolubility in most solvents characteristics of cellulosic material.[24,25]

Considering cellulose polymeric nature, it is possible to define certain parameters typical of polymers. One of them is the degree of polymerization (DP), which is defined as the number of monomeric units in a macromolecule or polymer.[29] For cellulose, this value is quite high, in the order of 10,000 glucose residues. Polydispersity (i.e., the ratio of weight average molar mass (M_w) to number average molar mass (M_n)) is also an important parameter for polymers, indicating the width of molar mass distribution. For cellulose, the polydispersity is rather low, less than 2, meaning that the chain lengths do not vary much over a wide range of molar masses. Cellulose content does not differ significantly between softwoods and hardwoods, with an average value of 40% over wood dry solids.[20]

3.1.2 Hemicelluloses

Hemicelluloses are the second most naturally occurring carbohydrates-based biopolymers.[30] They owe their name to the fact that they were thought to be intermediates in the cellulose biosynthesis, even though now it is known that they represent a distinct and separate group of plant polysaccharides. Together with cellulose, they are regarded as structural carbohydrates due to their function of supporting material in the cell walls, where they are found in the matrix between different cellulose fibrils.[30] The components in lignocellulosic materials are tightly associated together and the separation of hemicelluloses from lignin and cellulose is quite difficult without modifying the hemicelluloses themselves. It is possible that hemicelluloses serve as interface between cellulose and lignin, maintaining the ordered spacing between fibrils and perhaps, regulating wall porosity and strength.[30]

In contrast to cellulose, hemicelluloses occur as non-crystalline heteropolysaccharides, mainly consisting in various β-(1→4)-linked backbone of monosaccharide residues that exist in different proportions.[23,25,30] The molecular chains are much shorter than cellulose, highly branched, and with different substituents. Their monomeric units are mainly hexoses (D-glucose, D-mannose, and D-galactose) and pentoses (D-xylose, L-arabinose, and D-arabinose) (**Figure 3**). Smaller amounts of deoxyhexoses and certain uronic acids are also present. They have lower crystallinity and lower degree of polymerization (100-200) compared to cellulose, which gives them less thermal and chemical stability.[23,25,30]

Regarding hemicelluloses, softwoods and hardwoods show characteristic differences. Firstly, the total content over wood dry solids is higher for hardwoods (30-35%) than softwoods (20-25%).[20] Secondly, the composition and structure of the hemicelluloses themselves are different (**Table 3**). In softwoods the major hemicellulose is partially acetylated galactoglucomannans (glucomannan) (15-20% of wood dry mass) and a smaller amount of arabinoglucuronoxylan (xylan) (5-10% of wood dry mass). In contrast, in hardwoods the predominant hemicellulose is partially acetylated (4-*O*-methyl)glucuronoxylan (20–30% of wood dry mass) with a small proportion of glucomannan (<5% of wood dry mass). Larches can be distinguished among softwoods, as their main hemicellulose component is arabinogalactan, which is generally less than 1% in conifers.[20,30]

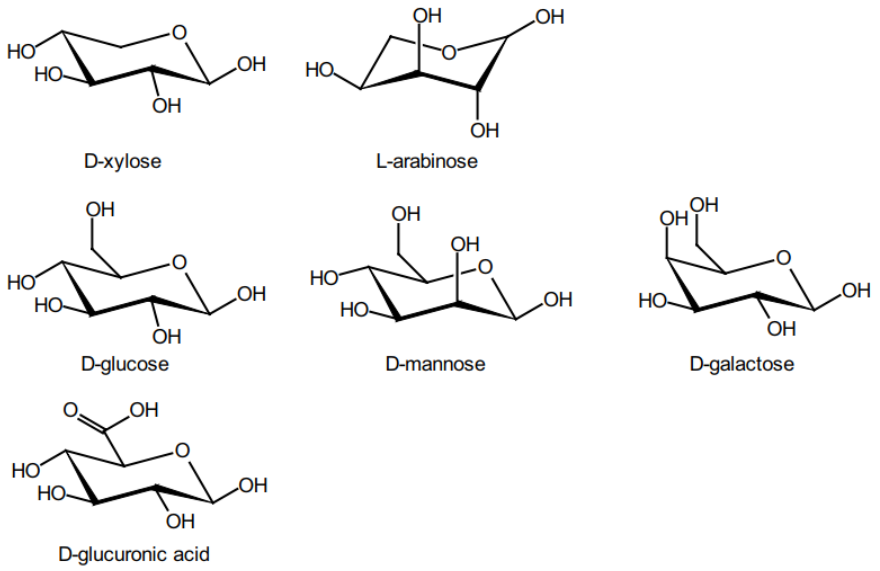

Figure 3. Main monosaccharides in wood hemicelluloses.[16]

Table 3. Comparison between major hemicelluloses in softwoods and hardwoods[30]

Occurrence	Hemicellulose	Amount, %[1)]	Units	Molar ratio[2)]	Linkage
Softwood	Galactoglucomannan	5–8	β-D-Man*p*	3–4	1→4
			β-D-Glc*p*	1	1→4
			α-D-Gal*p*	1	1→6
			O-Acetyl	1	
Softwood	Glucomannan	10–15	β-D-Man*p*	3–4	1→4
			β-D-Glc*p*	1	1→4
			α-D-Gal*p*	0.1	1→6
			O-Acetyl	1	
Softwood	Arabinoglucuronoxylan	7–15	β-D-Xyl*p*	10	1→4
			4-OMe-α-D-Glc*p*A	2	1→2
			α-L-Ara*f*	1.3	1→3
Larch wood	Arabinogalactan	3–35	β-D-Gal*p*	6	1→3, 1→6
			L-Ara*f*	2/3	1→6
			β-D-Ara*p*	1/3	1→3
Hardwood	Glucuronoxylan	15–35	β-D-Xyl*p*	10	1→4
			4-OMe-α-D-Glc*p*A	1	1→2
			O-Acetyl	7	
Hardwood	Glucomannan	2–5	β-D-Man*p*	1–2	1→4
			β-D-Glc*p*	1	1→4
			O-Acetyl	1	

[1)] By dry weight
[2)] Approximate value

3.2 Lignin

The term “lignin”, already introduced in 1819, is derived from the Latin word for wood “lignum”.[25] Lignin is the third main structural component of biomasses and it differs largely from cellulose and hemicelluloses for its complex structure, being a mixture of aromatic and aliphatic moieties. It is chemically and physically bonded to the carbohydrates and is the main responsible for plants mechanical strength and cell walls

rigidity.[27] Its content is clearly higher in lignocellulosic biomasses, especially in wood, with slightly high amount in softwoods (25-30%) than hardwoods (20-25%).[20] Lignin is generally defined as an amorphous polyphenolic material obtained via enzymatic polymerization of three main phenylpropanoid (C_3C_6) units: *trans*-coniferyl, *trans*-sinapyl, and *trans*-*p*-coumaryl alcohol (**Figure 4**). They are present in different proportion depending of the lignin origin.[20]

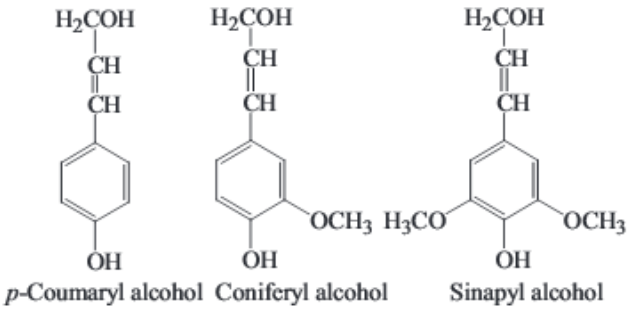

Figure 4. Lignin main precursors.[27]

The biosynthesis process involves a series of oxidative coupling reactions of the resonance-stabilized radicals obtained from the C_3C_6 precursors. [23,24] These reactions originate a non-linear and randomly cross-linked macromolecule. The linkages between the building blocks are mainly ether (C-O-C) or carbon-carbon (C-C) bonds, from which the ether type is dominant in wood, as a β-*O*-4-structure. They are distributed randomly, with result of creating a three-dimensional and unorganized structure. A part from inter-linkages between lignin precursors, the presence of chemical bonds between lignin and carbohydrates has been investigated due to the close physical and chemical interactions of these two components. The complex nature and the amount of linkages are not yet fully understood, but the terms "lignin-polysaccharide-complex" (LPC) or "lignin-carbohydrate-complex" (LCC) are used to indicate covalent bonds between the two macromolecules. Benzyl ether, benzyl ester, and phenyl glycoside linkages are the most frequently suggested types of bonds, with the α carbon (C_α) of the phenyl propane units being the most probable connection point between lignin and hemicellulose blocks.[23,24]

The determination of the polymeric properties of lignin is limited by its low solubility and lack of non-destructive isolation methods of lignin from other wood components.[24] Different measuring methods have suggested a DP of 75-100 for softwood, with slightly

lower value for hardwoods, as well as relatively high polydispersity (2.3-3.5) if compared to cellulose.[23]

3.3 Inorganics

Inorganics are together with extractives classified as non-structural components of wood. The amount of inorganic is measured as ash, which is the residue obtained after proper combustion of organic matter.[23-25] The ash contains mainly different metal salts, such as carbonates, silicates, oxalates, and phosphates, with calcium, potassium, and magnesium being the most common cations. Chiefly these inorganic components play important roles in the plant growing process but they can cause problems during pulping or other wood utilization practices.[23-25]

Wood usually contains a rather small amount of inorganics (<1% of wood dry solid) but their content is largely influenced by environmental growth conditions (tropical woods can contain even 5%) and the part within the tree, as ash content in needles, leaves, and bark can be much higher than in the stem.[25]

3.4 Extractives

Extractives comprise a very large variety of wood components, regarded as non-structural components (NSCs) found in plants and trees alongside the main structural one (**Table 4**). Extractives owe their name to the fact that they can be extracted, as they are soluble in neutral organic solvents or water. They range from lipophilic fats, resin acids, and waxes to water-soluble carbohydrates and inorganic salts, mainly with low molar masses.[8,23,25]

Table 4. Classification of non-structural components (NSCs) in trees[8]

Main class	Terpenoids	Fats	Polyphenols	Carbohydrates	Inorganics
Subclasses	Monoterpenoids Resin acids Other terpenoids	Triglycerides Steryl esters Fatty acids Sterols	Lignans Flavonoids Stilbenes Tannins	Sugars Starch Gums Pectins Glycosides	Various salts
Main function	Protection	Physiological	Protection	Biosynthesis Nutrient reserve Protection	Photosynthesis Biosynthesis
Occurrence	Oleoresin canals Heartwood Knots Bark	Parenchyma cells	Heartwood Knots Bark (condensed tannins) Foliage (hydrolysable tannins)	Sapwood Cambium Heartwood	Ascending water in sapwood Sap in inner bark
Tree species	Softwood	All species	All species, especially soft-woods	All species	All species
Solubility	Non-polar solvents	Non-polar solvents	Polar solvents Water (limited)	Water	Water

The composition of extractives is influenced by growth conditions, geographical site, and season, and varies widely between tree families and genera.[31] For example, in Scots pine (*Pinus sylvestris*) extractives concentration is in the range of 2.5-4.5%, while in silver birch (*Betula pendula*) between 1.0% and 3.5% of the wood dry solid (**Table 5**).[23] Different parts of the same tree also differ for extractives content and composition, as showed in the following (**Figure 5)**.

Table 5. Content of extractives in different wood species (extraction with diethyl ether)[32]

Species	Content %
Pine (*Pinus sylvestris*)	2.5-4.8
Spruce (*Pices abies*)	1.0-2.0
Birch (*Betula pendula*)	1.1-3.6
Aspen (*Populus tremula*)	1.0-2.7
Beech (*Fagus grandiflora*)	0.3-0.9

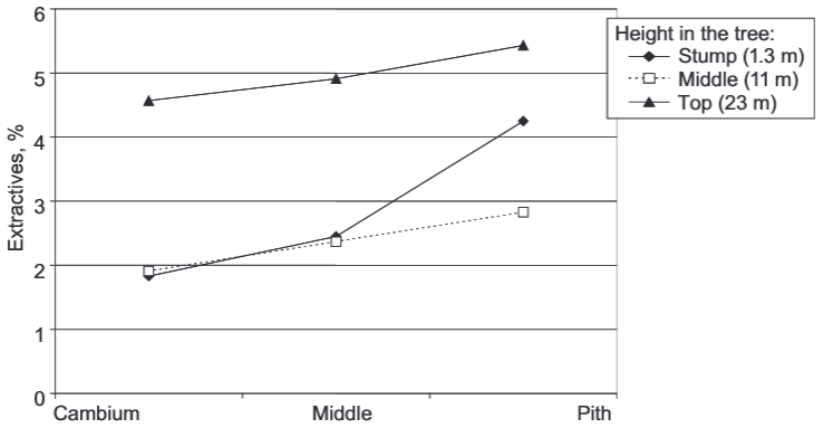

Figure 5. Acetone-extracted compounds across the stem of a birch tree determined at three different heights.[32]

Extractives occupy certain morphological sites in the wood structure. For example, resin acids are located in the oleoresin canals, whereas the fats and waxes can be found in ray parenchyma cells. Phenolic extractives are present mainly in the heartwood and bark. This happens because different extractives types are necessary to maintain the biological functions of the tree:[25,31] fats and waxes constitute the energy sources of the wood cells, while most resin and phenolic compounds protect the trees from natural treats, like microbiological damage or insect attacks.

Extractives have been utilized and appreciated since ancient time, one example is the fossilized resin obtained from coniferous tree named Amber or the degradation product of exuded resin for waterproofing wood and ropes, as well as tanning agents and dyes.[25,31] Nowadays, the class of extractives is of great interest as valuable raw material for making organic chemicals[20,25] due to their complex and naturally functionalized structures. Extractives have been largely studied by pulp and paper makers, since they can cause deposits and problems in the processes, influence paper properties, and contribute to the toxicity of effluents.[32] Since they comprise such a large group of compounds, they find today innumerable applications. Extraction and refining of oleoresin and lipid components of trees have already an established industry, providing turpentine and rosin products for production of commodity chemicals, such as paper sizes, adhesives, inks, and paints. Other extractives types have shown interesting properties as food supplement in food industry; like plant sterols able to lower the level of serum cholesterol in humans and animals. They also show different beneficial properties, which could be exploited in pharmaceutical and cosmetics industries.

Among the most famous examples, there is salicin, the active ingredient found in willow bark, which has been used already since long time for its pain relieving properties (i.e., as a precursor of the modern aspirin).[8] The next section describes an important class of compounds within extractives; terpenes and terpenoids.

4 Terpenes and terpenoids

Terpenes and their derivatives comprise one of the widest families of naturally occurring compounds with different characteristics and abundance in different plant species. Currently, about 30,000 terpenes are known in literature.[33] Terpenes are primarily famous for giving pleasant flavor and fragrance to many natural plants, such as conifer wood, citrus fruits, coriander, thyme, rosemary, lavender, peppermint species, rose, violet, and many others. Terpenes can be extracted or steam distillated for recovery of so-called "essential oils", which can be used not only for perfumery and improvement of food aroma, but also to produce phytomedicines from plant origin.[33]

Most terpenes share isoprene (2-methyl-1,3-butadiene) with a molecular form of C_5H_8 (**Figure 6**) as a common carbon skeleton building block.[23,25,33]

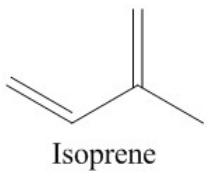

Figure 6. Isoprene (2-methyl-1,3-butadiene) structure.[34]

This structural relationship was identified by Wallach in 1887,[35] who recognized that most terpenic structures result from the head-to-tail condensation of isoprene units and this became known as the "isoprene rule".[7] The isopropyl part of the 2-methyl-1,3-butadiene is defined as head, while the ethyl residue as tail.[33]

The term "terpenes" refers generally to pure hydrocarbons, whereas the compounds collectively called as "terpenoids" carry one or more functional group containing oxygen, such as in hydroxyl, carbonyl or carboxylic acid groups.[23,25] Nevertheless, for simplicity, there is the tendency to use the term "terpenoids" generically referring to terpene-based compounds, both hydrocarbons and their oxygenated compounds. Terpenes and terpenoids can be classified according to the number of isoprene units linked together: mono-, sesqui-, di-, tri-, and polyterpenoids (**Table 6**). Even if the biosynthetic relationships are obvious, the total number of carbon atoms can deviate from the precursor due to further processes involving cleavage or addition reactions. In addition to classification by the number of carbons, they can also be divided according

to the number of rings within a structure (acyclic, monocyclic, bicyclic, tricyclic, and tetracyclic) (**Figure 7**).[23,25]

Table 6. Classification of the main terpenes types in wood tissues [23]

Name	Number of ($C_{10}H_{16}$) units	Molecular formula
Monoterpenes	1	$C_{10}H_{16}$
Sesquiterpenes	1.5	$C_{15}H_{24}$
Diterpenes	2	$C_{20}H_{32}$
Triterpenes	3	$C_{30}H_{48}$
Polyterpenes	>4	$>C_{40}H_{64}$

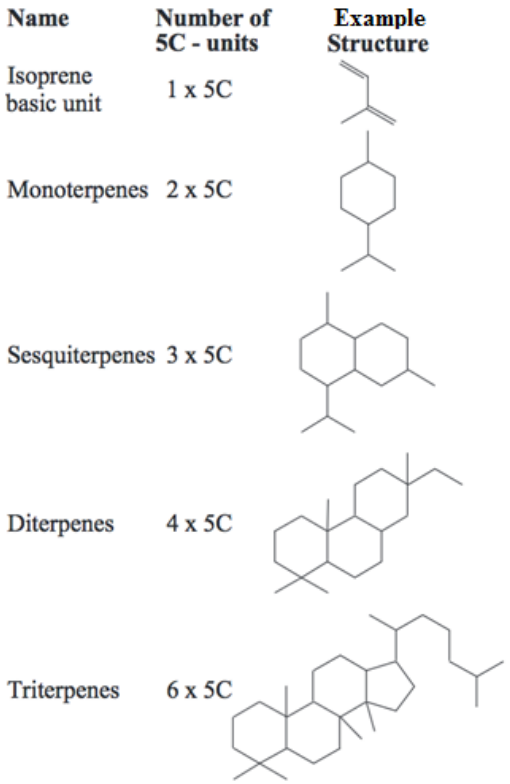

Figure 7. Basic structures of different terpenes.[32]

Monoterpenes/-terpenoids are volatile compounds and contribute mainly to the odor of wood and fragrance of plants and flowers, thus the name "essential oils".[23] Chemically they are mostly hydrocarbons and alcohols, mainly alicyclic or monocyclic and only fewer are aromatic and contain oxygen (**Figure 8**). They occur mainly in softwoods oleoresin, while being usually rare in hardwood species. They represent, together with diterpenes and some fatty acids and their glycerides, one of the most important constituents of oleoresin and exudates of softwoods.[23] However, their

composition is very species-dependent and there are considerable differences even between same species. For softwood pines, the most important monoterpenes are α- and β-pinene, giving the characteristic scent. Commercially semi-volatile monoterpenes are really important, since they are the source of various turpentine products, recovered from the kraft pulping process.[23]

Sesquiterpenes/-terpenoids can also be found as components of canal resin as well as deposits in the heartwood of softwoods (**Figure 8**). They are found in many tropical hardwoods but they are rare in temperate zone hardwoods. Since they occur usually in small amounts, they are industrially less important.[23,25]

As mentioned above, **diterpenes/-terpenoids** constitute a major part of the canal extractives (oleoresin) in softwoods and especially, in pine wood, which has larger canals than other conifers.[23,25] Chemically, they exist either as hydrocarbons or as derivatives with hydroxyl, carbonyl or carboxylic groups, and mostly with tricyclic structure (**Figure 8**). They are of great industrial importance in the form of "resin acids", with the most important being the abietane and pimarane types of resin acids. Biologically diterpenes resin acids are important for acting as defense against external attacks and pathogens.

Triterpenes/-terpenoids are widely distributed in the plant kingdom and both in softwoods and hardwoods. This class comprises mostly oxygenated compounds, traditionally divided into two subgroups, triterpenoids and steroids, which are both structurally and biogenetically closely related. They occur mainly as fatty acid esters and as glycosides, but also in the free form (**Figure 8**).[23,25]

Polyterpenoids are abundant in higher plants, especially leaves but not in wood, with some exceptions. An example is special types of polyprenols (acyclic primary alcohol of polyisoprenoids), called "betulaprenols" and present in silver birch, built up of 6 to 9 isoprene units. Some trees produce rubber and gutta, where the DP of isoprene units is typically very high.[23,25]

Softwoods and hardwoods show clear difference in terpenes composition;[32] generally the former includes mainly mono- and sesquiterpenes, typical compounds in the wood of pine that give the characteristic pine aroma, but also diterpenes and sterols.

Hardwoods instead mainly contain sterols, triterpenoids, and higher-molar-mass terpenes (rubber, gutta, and betulaprenols).

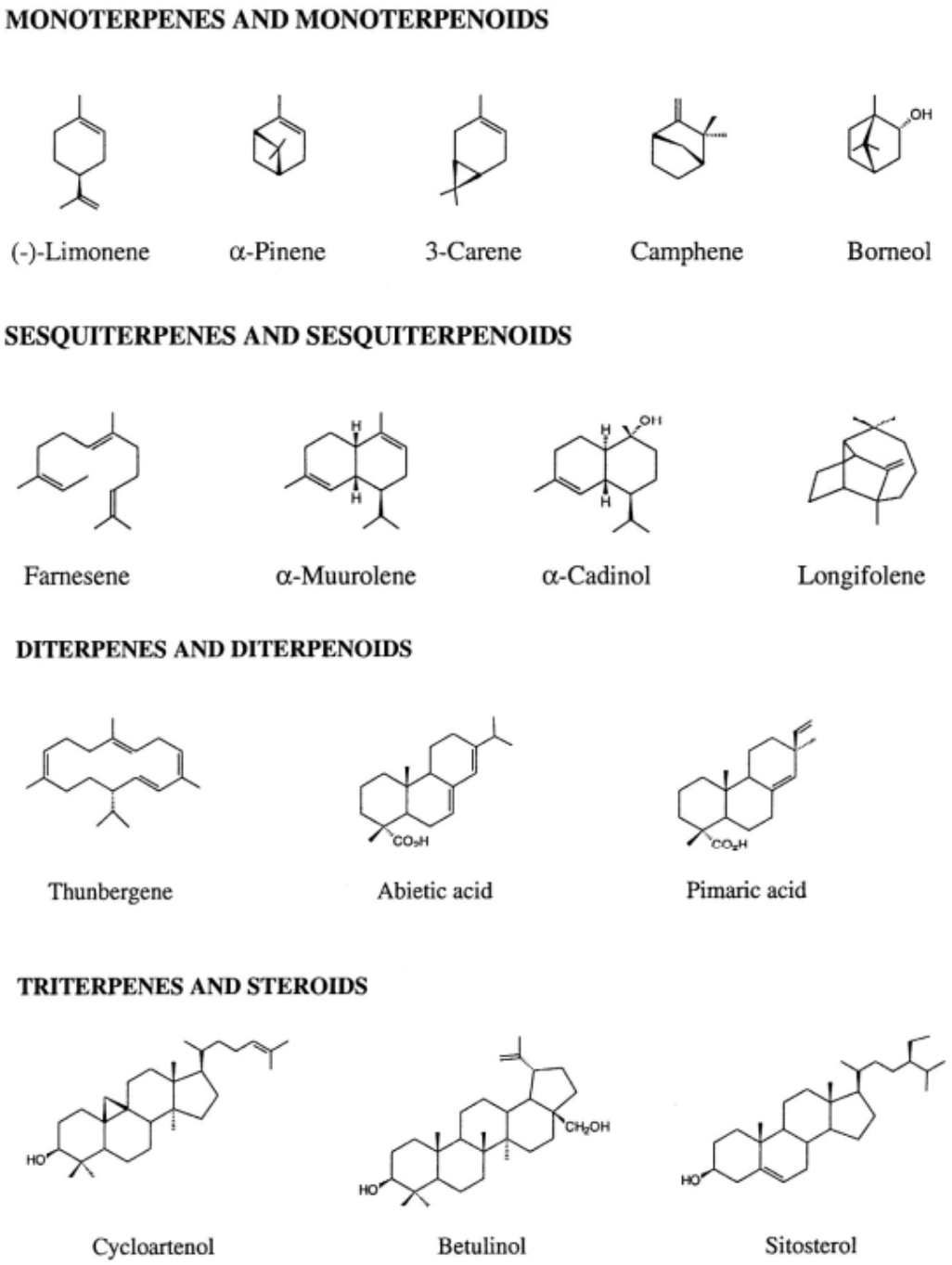

Figure 8. Chemical structure of some common terpenes and terpenoids.[23]

4.1 Diterpenes and diterpenoids: abietic acid

As already mentioned, the primary natural source of diterpenoids is the oleoresin contained in resin canals of different coniferous species, and especially abundant in pines. Because of being rich in oleoresin, pine trees have been utilized for the production of pitch and tar since ancient times.[36] They have been critical for waterproofing ships hulls and ropes, and made possible the era of giant sailing vessels.

Oleoresin is composed mainly of semi-volatile monoterpene hydrocarbons, non-volatile diterpenic monocarboxylic acids (resin acids), and small amounts of sesquiterpenoids and diterpernoids alcohol and aldehydes.[8] There are eight most common resin acids in conifer oleoresin, which share the same phenanthrene ring skeleton and the carboxylic group at the same position, as shown in **Figure 9**. However, they differ for the side groups at the third ring and the number and position of double bonds.[8]

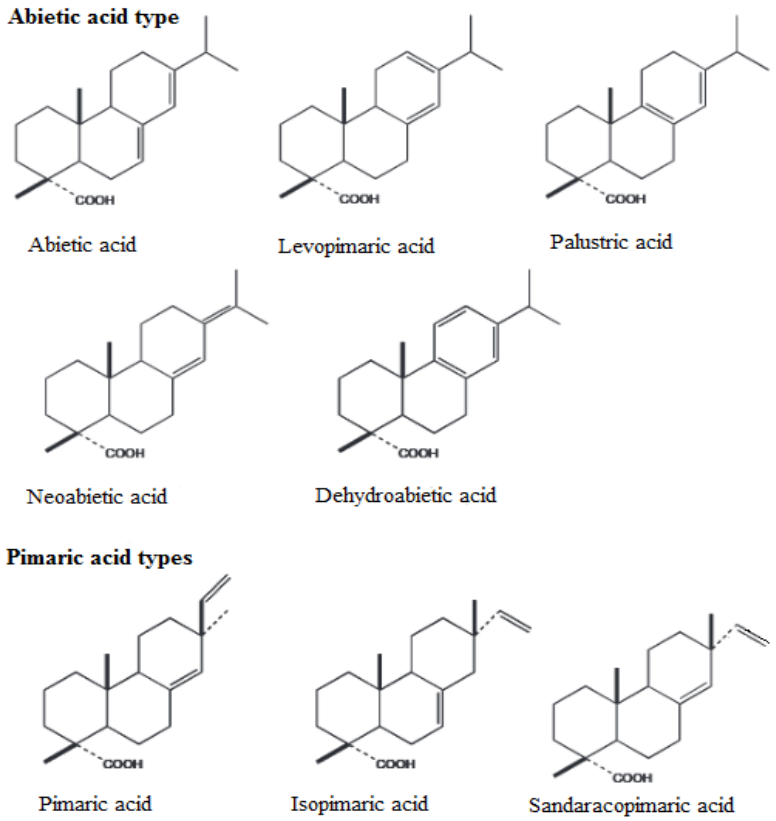

Figure 9. Structure of the most important resin acids found in pine and spruce.[32]

The most common resin acids found in pine rosin are derived from the three basic tricyclic carbon skeletons called “abietane”, “pimarane”, and “isopimarane”.[7] The

pimarane-type compounds have vinyl and methyl groups at the C-13 position, while abietane (**Figure 10**) has isopropyl or isopropenyl group at that position. The structure of abietane skeleton shows the presence of a conjugated double bond, which is an important feature in terms of chemical reactivity, while pimarane-type acids have different basic skeleton structure.[7] The overall reactivity of the resin acids is determined by the presence of both the double-bond system and carboxylic group. The carboxylic group is mainly involved in esterification, salt formation, decarboxylation, and nitrile and anhydrides formation, which are relevant for both abietic- and pimaric-type of acids. The olefinic system can be involved in oxidation, reduction, hydrogenation, and dehydrogenation, which are more likely for abietane compounds.[7]

Abietic acid $C_{20}H_{30}O_2$
ABI Abietic acid 85%
CAS# 514-10-3
Molecular mass: 302.451 g/mol

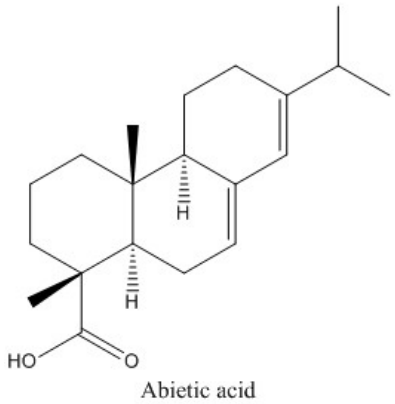

Figure 10. Chemical structure of abietic acid, one of the most common resin acids.[34]

Nowadays, diterpenoids are of great industrial importance, since resin acids are dominant constituents of rosin products and wood tars, obtained by destructive distillation (pyrolysis) of resinous wood.[8] Rosin is the common designation given to the solid residue originated from the distillation of the liquid resin exuded by many conifer trees. Regardless its origin, it is chiefly composed of resin acids, with a generic formula of $C_{19}H_{29}COOH$.[7] In fact, rosins can be obtain via extraction with solvent from pine stumps (wood rosin) or collection of fresh oleoresin exudates from standing trees (gum rosin), as well as from tall oil (TOR, tall oil rosin) obtained from crude tall oil (CTO).[8] CTO is a by-product of the Kraft pulping process used by many pulp mills and it is mainly a mixture of fatty and resin acids. The black liquor obtained from the pulping process is concentrated and then let to settle so that the top layer, known as tall oil soap, can be skimmed off. Sodium salts of fatty and resin acids are collected and then reacted with acid to yield CTO, which is refined into a number of commercially important products, like paper sizes, adhesives, and ink and paint ingredients.[25,32]

4.2 Triterpenes and triterpenoids: betulinol

The compounds belonging to the class of triterpenes are widely distributed in plants and this class comprises both triterpenoids and steroids.[25] They can be treated as part of the same group of compounds due to similarity in structure and biogenetics. Their biosynthesis starts from the same squalene precursor and proceeds towards different pathways originating slight differences in their structures.[25]

Triterpenoids are common in both softwoods and hardwoods, although generally in relatively small amounts. For both softwoods and hardwoods, the most abundant compound is sitosterol, but the wood of *Betula* species, especially birch, contains beside sitosterol, also lupane-type pentacyclic triterpenoids (lupeol, betulinol, and betulinic acid).[23] Both sitosterol and betulinol (**Figure 11**) are potential raw material for making wood-based chemicals.

Betulinol $C_{30}H_{50}O_2$
BET Betulin 98%
CAS# 473-98-3
Molecular mass: 442.717 g/mol

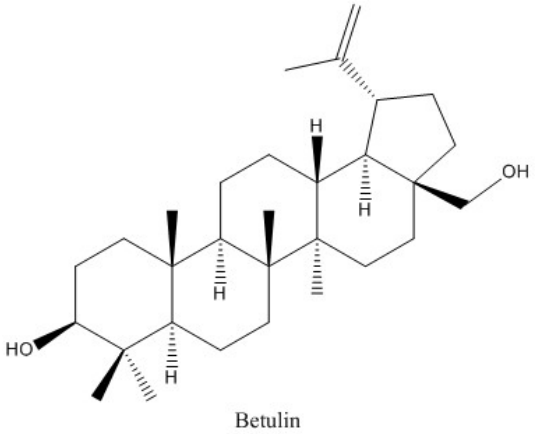

Figure 11. Chemical structure of betulinol.[34]

In Nordic countries and Eurasia, birch is the most abundant hardwood specie, with silver birch (*Betula pendula*) and downy birch (*Betula pubescens*) predominant ones. The bark of tree has two clearly distinguishable components: outer and inner bark. The outer bark of silver birch, accounting for only 3.4% of the wood log, is composed for about 40% of extractives. The rest is made up of 45% suberin, 9% lignin, 4% hemicelluloses, and 2% cellulose.[8] Among the extractives, betulinol is the largest component, accounting up to 30% of the birch outer bark and one of the first natural products isolated from plants. Betulinol can be naturally found as a chemically stable, white, and crystalline powder, which is the main reason for the white color of the birch bark.[8]

Extraction and utilization of betulinol have been investigated for many decades. Betulinol has been used for the production of cosmetic creams due to its unique property of stabilizing water-in-oil emulsion, thus enabling emulsifier-free creams. It has been stated that betulinol and some of its derivatives, like betulinic acid, have a wide range of beneficial properties, such as antibacterial, anti-mycotic, anti-itching, and anti-inflammatory properties as well as they are cytotoxic to some skin cancer cells.[8]

5 Biomass conversion routes

There is a considerable amount of documentation in literature[13,21,37-39] about the different technologies available for converting biomass feedstock into energy (heat and electricity), transportation fuel, and chemicals. The bulky and inconvenient form of biomass provides a major motivation for converting it into a form easier to handle and store.[38] This conversion can be achieved using many different routes, each of them with specific advantages and disadvantages. The main ones are considered to be physical, biochemical, and thermochemical conversion routes (**Figure 12**).[2,21,39-41] The actual selection of the conversion technology strongly depends upon the form in which the energy is required, so ultimately the type of products.[41]

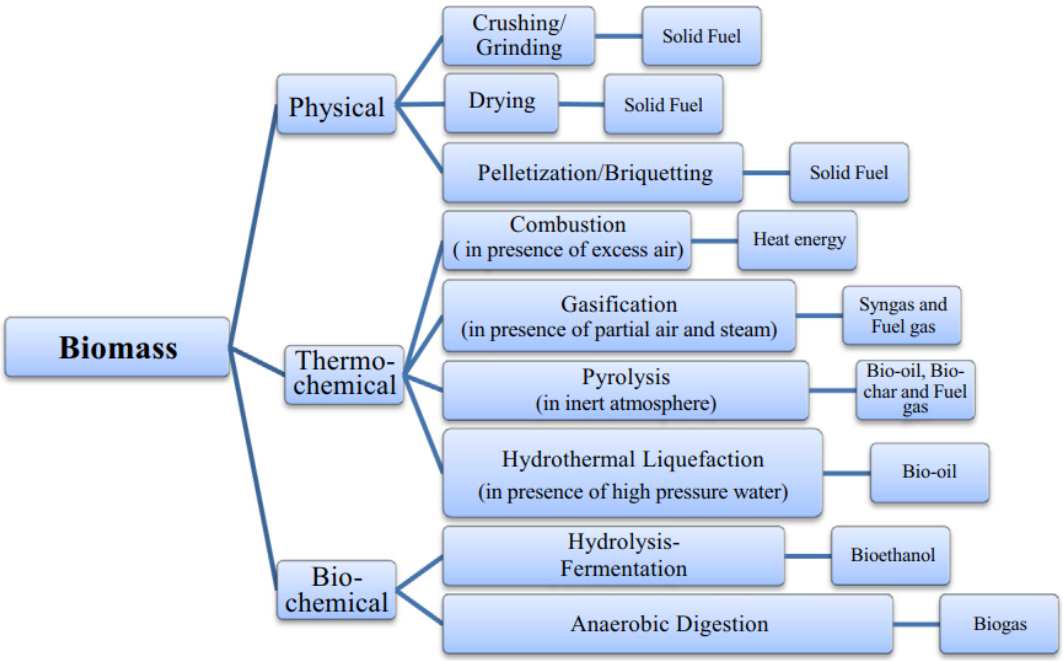

Figure 12. Biomass conversion pathways.[2]

Physical conversion of biomass uses densification techniques including crushing, heat, and pressure, mainly for the purpose of converting biomass into solid fuels.[2] On the other hand, biochemical process entails the utilization of enzymes or bacteria able to break down the main components of biomass into their smaller units. The most common and already established technologies are aerobic and anaerobic digestion for the production of compost and methane, respectively, fermentation to obtain mainly ethanol, and enzymatic or acid hydrolysis for pre-treatment of lignocellulosic materials.[21,37] The biochemical process is much slower than the thermochemical conversion but it does not require high external energy input. The main drawback is that

only cellulosic material can be treated conveniently while lignocellulosics, which are more resistant to biological treatments, require a pre-treatment with additional costs involved.[21]

During thermochemical conversion, the entire mass is converted by the means of heat into three main products:[39] solid, liquid, and gas. Thermochemical processing has several advantages over biochemical ones, such as the ability of producing a diversity of oxygenated and hydrocarbon compounds, shorter reaction times, lower cost of catalysts, and the possibility to easily recycle them. Furthermore, thermochemical conversion offers the advantage of rapid conversion of diverse feedstocks, including recalcitrant material, like lignocellulosic.

The four main thermochemical paths for conversion of biomass are:[2,21,42,43] direct combustion for heat, electricity, and power generation, pyrolysis and gasification for fuel and chemicals, and liquefaction for production of liquid oily fuel from wet substrates (**Table 7**). From the technical point of view, combustion involves high temperatures and excess air or oxygen condition. Similarly, gasification also requires high temperatures, but in an oxygen-deficient environment for maximizing gas production. Pyrolysis, on the other hand, takes place at a relatively low temperature in the total absence of oxygen. In liquefaction, the temperature is even lower and an essential requirement is the presence of a catalyst.[21,39,42]

Among these four thermochemical conversion processes, pyrolysis is estimated to be a well-established and promising method for biomass treatment due to its technical characteristic and variety of products.[40] Therefore, the following chapters will present on overview of the main features regarding biomass pyrolysis process.

Table 7. Comparison of the four major thermochemical conversion processes[21,42]

Process	Temperature (°C)	Pressure (MPa)	Catalyst	Drying
Combustion	700-1400	>0.1	Not required	Not essential, but may help
Pyrolysis	300-650	0.1-0.5	Not required	Necessary
Gasification	500-1300	>0.1	Not essential	Necessary
Liquefaction	250-330	5-20	Essential	Not required

6 Pyrolysis

6.1 Principles and products

Pyrolysis is defined as a thermochemical decomposition of biomass, either in total absence or limited supply of oxidizing agent that does not permit gasification.[21] In other words, it allows the conversion of a biomass sample through the agency of thermal energy alone. It is worth noting that pyrolysis is not only a thermal conversion technology by itself, but also the first stage of both combustion and gasification.[3,21,42] During pyrolytic process, long chains of carbon, hydrogen, and oxygen in the complex biomass macromolecules are broken down into smaller and simpler molecules, providing the three main products:[21] gas, condensable vapors (tars or oils), and char (solid residue) (**Figure 13**). The proportion of these three products can vary depending on pyrolysis process and conditions.

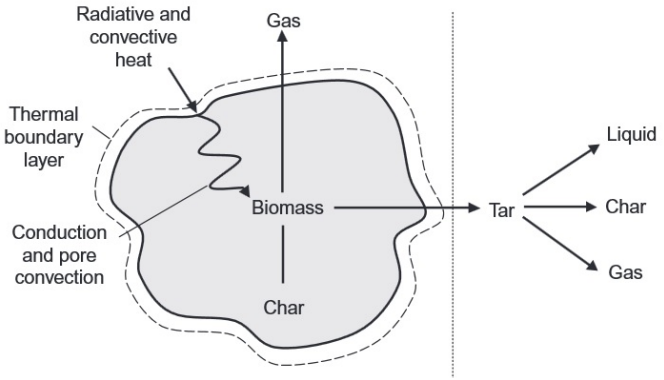

Figure 13. Three main products from pyrolysis of biomass.[44]

Because of the mentioned characteristics, pyrolysis results as a good option for studying biomass behavior, due to the fast heating mode and reaction rate (conversion within two seconds).[40] In conjunction to this, it is also relatively inexpensive, since it requires lower temperature than gasification and combustion, and no oxidizing agent.[2,21,42] Furthermore, it is an efficient conversion method compared to other thermo-chemical technologies and allows feedstock flexibility.[3,45] The main objective is obtaining products with better properties compared to the initial biomass.[3] This is why especially the production of liquid bio-oil from fast pyrolysis in the last decades has attracted large attention.

6.2 Pyrolysis mechanisms

Biomass pyrolysis is very complex process, involving both simultaneous and successive reactions that are taking place when the organic feedstock is heated in a non-reactive atmosphere.[3] Due to the large variability of biomass in structure and composition, pyrolysis processes show different reaction pathways. In fact, the main biomass components (carbohydrates and lignin) decompose through different mechanisms, at different rates of degradation, and different temperature ranges.[21,43]

Investigations on the decomposition path of single components show that hemicelluloses are the first to decompose, between 250-350°C, followed by cellulose at 300-400°C with levoglucosan as the main pyrolysis product (**Figure 14**).[13,43,46] The last compound to be degraded is lignin, which breaks down over a wide temperature range of 250-550°C, thus appearing the more thermally stable. Studying the thermal behavior of each single component is one approach for knowing more about pyrolytic behavior of biomass, but the interaction between these components during pyrolysis makes it difficult to predict biomass behavior simply based on the single element.[22,43]

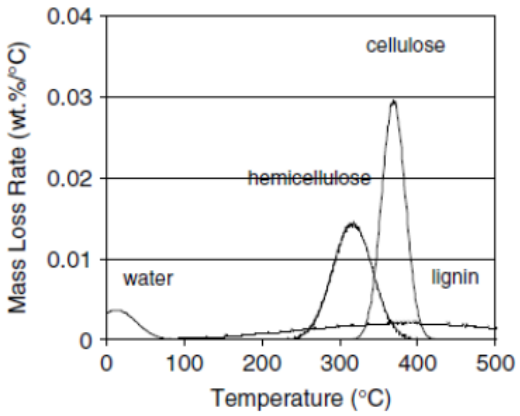

Figure 14. Decomposition rate of individual biomass components with pyrolysis temperature.[3]

From a thermal point of view, the changes happening inside each biomass particle during pyrolysis can be divided into different stages, which are not sharply defined but overlap one into each other.[21,43] In this contest, thermal analysis is a useful tool for observing the transition and behavior of biomass in different stages.

Firstly, a drying phase takes place at ~100°C, when free moisture and some loosely bound water is released, and heat transfer increases temperature.[21,46] Secondly, during an initial stage between 100-300°C, exothermic dehydration causes the release of water

and low-molar-mass gases, like CO and CO_2. Then follows a decomposition stage at temperatures >200°C, when primary pyrolysis reactions start to decompose the large biomass molecules into char (called "primary char"), condensable gases (precursors of bio-oil) and non-condensable gases. Finally, during the last stage between ~300-900°C condensable gases may break further by secondary cracking reactions into char (called "secondary char") and non-condensable gases, such as CO, CO_2, H_2, and CH_4. The condensable gases must be removed quickly from the reaction zone, in order to condensate them as tar or bio-oil. The overall decomposition happens partially in gas-phase homogeneous reactions and partly through gas-solid-phase heterogeneous thermal reactions, catalyzed by char.[21,46] **Figure 15** and **Figure 16** show possible reaction pathways for pyrolysis of biomass, considering both chemical and physical processes taking place inside a biomass particle.

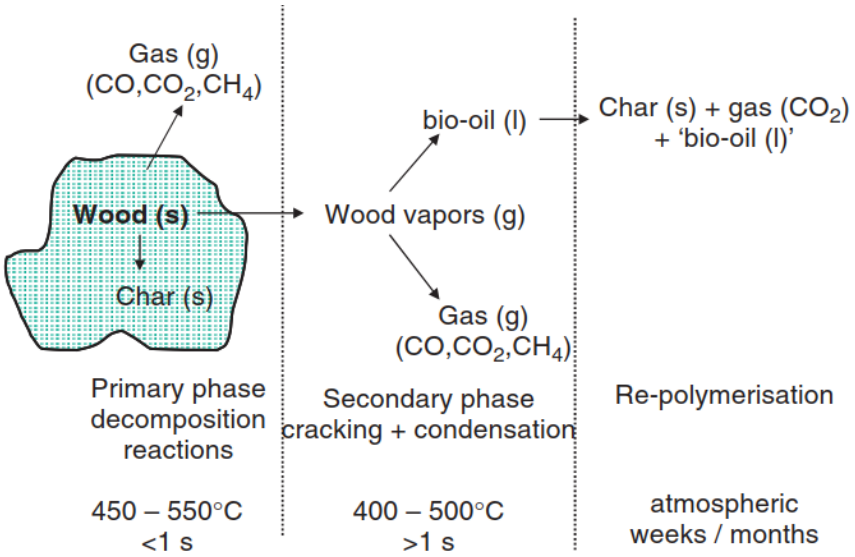

Figure 15. Representation of pathways for pyrolysis in wood substrate.[3,46,47]

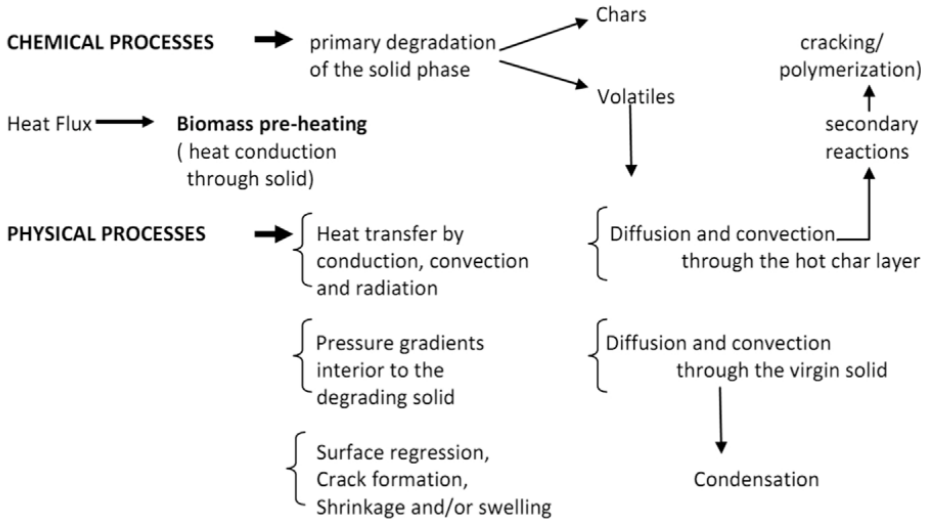

Figure 16. Chemical and physical processes inside a biomass particle during pyrolysis process.[2]

6.3 Parameters and their influence on products

The thermochemical conversion of biomass during pyrolysis is influenced by different factors, which ultimately affect the conversion time, as well as distribution and quality of the products. The most important parameters to consider are feedstock composition and its physical and chemical characteristics, the design of the pyrolytic unit, as well as operating parameters as temperature and pressure, heating rate, and vapor or solid residence time in the reaction zone.[2,3,21,43]

The **type of biomass** being pyrolyzed and its composition influences the process and products in several ways.[43] Cellulose, hemicelluloses, and lignin, together with extractives and inorganic compounds are present in different proportions depending on the biomass type, and their interactions differ from biomass to biomass, influencing consequently pyrolysis performance and product distribution.[2] Each component features unique pyrolysis reaction pathways and thermochemical characteristics, thus originating different products.[43]

In general, the main biomass components contribute to products yields in characteristic way;[2] volatiles derive mainly from cellulose and hemicelluloses, while lignin originates predominantly char residues. Extractives contribute to liquid and gas products either through simple volatilization or decomposition. In contrast minerals, especially, alkali metals, generally remain in the char with catalytic effects, which increases the char yield and degrades the oil quality. Moreover, pyrolysis process can be influenced by physico-chemical properties of the biomass, such as thermal conductivity and

emissivity, permeability and density, specific heat capacity and heat reaction, particle shrinking, and moisture content.[2] **Particle size** has a significant effect on heat and mass transfer phenomena, since larger particles imply larger thermal gradients, longer resident time, and possibility of secondary cracking, thus reducing liquid yields.[2] Particle shape and orientation can also influence biomass pyrolysis due to the biomass anisotropic behavior.

Temperature significantly influences distribution and properties of products. As it is possible to find out in **Figure 17**, liquid products increase with the pyrolysis temperature but only until a maximum value, usually between 400°C and 550°C, when bio-oil yield reach its peaks.[2,43] For temperature higher than 600°C gas is predominant, as bio-oils and char are converted into non-condensable gas due to secondary cracking reactions. Usually, the higher the temperature, the less is the char yield, due to higher stripping of volatile material from the char.[2,43]

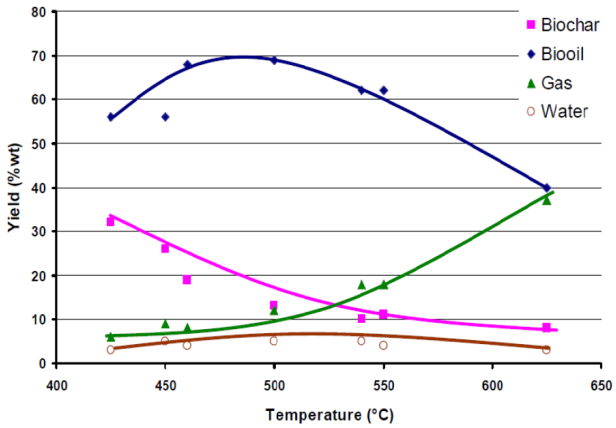

Figure 17. Relative distribution of pyrolysis end products over temperature range.[3]

Heating rate is the main parameter defining the type of pyrolysis method (slow, fast, and flash) and it also largely influences the products yield.[2,43] Fast heating rate means a quick fragmentation of biomass, thus more gas and less char. Rapid heating and cooling of primary vapor is required to enhance the bio-oil production and minimize secondary reactions, which have negative impact on liquid yields and quality. On the contrary, slow heating rates lead to more char production.[2,43]

Furthermore, **vapor residence time** can also influence the type of products, since it affects the contact time between char and vapors, thus ultimately affects the intensity of secondary reactions and the properties of volatiles.[2] For example, a quick removal of

vapors from reaction zone will minimize secondary reactions, thus increasing bio-oil yields.[43]

Another parameter to consider is the operating **pressure** at which the pyrolysis is performed, as it has been found that higher pressure leads to higher concentration of volatiles, thus increasing the decomposition rates through secondary reactions and higher char fraction.[2]

As can be seen above, operating conditions are possible to be adjusted in order to obtain the desired products and change the relative yields of gas, solid, and liquid. Given specific operating conditions, each process has its characteristic products and applications.[21]

When considering heating rate, temperature, and gas residence time (the most influential factors on the result products) general patterns can be individuated. For instance, charcoal production is generally maximized by slow heating rate, low final temperature (300-600°C), and long gas residence time.[21] Higher liquid yields, on the contrary, can be obtained by high heating rate, moderate final temperature (450-600°C), and short gas residence time as rapid cooling of the produced vapor, which allows condensing them into liquids.[21,47] Lastly, gas fraction can be maximized by slow heating rate, high final temperature (700-900°C) and long gas residence time.[21]

6.4 Methods

Considering the different operating parameters, and in particular, heating rate and residence time, pyrolysis processes can broadly be divided into three main categories:[43] slow (or conventional), fast, and flash pyrolysis. As seen above, the distribution of products is largely influenced by the operating parameters, which also define the type of pyrolysis being performed.[3] In slow pyrolysis and carbonation, carbonization is the primary process, which maximizes the production of charcoal, whereas in fast pyrolysis, bio-oil is the main product of interest.[47] **Table 8** summarizes the main pyrolysis methods, together with the information related to the most important parameters and products.

Table 8. Main pyrolysis methods, important parameters and products[3,21,38,43,45,48]

Pyrolysis method	Residence time	Temperature (°C)	Heating rate	Products
Carbonation	Days	~400	Very low	Charcoal
Slow	5-30 min	~500/600	Low, 0.1-1°C /s	Oil, gas, char
Fast	0.5-10 s	<650	High, 10-200°C/s	Bio-oil
Flash	<1 s	<650	High, > 1000°C/s	Bio-oil, chemicals, gas
Ultra-rapid	<0.5 s	~1000	Very high	Chemicals, gas

Normally pyrolysis is carried out in the absence of a medium, such as air or oxygen, but in an attempt to investigate further pyrolytic processes, other pyrolysis types have been performed.[21,45] Thus, further classification can be made depending on the atmosphere in which the pyrolysis takes place, such as hydro-pyrolysis in presence of water, methano-pyrolysis with methanol, and vacuum pyrolysis in vacuum conditions.[21,45]

Slow or conventional pyrolysis consists of slow heating rate of relatively large solid particle for long vapor residence times, usually at a temperature lower than fast pyrolysis.[2] The vapor residence time is so high that the components in the vapor phase continue to react with each other, resulting in increasing formation of solid char.[3] On the opposite, **fast pyrolysis** is a high temperatures process, characterized by rapid heating and short vapor residence times.[48] Feedstocks consisting of small particles are preferred and it is important to remove the vapors quickly to avoid further contact with the hot solid particles, which catalyzes secondary cracking reactions.[2,46] After cooling and vapor condensation, a liquid product is formed, with heating value which is about half of conventional fuel oil.[48] Fast pyrolysis technology is receiving great attention for producing liquid fuels, as well as a variety of commodity and specialty chemicals that have much higher added value than fuels.[38] It has relatively low investment cost and high-energy efficiency.[3] Carefully controlled parameters can yield 60-75% (on dry feed basis) liquid bio-oil, 15-25% solid char, and 10-20% non-condensable gases, depending on the feedstock.[48] Furthermore, **flash pyrolysis** can achieve up to 75% bio-oil yield, applying even higher temperature and shorter residence time then fast pyrolysis.[3,38] The major disadvantages of these technologies is the low quality and stability of the oil produced, which is affected by the presence of char, responsible for catalyzing repolymerization reactions inside the oil and increasing viscosity. As a result, upgrading processes of the bio-oil are usually needed.[38] These different types of pyrolysis

processes prove very clearly that any change in the operating conditions has a significant effect on the product yields of gas, tar, and char.[2,46]

6.5 Reactors

Different pyrolytic units have been developed for the purpose of thermal degradation in absence of oxygen. The reactor has a core role in the pyrolysis process and large research has been focused towards the improvement of the reactor unit.[3] The modern reactor configurations mainly include fixed bed, fluidized bed, heated kiln, and rotating cone pyrolyzers, already at commercial level, while ablative, screw feeder/auger, and vacuum pyrolyzers mainly at pilot or laboratory scale.[21,42,43,47]

The main reactor types for fast pyrolysis process are ablative systems, fluidized beds, and rotating cone systems.[3] Fluidized-bed reactors (FBRs) are well-known reactor also in the petrochemical industry, with a variety of applications. The feedstock particles and the hot send are fluidized by recirculation of the product gas. One very influential parameter when it comes to reactor selection is the medium of transfer of heat to the biomass particles inside the reactor. FBRs have very good temperature control, as well as heat and mass transfer, which allow a rapid heating of the feedstock particles.[2] This can lead to a production of 70-75% of bio-oils yield on biomass dry basis. However, one drawback of this technology is that the operating costs are usually high.[21,49] Rotating cone types of reactors, instead, are especially suitable for flash pyrolysis due to rapid heating rate and short residence time typical of this system. Compared to other technologies the operating costs are lower, due to lower need for carrier gas.[49]

For slow pyrolysis instead different types of technologies are used, such as fixed-bed reactors (batch or continuous), agitated drum, rotary kilns, vacuum, and screw pyrolyzers.[3] Among them, a fixed-bed reactor is the oldest pyrolyzer type. It is usually used for the production of char through slow pyrolysis, thus with long residence time and slow heating rate. In some cases, an inert gas is used for the removal of product gases form the reaction zone. This technology is simple but not very flexible to process changes.[49] In order to have an overview, **Table 9** compares different characteristics of the main modern reactor types.

Table 9. Characteristics of pyrolysis reactors[43]

Reactor type	Feed size requirement	Feed moisture	Bio-oil yield	Complexity	Status	Scale	Product quality
Bubbling fluidised bed	< 2 mm	< 10%	75%	Medium	Commercial	2–20 t/h	Water and high level of ash and charcoal particles in oils.
Circulating fluidised bed	< 6 mm	< 10%	75%	High	Commercial	2–20 t/h	Water and high level of ash and charcoal particles in oils.
Heated kiln	5–50 mm	< 10%	/	Low	Commercial	< 4000 kg/h	/
Rotating cone	< 0.2–6 mm	< 10%	70%	High	Commercial	200–2000 kg/h	Water, ash and charcoal particles in oils.
Ablative	< 20 mm	< 10%	75%	High	Laboratory	1–20 kg/h	Water and some ash and charcoal particles in oils.
Auger/screw feed	5–50 mm	< 10%	60%	Medium	Pilot	20–200 kg/h	Gas can contain particulates and tar, may be very acidic. High moisture content in gas and/or oil if feed is not dried before pyrolysis
Vacuum	5–50 mm	< 10%	60%	High		200–2000 kg/h	Hard

6.6 Utilization of pyrolysis oils for chemicals

Between the three main pyrolytic products, the production of liquid oils from biomass has drawn considerable attention due to different reasons. Firstly, pyrolysis oils have higher energy density and thus, they can reduce transport and handling costs. Furthermore, they can be used as substrate for conventional fuels in many applications, such as combustion engines, boilers, and turbines.[3,48] In addition to this, pyrolysis oils represent a great possibility as feedstock for production of value-added chemicals that can substitute petrochemical products.[13,46] On the other hand, the main drawback is their complex chemical and physical characteristics: their instability, high water content, corrosive property, the possible presence of oxygenated and aromatic compounds, as the case of bio-oil obtained from wood material.[46]

The chemical composition of pyrolysis oils is a combined result of biomass material properties, pyrolysis operation parameters, oil recovery, and storage conditions. Due to its complex nature, the exact analysis of this liquids results to be a difficult task. Even though value-added chemicals from bio-oils are interesting possibilities and technically possible, the recovery costs and their low concentration in the oil are the main reasons why it is still economically unattractive on a large scale.[46,50]

Despite the continuous improvements in technologies, bio-products economic feasibility still cannot compete with petrochemicals.[19] The biomass products should be at low cost and perform as well as petroleum-counterparts for being economically attractive. The starting point could be increasing the production of large-volume chemicals, which have high demand. Lubricants, surfactants, monomers for plastics and fibers, and industrial

solvents from biomass can have the potential to satisfy large portion of the market and impact positively the sustainability of biochemicals production.[19] Current exploitation of pyrolysis oils for chemicals includes the recovery of phenolic compounds from lignin fraction, resins, sugars, hydroxyacetaldehyde, and furfural derivatives.[46] Nevertheless, improving the understanding of the chemistry behind pyrolysis process and products characteristics is a primary need.[46]

7 Analytical pyrolysis

Many organic substances found in Nature, due to their complex and varying polymeric structure, are unsuitable for direct analysis. In order to investigate them, different chemical and physical degradative techniques have been used, pyrolysis being one of them.[51,52] Analytical pyrolysis is a simple, rapid, and reliable analytical technique, especially for the analysis of polymeric and composite organic materials. The samples are usually not volatile and have low solubility in most solvents, thus not suitable for direct analytical determinations.[52]

Analytical pyrolysis is defined as "the technique of studying molecules either by observing their behavior during pyrolysis or by studying the resulting molecular fragments".[53] It is a small-scale analytical technique, where the sample is pyrolyzed by rapid application of heat in an inert atmosphere. Pyrolysis itself does not produce any analytical data unless associated analytical instruments. This is why analytical devices for separation and quantification of the volatile fragments are usually connected the pyrolyzing unit.[51,52]

The analytical pyrolytic unit has a fundamental requirement; reproducibility.[51] This means that the same product profiles should be obtained from replicate analysis. As could be seen from the general pyrolysis process, in order to obtain reproducible results, different operating parameters must be accurately controlled.

The reactions responsible for breaking biomass compounds bonds are strongly dependent on temperature, which consequently influences the final product distribution.[51] This is why precisely controlled temperatures must be used.[51] For the purpose of analytical pyrolysis, temperatures in the range of 600-800°C are preferred because when the pyrolysis temperature increases, the pyrogram is influenced by smaller and less characteristic fragments.[51] A second important parameter is the temperature time profile, which allows the sample to be heated in a controlled and reproducible manner. In this way, the sample will be decomposed over the same temperature range, hence major control of pyrolytic behavior.[51] The temperature rise time is also crucial, as the heating rate should be rapid compared to the degradation rate of the sample for preventing degradation to be already over before reaching the actual pyrolysis temperature. Ultimately, rapid cooling rate will ensure that the products

escape quickly from the pyrolysis zone and can be transmitted entirely to proper analytical device coupled with the pyrolytic unit.[51]

When temperature, heating rate, and time can be reproduced and controlled in a consistent way, the original macromolecule will always break down according to characteristic fragmentation pattern.[53] Similar fragments obtained in the same conditions will then give information about the nature, arrangement, and identity of the original sample as a fingerprint.[53]

A diversity of analytical approaches is required to understand the complex composition of biomass and its degradation products.[54] In order to do that, different analytical techniques have been applied to study biomass thermochemical behavior. These techniques include physical and elemental analyses, as well as thermo-analytical techniques, like thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). Furthermore, chromatographic analytical technique as gas chromatography (GC) can be used for analysis of gas products and high-performance liquid chromatography (HPLC) for liquid ones. Together with these chromatographic methods, mass spectrometric techniques, but also infrared (IR), Raman, near-infrared (NIR) spectroscopic techniques, as well as nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and microscopic techniques (light microscopy (LM) and scanning electron microscopy (SEM)) are frequently used for the analysis of biomass fragmentation products.[55]

7.1 Pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS)

Analytical pyrolysis has a long history in characterizing complex samples in fields ranging from forensic science to geochemistry, archeology, and art.[53] The coupling of the pyrolytic unit with appropriate analytical devices is fundamental for obtaining comprehensive qualitative and quantitative results. It follows that combining pyrolysis with modern analytical techniques, such as high-resolution capillary GC and mass spectrometry (MS), originates a powerful tool for the investigation of complex organic materials.[56]

An optimal analytical pyrolysis device should produce degradation products that are representative of the sample, reproducible, and capable of successful separation and elution in the gas chromatograph for further detection.[53,56] Despite some limitations, Py-

GC/MS permits the study of a wider range of molecules compared to the ones that can be detected by simple GC/MS, especially in the case of intractable, non-volatile, and high boiling point components.[57] In fact, Py-GC/MS allows direct analysis of the original natural material, since the pyrolytic unit is able to produce volatile fragments, which can then be analyzed using GC/MS.[58] Therefore, Py-GC/MS is a useful method for the qualification of pyrolysis products and it has a great potential for studying the decomposition pathways of various biomass types and their components.[59]

The Py-GC/MS unit (**Figure 18**) consists in a pyrolyzing system that makes possible thermal degradation of the sample by rapid application of heat. An inert gas stream, usually helium (He), sweeps the volatile products into the gas chromatographic column, where oven temperature programing separates them. Lastly, a spectrometric detector allows identification with the aid of a mass spectral library, for the qualitative assessment of the fragments.

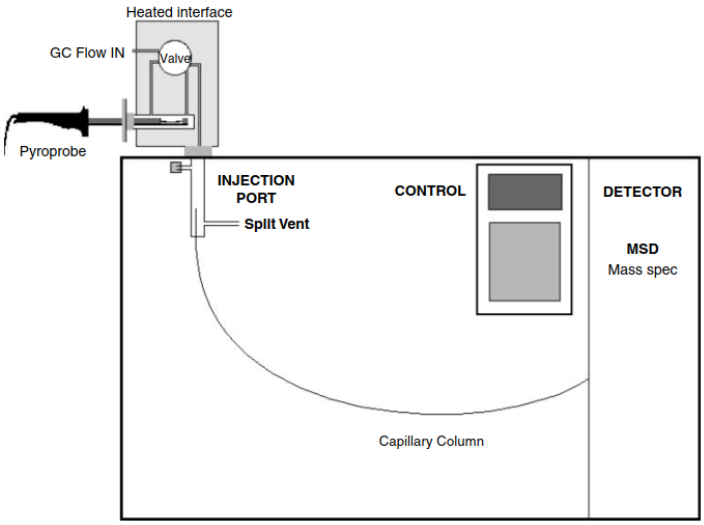

Figure 18. Pyrolysis-gas chromatography/mass spectrometry unit.[50]

The three commercial and most common pyrolyzing instruments for analyzing solid and non-volatile liquids are isothermal furnace, Curie-point (inductively heated) filaments, and resistively heated filaments pyrolyzers, each having their own specific design advantages.[53,56] In resistively heated filament pyrolyzer very fast heating rates are achieved by a controlled current passing through a small filament. This means that the mass of the sample analyzed should be quite small, usually in the range of micrograms, in order to be compatible with the filament and successively with the chromatographic column capacity.[53] The heated-filament is contained in a pyroprobe design, which

allows precise control of temperature, time, and heating rate. The pyroprobe is placed into a heating chamber, generally connected to the injection port of the analytical device, with the column gas carrier flowing through it, as shown in **Figure 18**.[53]

In order to exploit the rapid heating capability of the pyrolyzer and obtain efficient heat transfer to the sample, this must be in intimate contact with the heater.[51] When the sample to be analyzed is in the form of fibers or fine powder, a small quartz tube is generally used. The sample is weighed and held in position with wool plugs inside the quartz tube, which is then inserted into the coil filament for pyrolysis, and consequent analysis. To ensure reproducibility of the results, sample handling is very important. Sample size should be small (lower than 1 mg) and homogeneous, thus representative of the all material.[53]

7.2 Thermal decomposition behavior

In order to achieve a better understanding of biomass pyrolysis mechanisms, intensive studies on pyrolytic behavior of its main components are required and have been pursued. Investigations by the means of Py-GC/MS on carbohydrates and lignin have been largely reported in literature.[22,40,59] In addition to that, the influence of the other biomass constituents, as inorganic ions and extractives, should also be considered when studying the thermal decomposition behavior of biomass material.[60] Different qualitative and quantitative studies have been performed on various types of biomass samples, which have allowed identification and quantification of the large variety of compounds comprised in the extractive class.[60-62] Since wood contains a large range of substances classified as extractives, studies usually focus on the analysis of a single compound group. However, studies on analytical pyrolysis of terpenoids have been difficult to find. This is why the present work aims at exploring terpenoids pyrolytic behavior and could be an interesting starting point for future investigations.

A molecular compound undergoes pyrolysis through one or more pyrolytic reactions, which can happen simultaneously or sequentially. Many chemical reactions are taking place during pyrolysis, most of them based on free radicals.[14] The pyrolysis products are consequently influenced by the structure of the initial molecule, together with experimental conditions.[52] Considering the precursor molecule, the products that will be originated depend on chemical bonds and functional groups present in the compound, as

well as on the stability of the resulting fragments.[53] The most common mechanisms taking place during pyrolysis include elimination and fragmentation reactions, rearrangements, and other types of reactions, such as oxidation, reduction, substitution, and addition.[45,52]

Previous investigation on resin acids under high-temperature pyrolytic conditions (800°C) found out naphthalene derivatives as major products.[63] Levopimaric acid, abietic acid, dehydroabietic acid, and methyl dehydroabietate were the main four compounds studied, which gave the same general spectrum of products, the major ones being toluene, styrene, indene, naphthalene, 2-vinylnaphtalene, acenaphthylene, phenanthrene, fluorine, and 2-phenylnaphtalene. It was assumed that the high yield of naphthalene products during pyrolysis of resin acids must arise from cleavage in the A-ring of the parent molecule before complete aromatization. This cleavage is likely to be facilitated by the ease at which the resin acids undergo decarboxylation.[45,63] Beside fragmentation and carboxylation reactions, dehydrogenation is another important reaction taking place in resin acids.[52]

7.3 Conclusions

Our world is very close to face both economic and environmental crisis, due to depletion of fossil resources and the climate effects of GHGs.[14] To address these issues, it is fundamental to develop new technologies based on the utilization of renewable resources, as biomass.

Lignocellulosic biomasses have been considered by various researchers as a promising resource to count on for future development due to the number of positive advantages. In order to best implement these resources, their structure and chemical composition should be studied in details. Therefore, the chemical characteristics of wood material have been presented at the beginning of this work. Within wood extractives, the attention was focused on di- and triterpenoids since they are an interesting substrate, currently available in by-products and wastes of already commercially established processes. Diterpenoid resin acids, as abietic acid, are largely found as by-products of Kraft pulping process, while triterpenoids, as betulinol, are highly concentrated in hardwood bark, which is usually a waste product since wood logs are debarked prior to

pulping and paper production. Their valorization could bring higher value to already existing processes.

Biomass pyrolysis is a promising technology, which has the potential to form part of the solution to the energy and environmental crisis.[14] A wiser way to implement pyrolysis of biomass and use the particularly valuable liquid fraction is the production of higher value-added products, like chemicals. To explore the feasibility of this, analytical pyrolysis represents a very useful tool. The analytical procedures and the results obtained from the Py-GC/MS experiments performed on the terpenoid model compounds are described in the following part of this work.

8 Experimental

8.1 Materials

The samples utilized were model compounds of abietic acid and betulinol, representing, respectively, the subclass of tricyclic diterpenoids and tetracyclic triterpenoids (**Table 10**). Both materials were obtained from the inventory of the Department of Chemistry at the University of Jyväskylä, specifically from the Laboratory of Applied Chemistry. Abietic acid was originally produced by ACROS organics (USA) while betulinol was extracted from birch (*Betula pendula*) bark by methanol.

Table 10. Information on model compounds utilized

Chemical substance	Grade (%)	Used as
Abietic acid **CAS# 514-10-3** 302.451 g/mol	85%	Model compound
Betulinol **CAS# 473-98-3** 442.717 g/mol	~95%	Model compound

Betulinol existed in a white, solid, homogeneous, and microcrystalline form, while abietic acid occurred as yellow, resinous chunk particles, which needed to be extensively milled. To achieve that, abietic acid was manually grinded in a mortar with a pestle, until it reached the state of a fine, homogeneous powder. This form was more suitable for pyrolysis since it minimized problems of mass and heat transfer and reduced temperature gradients within the sample.[64]

Sample amounts of ≈ 0.2 mg of abietic acid and betulinol were accurately weighed in a μg precision scale with a Mettler MT5 balance and properly placed in open ended quartz tubes between two wool plugs in order to hold the sample in place as shown in **Figure 19**. Sample handling and precision of the quartz tube placement with respect to the pyrolyzer heated filament coil proved to be a crucial task regarding the response and repeatability of the resulting chromatogram.

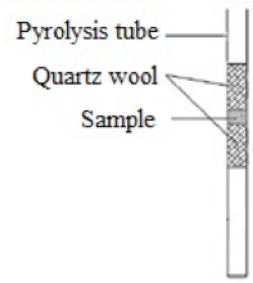

Figure 19. Sample preparation for Py-GC/MS.[50]

8.2 Py-GC/MS

The characterization of pyrolysis fragment products obtained from model compounds could be pursued by Py-GC/MS. Fast pyrolysis experiments were carried out with a CDS Pyroprobe 1000 (Chemical Data System, USA), equipped with a resistively heated platinum filament coil, which held the quartz tubes with the sample. Once the quartz tube was added to the pyroprobe, this was then inserted into the pyrolysis chamber interface having a temperature of 280°C and pyrolysis was performed after an equilibrium period of 30 seconds.

The products of pyrolysis were separated by interfacing the pyrolyzer to a GC system (HP 5890 II), provided with a thin capillary column (INFERNO ZB-35HT, 30 m length × 0.25 mm diameter × 0.25 μm film thickness), and the temperature of the GC inlet system, connecting the pyrolyzer to the GC, was 280°C. The GC oven temperature program was elaborated on the basis of previous works done with similar compounds.[45] The initial oven temperature was kept constant at 40°C for the first 5 minutes, then it was increased at different rates until finally reaching a temperature of 320°C, which was kept stable for other 10 minutes to clean the column. The same oven program was used for both samples in order to be able to compare the products' retention times.

Qualitative detection was performed by coupling GC with a quadrupole mass selective detector (HP 5973), operating in electron impact ionization (EI) mode, with an electron energy of 70 eV and a scanning mass range of 50-500 *m/z*. The inert gas used in the pyrolysis interface atmosphere and as carrier gas in the column was helium (He), injected into the system and kept at a flow of 1 mL/min during the GC analysis. Injection mode was split-less.

Trial analyses were carried out at different pyrolysis time, varying between 5 and 20 seconds and different temperatures, ranging from 400 to 700°C, according to literature examples on analytical pyrolysis studies of lignocellulosic material[57,64-68], with a pyrolysis heating-up time of 20°C/ms. The temperatures of 500, 600, and 700°C and the two pyrolysis times of 5 and 20 seconds were considered to be the most relevant ones for obtaining indicative differences in the formation of products. However, it had to be remembered that a difference existed between the actual temperature of the sample and the temperature specified by the equipment manufacturer, usually due to poor thermal conductivity of lignocellulosic material.[64,66] **Table 11** summarizes all the parameters utilized in the Py-GC/MS experiments of abietic acid and betulinol.

Table 11. Experimental parameters of Py-GC/MS analysis

Experimental Py-GC/MS parameters	
Pyrolysis	
Heating rate [°C/ms]	20
Py-GC-interface temperature [°C]	280
Pyrolysis temperature [°C]	500, 600, 700
Pyrolysis time [s]	5, 20
GC	
Column	ZB-35HT
Length [m]	30
Inner diameter [mm]	0.25
Film thickness [μm]	0.25
Carrier gas, He [mL/min]	1
GC-over temperature program	40°C (5min) →5°C/min→125°C/min →3°C/min→285°C/min →5°C/min →320°C (10min)
MS	
Detector temperature MSD [°C]	280
Injector [°C]	280

8.3 Data handling

The peaks in the pyrolysis-chromatograms (pyrograms) obtained were integrated and the mass spectra were interpreted with Agilent Data Analysis software. The interpretation of the peaks was made by matching each peak with the compound listed in spectral libraries provided by the software (W8N05ST and Wiley 138n). For a proper and accurate interpretation of the results, online database (NIST Chemistry WebBook) and literature references were also consulted.[45,63,69,70] Only quality matches above 85% were reported, but in very few cases, also lower quality matches were considered (the lowest was 70%), when the degradation fragments seemed more appropriate.

The nature of this work was primarily qualitative; in fact Py-GC/MS analysis did not provide quantitative information without a proper calibration with internal standards. Nevertheless, it has been assumed in previous analytical studies of this type that the chromatographic peak area of a compound can be considered linear with its quantity and similarly, the peak area percentage linear to its content.[65-67] It follows that even without absolute quantitation is possible to observe changes in the relative content of products by comparing the peak area percentage of each detected compound under different reaction conditions.[65-67]

Under this light, after the identification of products, they were classified according to their chemical structures and the relative yield of each compound group was represented graphically with stacked columns (**Figure 23** and **Figure 27**) in the results and discussion section. The calculations were based on the peak area percentage obtained after integration of each detected compound and reported in the library search report provided by Agilent Data Analysis software.

9 Results and discussion

The main objective of the analysis was to investigate under varying pyrolytic conditions the product profiles and the characteristic fragmentations of the model compounds studied, as well as the influence of specific variables (pyrolysis temperature and time) on pyrolysis products.

The pyrolysis experiments indicated that the fragments obtained from abietic acid and betulinol, under the chosen conditions, were mainly aromatics in nature, especially at the higher temperatures. As a common feature, the beginning of each run showed generally a significant amount of lighter and volatile compounds, primarily alkanes and alkenes, but also other volatile compounds, which could not be accurately identified due to a poor chromatographic resolution. One reason for this was the nature of the GC oven program applied; the temperature was kept constant at 40°C for the first 5 minutes, leading to the most volatile products to be eluted together in a narrow window of time. In case of betulinol, it was possible to identify among them isoprene, the basic unit of a terpene structure. The identified products were grouped into five categories mainly based on their aromaticity (presence or absence), and according to the number of rings within the aromatic structure, labeled in the following way:

X = alkanes/alkenes and cycloalkanes/cycloalkenes
I = indane/indene and their derivatives
A1 = aromatics with one benzene ring, benzene and its derivatives
A2 = aromatics with two benzene rings, naphthalene and its derivatives
A3 = aromatics with three benzene rings, phenanthrene/anthracene and their derivatives.

The pyrograms of abietic acid and betulinol at 700, 600 and 500°C are reported in **Appendix A** and **Appendix B**, respectively**.** All the pyrolytic products identified under each condition were listed and grouped according to the above-mentioned labels (**Table 12, Table 13,** and **Table 14,** and **Table 16, Table 17,** and **Table 18).** The compounds were associated with the respective retention time (RT) in minutes, as well as the characteristic mass to charge ratio (*m/z*), with the underlined number corresponding to the base peak. Finally, the peak area percentages of each compound identified, for pyrolysis times of 20 and 5 seconds, were separately reported on the right columns.

Some problems were encountered due to accumulation of deposits on the equipment lines and on the inlet system connecting the pyrolyzer to the GC, especially at 500°C and during trial analyses at lower temperatures. This complication was probably related to the nature of the sample treated.[71] For this reason, cleaning runs were performed after every pyrolysis experiment, in order to avoid dirt deposition and base line raise, which can be seen in **Figure 20**.

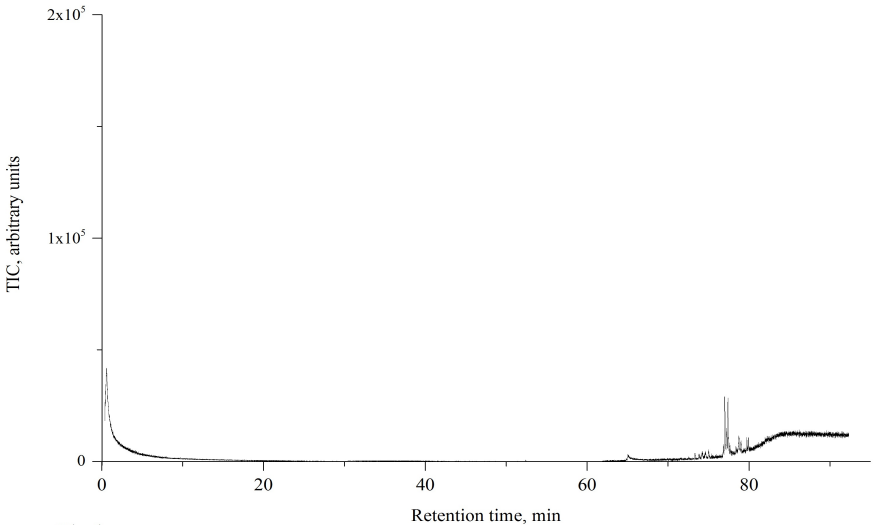

Figure 20. Effect of residuals and dirt on a blank Py-GC/MS run.

9.1 Abietic acid

9.1.1 Treatment at 700°C

Pyrolysis of abietic acid at 700°C yielded primarily aromatics, having one to three benzene rings (**Table 12**). The products eluted at the beginning of the run, within the first five minutes, could not be accurately identified due to the low resolution of these low-molar-mass compounds. However, a low amount of short aliphatic hydrocarbons could be detected, especially at a pyrolysis time of five seconds. Some phenolic compounds were also formed in a lesser amount, which was why they were grouped together with benzene derivatives and not in a separate category. The dominant products were benzene, xylene, and toluene, as well as methyl-, dimethyl-, and trimethyl-substituted naphthalenes. After carefully studying the mass spectra, at RTs of 14.86 and 18.15 minutes, two different compounds were suggested for the same peak since it seemed that the two reported compounds were both present. Being both benzene derivatives, the peak area percentage was included in the aromatic group with one benzene ring.

Table 12. Identified pyrolysis products of abietic acid at 700°C (for X, I, A1, A2, and A3, see Chapter 8)

Type	RT (min)	Compounds	m/z	20s	5s
X	5.27	1,3,5-Hexatriene, 3-methyl	94/79/65	0.33	0.59
X	7.02	1,3-Hexadiene, 2,5-dimethyl	110/95/77/67	-	2.60
X	9.00	1,3-Cyclohexadiene, 1,4-dimethyl	108/93/77	-	0.74
			total	**0.33**	**3.93**
I	16.91	1*H*-Indene, 2,3-dihydro	117/103/91	0.45	0.32
I	21.01	1*H*-Indene, 1-methyl	130/115/102	1.23	1.15
I	21.32	1*H*-Indene, 2-methyl	130/115/102	1.74	1.45
I	24.18	1*H*-Indene, 1,3-dimethyl	144/129/115/102	0.66	0.72
I	24.46	1*H*-Indene, 4,7-dimethyl	144/129/115	0.77	0.79
I	26.25	1*H*-Indene, 2,3-dihydro-1,1,3-trimethyl	160/145/128/115	0.20	0.25
			total	**5.05**	**4.68**
A1	3.90	Benzene	78/51	3.53	2.28
A1	6.49	Benzene, methyl (toluene)	91/65	5.65	3.68
A1	9.88	Benzene, 1,2-dimethyl (*o*-xylene)	106/91/77	1.27	-
A1	10.19	Benzene, 1,3-dimethyl (*m*-xylene)	106/91/77	2.85	2.94
A1	11.24	Benzene, 1,4-dimethyl (*p*-xylene)	106/91/77	1.06	1.03
A1	11.64	Benzene, ethenyl (styrene)	104/78/51	1.06	1.00
A1	12.09	Benzene, (1-methylethyl)	120/105/91/77	0.34	0.51
A1	13.19	Benzene, propyl	120/105/91/78	0.13	0.31
A1	13.57	Benzene, 1-ethyl-3-methyl	120/105/91/77	1.04	0.97
A1	14.36	Benzene, 1-ethyl-2-methyl	120/105/91/77	0.51	0.52
A1	14.86	Benzene, (1-methylethenyl)	118/103/91	0.85	0.91

		Benzene, 1,2,4-trimethyl	120/105/91/77		
A1	15.34	Benzene, 1-ethenyl-2-methyl	117/103/91	0.99	0.71
A1	15.49	Benzene, 1-methyl-4-(1-metylethyl)	134/119/105/91	0.82	0.97
A1	16.07	Benzene, 1,3,5-trimethyl	120/105/91/77	0.58	0.70
A1	17.56	Benzene, 1-ethyl-3,5-dimethyl	134/119/105/91	0.09	-
A1	17.72	Benzene, propynyl	115/89/63	1.23	0.88
A1	18.15	Benzene, 1-methyl-4-(1-methylethenyl)	132/117/105/91	0.58	0.55
		Benzene, 1-ethyl-4-(1-methylethyl)	148/133/119/105		
A1	19.08	Phenol, 4-methyl	107/90/77	0.49	0.50
A1	19.60	Benzene, 1,3-dimethyl-5-(1-methylethyl)	148/133/115/105	-	0.27
A1	19.89	Benzene, 1-methyl-2-(1-methyl-2-propenyl)	146/131/115/91	0.53	1.10
A1	20.11	Phenol, 2,6-dimethyl		0.21	0.28
A1	20.23	Benzene, 1-methyl-4-(2-propenyl)	132/117/105/91	0.25	0.25
A1	20.66	Benzene, 2-ethenyl-1,4-dimethyl	132/117/105/91	0.40	0.51
A1	23.77	Phenol, 4-(1-methylehtyl)	136/121/103/91	0.66	0.71
			total	**25.12**	**21.58**
A2	22.88	Naphthalene	128/102	1.20	0.79
A2	25.30	Naphthalene, 1,2-dihydro-6-methyl	144/129/115	0.86	0.90
A2	26.41	Naphthalene, 1-methyl	142/115/89	1.39	1.07
A2	27.17	Naphthalene, 2-methyl	142/115/89	1.36	0.86
A2	29.07	Naphthalene, 1,2,3,4-tetrahydro-2,2-dimethyl-1-methylene	172/157/142/129/115	0.69	0.75
A2	29.68	Naphthalene, 2-ethyl	156/141/128/115	0.98	0.48
A2	30.11	Naphthalene, 1,7-dimethyl	156/141/128/115	0.81	0.69
A2	30.67	Naphthalene, 2,7-dimethyl	156/141/128/115	0.24	0.21
A2	30.94	Naphthalene, 2,6-dimethyl	156/141/128/115	0.99	0.79
A2	31.58	Naphthalene, 2-methylethyl	170/155/141/128	1.48	1.00
A2	31.86	Naphthalene, 1,6-dimethyl	156/141/128/115	0.26	0.22
A2	33.05	Acenaphthylene	152/76	0.38	-
A2	33.48	Naphthalene, 1,4,6-trimethyl	170/155/141/128	0.62	0.49
A2	34.31	Naphthalene, 1,4,5-trimethyl	170/155/141/128	0.79	0.50
A2	34.61	Naphthalene, 2-(1-methylethenyl)	168/153/141/128	0.70	0.47
A2	36.18	Naphthalene, 1-methyl-7-(1-methylethyl)	184/169/154/141	1.60	1.52
A2	39.30	1-1'-Biphenyl, 4-4'-dimethyl	182/167/152	0.36	0.27
A2	40.32	Naphthalene, 1,6-dimethyl-4-(1-methylethyl)	198/183	0.39	0.18
A2	42.99	Biphenyl, 4-isopropyl	196/181/165/152	0.52	0.28
			total	**15.62**	**11.47**
A3	45.91	Phenanthrene	178/152	0.28	0.17
A3	49.69	Phenanthrene, 2,3,4,4a,9,10-hexahydro-1,4a-dimethyl-7-(1-methylethyl) (19-norabieta-4,8,11,1)	254/239	-	0.27
A3	50.73	Phenanthrene, 2-methyl	192/165/94	0.33	0.26
A3	54.10	Phenanthrene, 7-isopropyl-1-methyl-1,2,3,4-tetrahydro (10,18-bisnorabieta-5,7,9(10),11,13-pentaene)	238/223/206/195	0.58	0.59

A3	58.80	Phenanthrene, 1-methyl-7-(1-methylethyl)	234/219/204/189	0.37	0.34
			total	**1.56**	**1.63**

The total amount of identified compounds was quite low, 48% of the total peak areas for the pyrolysis time of 20 seconds and 44% for five seconds. Based on the interpretation of the MS spectra, it could be assumed that the large majority of those unidentified compounds consisted of a wide range of mono- and polyaromatic hydrocarbon derivatives, in accordance with previous studies on resin acids.[45,63,69,70] In fact, besides benzene, the main products of abietic acid were naphthalene derivatives, which were assumed to be primarily originated from the decomposition of the parent resin acid molecule before aromatization.[63] The main reactions taking place were fragmentation and decarboxylation and it was hypothesized that dehydrogenation also played an important role for the stability of the phenanthrene ring structure.[69,70] This was probably the reason why it was also possible to observe phenanthrene types of compounds among the pyrolysis products of abietic acid.

9.1.2 Treatment at 600°C

Analytical pyrolysis of abietic acid at 600°C resulted in very similar types of products compared to the previous ones at 700°C (**Table 13**). Even at this temperature, the dominating products were aromatics, with a significant variation in the yields of benzene and its derivatives, and it was higher at the shortest pyrolysis time. Again at RTs 14.83 and 18.12 min two compounds were present. The amount of total identified compounds was lower than that before for pyrolysis at 20 seconds (only about 40% of the total peak areas), while the same amount as that before was identified for 5 seconds (44%). In the present case, it seemed that shorter pyrolysis residence time led to an increase in the amount of the detected compounds. This anomaly with respect to the trend observed at 700°C could be due to the influence of different errors related to sample weighing, handling, and placing in the quartz tube as well as its position with respect to the heating filament coil.

Table 13. Identified compounds from pyrolysis of abietic acid at 600°C (for X, I, A1, A2, and A3, see Chapter 8)

Type	RT (min)	Compound	m/z	20s	5s
X	4.87	2,4-Hexadiene, 2-methyl	96/81/67/53	2.10	1.88
X	5.80	1,3,5-Hexatriene, 3-methyl	94/79/65	1.45	2.26

X	7.03	Cyclohexene, 1,3-dimethyl	110/95/82/67	2.55	3.82
			total	**6.10**	**7.96**
I	16.88	Indene, 2,3-dihydro	117/103/91	0.48	0.25
I	20.98	1*H*-Indene, 2-methyl	130/115/102	0.87	0.74
I	21.29	1*H*-Indene, 1-methyl	130/115/102	1.35	0.88
I	24.40	1*H*-Indene, 1,3-dimethyl	144/129/115	0.63	0.55
I	26.19	1*H*-Indene, 2,3-dihydro-1,1,3-trimethyl	160/145/128/115	0.22	0.18
			total	**3.55**	**2.60**
A1	3.81	Benzene	78/51	1.89	1.98
A1	6.45	Toluene	91/65	2.62	4.68
A1	10.16	*m*-Xylene	106/91/77	2.59	4.02
A1	11.21	*p*-Xylene	106/91/77	0.87	1.40
A1	12.00	Styrene	104/78/51	0.78	1.58
A1	12.05	Benzene, (1-methylethyl)	120/105/91/77	0.55	0.86
A1	13.54	Benzene, 1-ethyl-2-methyl	120/105/91/77	0.97	1.38
A1	14.32	Benzene, 1-ethyl-3-methyl	120/105/91/77	0.55	0.84
A1	14.83	Benzene, (1-methylethenyl)	118/103/91	0.84	1.28
		Benzene, 1,2,4-trimethyl	120/105/91/77		
A1	15.31	Benzene, 1-ethenyl-2-methyl	117/103/91	0.67	0.88
A1	15.46	Benzene, 1-methyl-4-(1-metylethyl)	134/119/103/91	0.94	1.33
A1	16.03	Benzene, 1,3,5-trimethyl	120/105/91/77	0.76	0.86
A1	17.69	Benzene, 1-propynyl	115/89/63	0.67	0.44
A1	18.12	Benzene, methyl-4-(1-methylethenyl)	132/117/91	0.47	0.43
		Benzene, 1-ethyl-4-(1-methylethyl)	148/133/119/105		
A1	19.07	Phenol, 4-methyl	107/90/77	0.51	0.32
A1	19.56	Benzene, 1,4-dimethyl-2-(1-methylethyl)	148/133/117/105	0.28	0.20
A1	19.85	Benzene, 1-methyl-4-(1-methyl-2-propenyl)	146/131/115/91	0.97	0.80
A1	20.08	Phenol, 2,6-dimethyl	122/107/91/77	0.30	0.18
A1	20.62	Benzene, 2-ethenyl-1,4-dimethyl	132/117/105/91	0.52	0.37
A1	23.74	Phenol, 4-(1-methylehyl)	136/121/103/91	0.66	0.53
A1	28.75	Benzene, 1,3,5-trimethyl-2-(1,2-propadienyl)	158/143/128/115	0.45	0.40
			total	**18.86**	**24.76**
A2	22.85	Naphthalene	128/102	0.54	0.46
A2	25.25	Naphthalene, 1,2-dihydro-6-methyl	144/129/115	0.76	0.64
A2	26.36	Naphthalene, 1-methyl	142/115/89	0.80	0.46
A2	27.12	Naphthalene, 2-methyl	142/115/89	0.76	0.73
A2	29.01	Naphthalene, 1,2,3,4-tetrahydro-2,2-dimethyl-1-methylene	172/157/142/129/115	0.61	0.60
A2	30.88	Naphthalene, 2,6-dimethyl	156/141/128/115	0.74	0.55
A2	31.49	Naphthalene, 2-isopropyl	170/155/141/128	0.67	0.45
A2	31.86	Naphthalene, 1,6-dimethyl	156/141/128/115	0.19	0.17
A2	34.25	Naphthalene, 1,4,5-trimethyl	170/155/141/128	0.45	0.31
A2	34.57	Naphthalene, 2-isopropenyl	168/153/141/128	0.38	0.38
A2	36.10	Naphthalene,1-methyl-7-(1-methylethyl)	184/169/154/141	2.05	1.75
A2	39.24	1-1'-Biphenyl, 4-4'-dimethyl	182/167/152/141	0.31	0.65
A2	40.24	Naphthalene, 1,6-dimethyl-4-(1-	198/183	0.37	0.48

		methylethyl)-			
A2	42.91	1-1'-Biphenyl, 4-(1-methylethyl)	196/181/165/153	0.26	0.48
A2	43.56	Naphthalene, 5-isopropenyl-3-isopropyl	210/195/180/165/153	0.28	0.30
			total	**9.17**	**8.41**
A3	54.00	Phenanthrene, 7-isopropyl-1-methyl-1,2,3,4-tetrahydro (10,18-Bisnorabieta-5,7,9(10),11,13-pentaene)	238/223/195	0.89	0.47
A3	58.72	Phenanthrene, 1-methyl-7-(1-methylethyl)	234/219/204/189	0.50	0.17
			total	**1.39**	**0.64**

9.1.3 Treatment at 500°C

The analysis of the pyrograms obtained at 500°C (**Table 14**) was rather complicated if compared to those at the previous temperatures due to the lower response and noisy base line; thus, fewer compounds could be identified, less than 40% of the total integrated area. The percentage of identified aliphatic hydrocarbons increased, while indene-types of compounds were found in very low amounts. The main products were benzene and its derivatives, while less polyaromatics than those before could be identified at this temperature. Nevertheless, judging from the pyrograms, some important peaks seemed to be present in the RT area of 45-60 min, which could not be matched with the spectral library. For example, the intense peak at 50 min could not be identified with reference from the library and its MS spectrum is reported in **Figure 21**. The fragment peaks in the spectrum showed clearly that was a decomposition product, which did not undergo aromatization and was obtained from direct fragmentation of the parent molecule after decarboxylation. The suggested interpretation of the spectrum is shown in **Figure 22**.

Table 14. Identified compounds from pyrolysis of abietic acid at 500°C (for X, I, A1, A2, and A3, see Chapter 8)

Type	RT (min)	Compounds	m/z	20s	5s
X	4.84	2,4-Hexadiene, 2-methyl	96/81/67	4.79	3.19
X	7.03	1,3-Hexadiene, 2,5-dimethyl	110/95/67	4.38	2.86
X	8.86	Cyclopentene, 3-methylene	108/93/77	1.53	2.97
X	9.80	1,3-Cyclohexadiene, 1,4-dimethyl	108/93/77	1.27	1.39
X	12.38	Cyclohexene, 3,3-dimethyl-6-methylene	122/107/91/79	0.91	0.84
X	23.52	2-Cyclopentene, 1-carboxylic acid, 1,2,3-trimethyl	154/109/91/67	1.74	1.99
			total	**15.27**	**13.87**

I	21.28	1*H*-Indene, 1-methyl	130/115/102	0.70	0.73
			total	**0.70**	**0.73**
A1	6.48	Toluene	91/65	2.05	1.35
A1	10.15	*m*-Xylene	106/91/77	2.00	1.96
A1	15.47	Benzene, 1-methyl-4-(1-metylethyl)	134/119/105/91	1.75	1.23
A1	16.03	Benzene, 1,2,4-trimethyl	120/105/91/77	1.32	0.70
A1	19.85	Benzene, 1-methyl-4-(1-methyl-2-propenyl)	146/131/115/91	1.07	1.04
A1	23.73	Phenol, 4-methylethyl	136/121/103/91	1.22	1.27
A1	26.77	Benzene, 1,2,4-trimethyl-5-(1-methylethyl)	162/147/119/91	0.35	0.42
			total	**19.52**	**15.94**
A2	23.02	Naphthalene, 1,2,3,4-tetrahydro-5-methyl	146/131/115	0.91	0.80
A2	25.24	Naphthalene, 1,2-dihydro-4-methyl	144/129/115	0.63	0.71
A2	30.89	Naphthalene, 2,6-dimethyl	156/141/128	0.55	0.32
A2	36.08	Naphthalene, 1-methyl-7-(1-methyltehyl)	184/169/154/141	1.01	1.18
			total	**3.10**	**3.01**
A3	49.59	Phenanthrene, 2,3,4,4a,9,10-hexahydro-1,4-dimethyl-7-(1-methylethyl) (19-norabieta-4,8,11,1)	254/239	0.62	0.35
A3	53.98	Phenanthrene, 7-isopropyl-1-methyl-1,2,3,4-tetrahydro (10,18-Bisnorabieta-5,7,9(10),11,13-pentaene)	238/223/195	0.78	0.82
			total	**1.40**	**1.17**

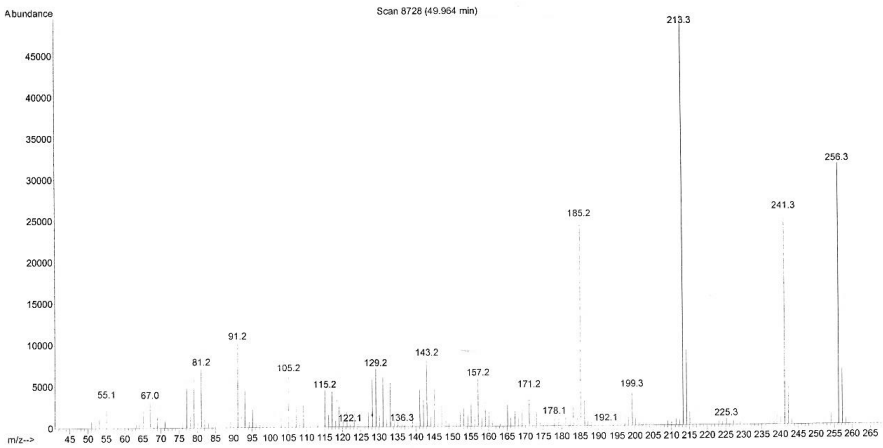

Figure 21. MS spectrum of the peak at RT 50 min.

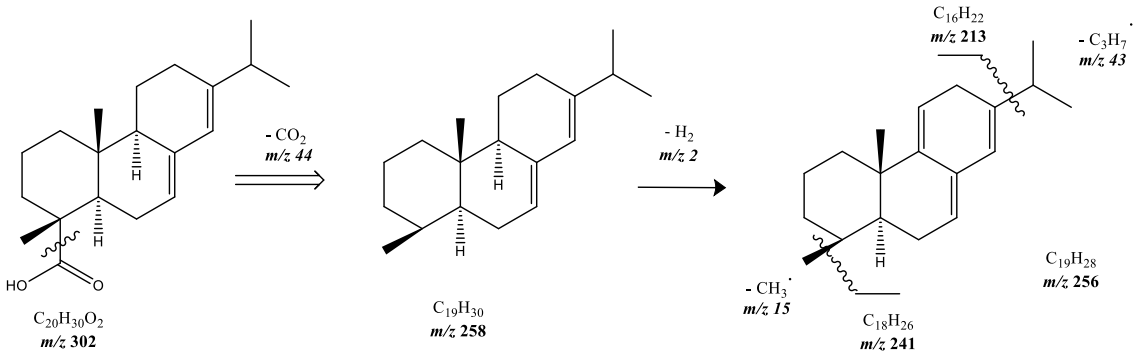

Figure 22. Suggested interpretation of the MS spectrum of the peak at RT 50 min (see **Figure 21**).

Overall, the results obtained from pyrolysis of abietic acid were in line with those expected from literature studies on resin acid mixtures and tall oil resin, which both contain abietic acid as one of their main components.[45,63]

9.1.4 Summary

The distribution of the product groups and the overall influence of temperature and time on them are summarized in **Table 15** and visualized graphically in **Figure 23**. In most cases, it seems that a higher temperature and a prolonged pyrolysis time promoted the formation of the detected compounds. The only exception was abietic acid at 600°C, which yielded more products at a lower pyrolysis time.

Table 15. Abietic acid products distribution at different pyrolysis condition (peak area %) (for X, I, A1, and A2, see Chapter 8)

Abietic acid							
Temperature (°C)	**Time (s)**	**X**	**I**	**A1**	**A2**	**A3**	**Total identified (%)**
700	20	0.33	5.05	25.12	16.17	1.56	48.23
	5	3.93	4.68	21.58	11.97	1.63	43.79
600	20	6.10	3.55	18.86	9.17	1.39	39.07
	5	7.96	2.60	24.76	8.41	0.64	44.37
500	20	14.62	0.70	19.52	3.10	1.40	39.34
	5	13.24	0.73	15.94	3.01	1.17	34.09

Figure 23 shows that the same fragmentation groups were found in every pyrolysis condition. The trend appeared to be an increase in the amount of lower-molar-mass compounds at lower pyrolysis temperature while indene, naphthalene, and their

derivatives increased at higher temperature and longer pyrolysis retention time. In general, in every condition benzene and the different benzene derivatives accounted for the main percentage of identifiable products.

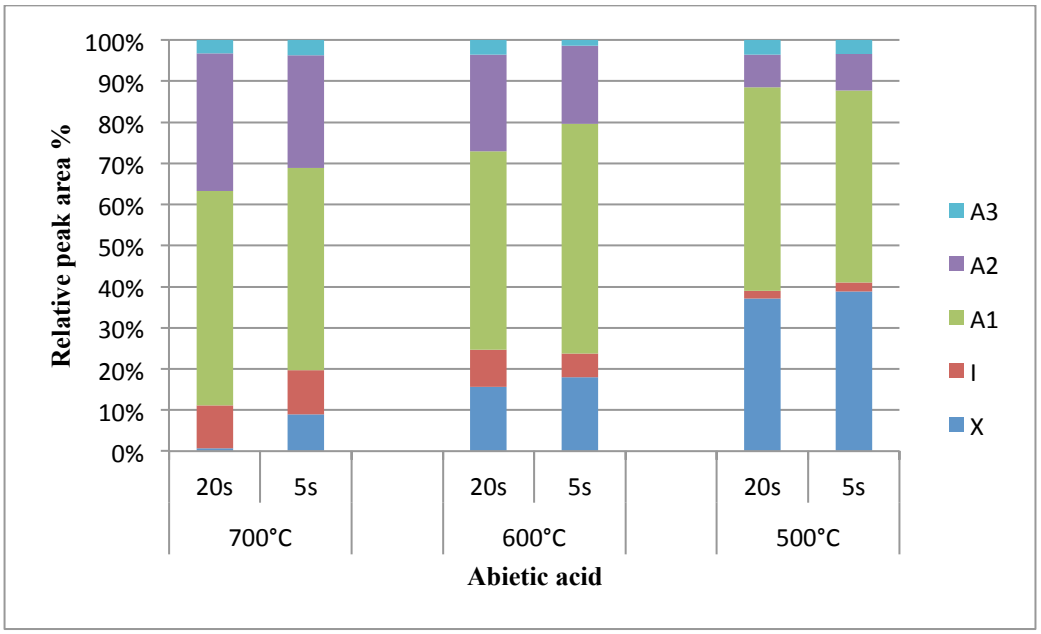

Figure 23. Effect of pyrolysis temperature and time on the abietic acid product composition (relative area %).

Figure 24 illustrates an estimation of the hypothetical product distribution in the case where the total integrated area of the chromatogram was taken into account and not only the area of the identified compounds. This estimation was based on the general analysis of the MS spectra of the unidentified compounds and the assumption that the large majority of them showed fragments characteristics of different mono- and polyaromatics derivatives.

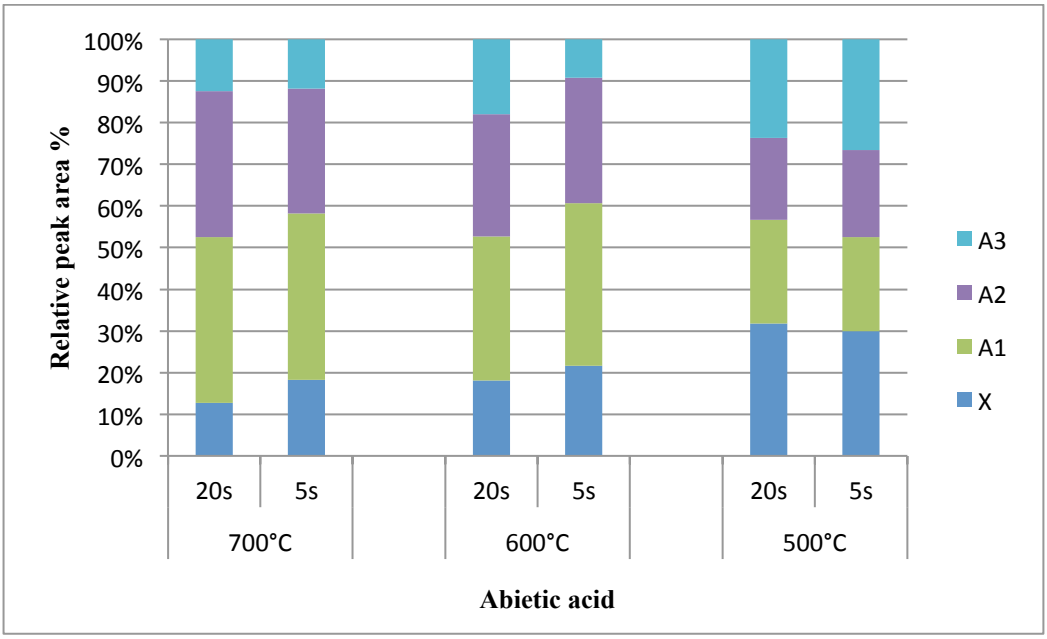

Figure 24. Estimation of the product distribution calculated on the total integrated area.

The main products were aromatics with one, two, or three benzene rings, considerably dominant especially, for the highest temperature. Indene derivatives were considered as part of the one benzene ring (A1) class in order to simplify the process. It can be noticed that **Figure 24** resembles the product distribution of **Figure 23**, because the underlying assumption was, of course, dependent on the information obtained from the identified compounds. Nevertheless, considering the total integrated area it could give a better perspective about the real relative distribution of the pyrolysis products. On the other hand, it had to be taken into account that the category of three benzene rings (A3) most likely also comprised other compounds than those of phenanthrene-type. Especially, at 500°C, when this class seemed increasing, the analysis of the MS spectra suggested that it contained mostly tricyclic but not aromatic products, deriving from the direct fragmentation of the parent molecule prior to aromatization, like it was seen at RT 50 minutes.

9.2 Betulinol

9.2.1 Treatment at 700°C

The analysis of the pyrograms obtained at 700°C showed that the pyrolysis of betulinol yielded mainly aromatics with one and two benzene rings. Various substituted aliphatic hydrocarbons were identified at the beginning of each run and for betulinol, it was decided to report the first peak at a RT of around 2.40 min; in this case, in contrast to abietic acid, high quality match was obtained. Three compounds were suggested (**Table 16)** not because they were all present at the same time, but because they had the same characteristic fragments and, due to their low molar mass, they could not be distinguished with certainty (MS detector lower limit of scanning mass was 50 *m/z*). As dominant fragmentation products it was possible to identify benzene, toluene, xylene, and methylindene, as well as methyl-, dimethyl-, and trimethylnaphthalenes. In contrast to abietic acid, no phenanthrene derivatives were obtained from the pyrolysis of betulinol.

Table 16. Identified products from pyrolysis of betulinol at 700°C (for X, I, A1, and A2, see Chapter 8)

Type	RT (min)	Compound	m/z	20 s	5 s
X	2.37	1,3- Butadiene, 2-methyl or 1,2-Pentadiene or cyclopropane, 1,2-dimethyl	67/53	5.95	5.26
X	5.06	1,3,5-Hexatriene, 3-methyl	94/79	0.76	0.86
X	8.16	1,4-Cyclohexadiene, 1,2-dimethyl	108/93/77/65	0.86	1.14
X	8.92	1,3-Cyclohexadiene, 1,4-dimethyl	108/93/77/65	0.50	0.62
X	15.05	Cyclohexane, 1,2,4-tris(methylene)	120/105/91/79	0.42	0.43
			total	**8.49**	**8.31**
I	20.95	1*H*-Indene, 1-methyl	130/115/102	1.74	1.67
I	21.24	1*H*-Indene, 2-methyl	130/115/102	2.37	1.61
I	24.06	1*H*-Indene, 1,3-dimethyl	144/129/115	0.84	0.78
I	24.35	1*H*-Indene, 2,3-dimethyl	144/129/115	1.04	0.92
I	24.60	1*H*-Indene, 4,7-dimethyl	144/129/115	1.50	1.39
			total	**7.49**	**6.62**
A1	3.78	Benzene	78/51	4.74	4.74
A1	6.39	Toluene	91/65/51	7.30	7.59
A1	9.76	Benzene, ethyl	106/91/77	1.76	1.84
A1	10.10	*m*-Xylene	106/91/77	5.28	5.11
A1	11.13	*p*-Xylene	106/91/77	1.80	1.75
A1	11.54	Styrene	104/78/63/51	1.59	1.56
A1	13.48	Benzene, 1-ethyl-3-methyl	120/105/91/77	2.20	2.03
A1	13.78	Benzene, 1,2,3-trimethyl	120/105/91/79	0.58	0.62

A1	14.26	Benzene, 1-ethyl-2-methyl	120/105/91/77	1.11	1.12
A1	14.76	Benzene, 1,2,4-trimethyl	120/105/91/77	1.69	1.63
A1	15.27	Benzene, 1-ethenyl-2-methyl	117/115/103/91	3.01	2.79
A1	15.97	Benzene, 1,3,5-trimethyl	120/105/91	0.91	0.89
A1	17.49	Benzene, 4-ethyl-1,2-dimethyl	134/119/105	0.32	0.30
A1	17.64	Benzene, 1-propynyl	115/89/63	1.45	1.19
A1	18.08	Benzene, 4-ethenyl-1,2-dimethyl	132/117/105/91	0.68	0.63
A1	18.36	Benzene, methyl-4-(1-methylethenyl)	132/117/115/105	0.42	0.41
A1	18.57	Benzene, 1-methyl-2-(1-methlethenyl)	132/117/105/91	1.47	0.73
A1	18.69	Benzene, 4-ethyl-1,2-dimethyl	132/119/115/105	-	0.32
A1	18.82	Benzene, 1-ethenyl-2,4-dimethyl	132/117/115/105	-	0.31
A1	19.68	Benzene, 2-ethenyl-1,4-dimethyl	132/117/105/91	1.11	1.06
A1	20.14	Benzene, 1-methyl-2-(2-propenyl)	132/117/105/91	0.69	0.49
A1	20.56	Benzene, 1-methyl-2-propenyl	132/117/105/91	0.65	0.56
A1	21.68	Benzene, (1-methylene-2-propenyl)	129/115	1.29	0.91
A1	22.23	Benzene, 2-ethenyl-1,3,5-trimethyl	146/131/115/105	0.60	0.60
A1	29.18	Benzene, 1,3,5-trimethyl-2-(1-propadienyl)	158/143/128/115	0.54	0.54
			total	**41.19**	**39.72**
A2	22.79	Naphthalene	128/102	1.24	1.06
A2	25.18	Naphthalene, 1,2-dihydro-6-methyl	144/129/115	0.96	0.87
A2	26.31	Naphthalene, 1-methyl	142/115	1.43	1.41
A2	27.07	Naphthalene, 2-methyl	142/115	1.34	1.18
A2	29.54	Naphthalene, 2-ethyl	156/141/128/115	0.88	0.82
A2	29.86	Naphthalene, 1-ethyl	156/141/128/115	0.32	0.29
A2	29.98	Naphthalene, 1,5-dimethyl	156/141/128/115	0.83	0.76
A2	30.54	Naphthalene, 2,6-dimethyl	156/141/128/115	0.63	0.58
A2	30.80	Naphthalene, 1,6-dimethyl	156/141/128/115	0.93	0.81
A2	31.71	Naphthalene, 1,7-dimethyl	156/141/128/115	0.33	0.29
A2	32.19	Naphthalene, 1,4-dimethyl	156/141/128/115	0.31	0.29
A2	32.90	Acenaphthylene/Biphenylene	152/126/76	0.31	0.27
A2	33.33	Naphthalene, 1,4,6-trimethyl	170/155/141/128	0.34	0.29
A2	34.16	Naphthalene, 1,4,5-trimethyl	170/155/141/128	0.26	0.24
A2	34.48	Naphthalene, 2,3,6-trimethyl	170/155/141/128	0.45	0.45
A2	37.00	Naphthalene, 1,6,7-trimethyl	170/155/141/128	0.29	0.26
			total	**10.85**	**9.87**
	17.77	UNKNOWN	122/107/96/81	**1.14**	**1.36**

Around 68 and 64% of the total area of integrated compounds could be identified with certainty, for pyrolysis at 20 and 5 seconds, respectively. The remaining portion did not give a good match, mainly due to broadening and overlapping of the peaks, which made the identification process quite complicated. An unknown compound, which could not be identified by comparison to mass spectral libraries, was observed at RT 17.7 min and its MS spectrum is shown in **Figure 25**. This compound was reported in **Table 16**, even if it was not identified, because its presence increased in the pyrograms obtained at 600

and 500°C, meaning that it might be an important product of betulinol fragmentation. A possible interpretation of the mass spectrum obtained at RT 17.7 min is suggested in **Figure 26.**

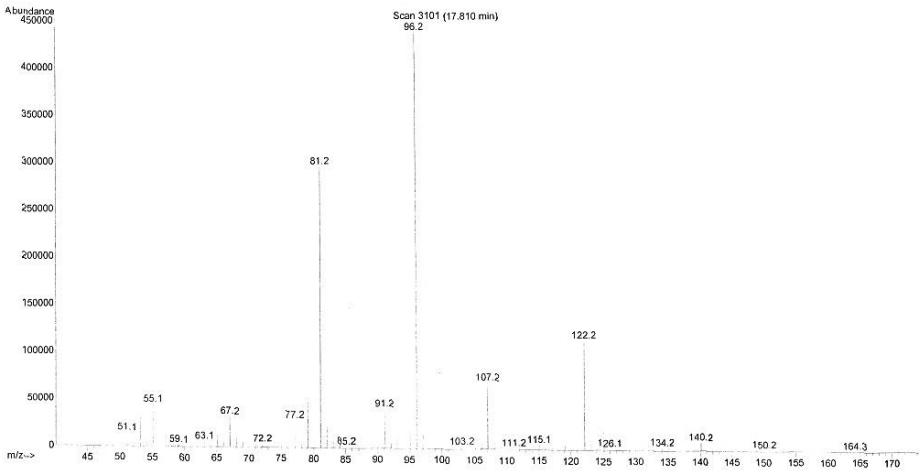

Figure 25. MS spectrum of the peak at RT 17.7 min found in all betulinol pyrograms.

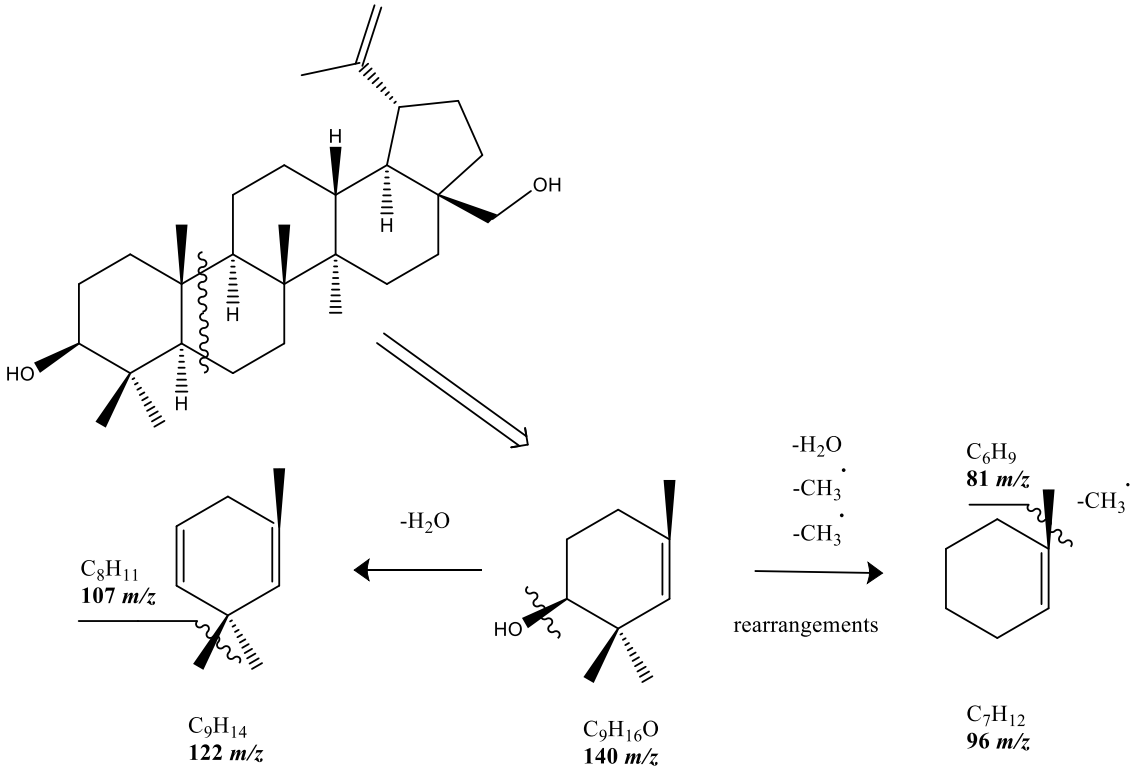

Figure 26. Suggested interpretation of the MS spectrum of the peak at RT 17.7 min (see **Figure 25**).

9.2.2 Treatment at 600°C

The analysis of the betulinol pyrograms obtained at 600°C (**Table 17**) was quite problematic due to a very noisy base line. Similar types of compounds found in the previous pyrograms could be found but they were less abundant and intense, due to lower temperature. The dominant products seemed to be aromatics with one benzene ring, mainly benzene, toluene, and xylene. A difference in the pyrograms of 20 and 5 seconds could be noticed in the area around RT 24 min (see **Appendix 2(2)**) where the base line was increasing considerably for a pyrolysis time of 5 seconds. This was not necessarily caused by an increase in the amount of products (for example, a higher amount of indene which was identified in this area) but probably again to some error in sample handling and preparation. The fragmentation product at RT 17.7 min seemed to increase with decreasing of pyrolysis temperature.

Table 17. Identified products from pyrolysis of betulinol at 600°C (for X, I, A1, and A2, see Chapter 8)

Type	RT (min)	Compound	m/z	20 s	5 s
X	2.49	1,3-Butadiene, 2-methyl or 1,3-pentadiene	67/53	8.98	8.09
X	5.80	1,3,5-Hexatriene, 2-methyl	94/79/65	6.21	2.89
X	8.61	1,3-Cyclohexadiene, 1,4-dimethyl	108/93/91/77	0.56	0.89
X	8.90	1,4-Cyclohexadiene, 1,2-dimethyl	108/93/91/77	1.39	1.29
X	15.10	Cyclohexane, 1,2,4-tris(methylene)	120/105/91/79	0.47	0.42
			total	**17.61**	**13.58**
I	20.98	1*H*-Indene, 2-methyl	130/115	0.95	1.00
I	21.28	1*H*-Indene, 1-methyl	130/115	1.02	1.64
I	21.83	1*H*-Indene, 2,3-dihydro-1,2-dimethyl	146/131/115	0.27	0.26
I	24.10	1*H*-Indene, 1,3-dimethyl	144/129/115	0.65	1.12
I	24.40	1*H*-Indene, 4,7-dimethyl	144/129/115	0.57	0.97
			total	**3.46**	**4.99**
A1	6.41	Toluene	91/65	6.24	2.60
A1	9.80	Benzene, ethyl	106/91/77	1.07	1.17
A1	10.14	*m*-Xylene	106/91/77	4.20	5.44
A1	11.18	*p*-Xylene	106/91/77	1.13	0.96
A1	11.59	Styrene	104/78/63	0.81	0.70
A1	12.02	Benzenemethanol, 4-methyl	122/107/91/79	0.76	0.70
A1	13.53	Benzene, 1-ethyl-3-methyl	120/105/91/79	1.29	1.17
A1	13.84	Benzene, 1,2,3-trimethyl	120/105/91/77	0.80	0.72
A1	14.30	Benzene, 1-ethyl-2-methyl	120/105/91/79	0.92	0.91
A1	14.80	Benzene, 1,2,4-trimethyl	120/105/91/77	1.39	1.28
A1	15.29	Benzene, 1-ethenyl-2-methyl	117/103/91	1.86	1.73
A1	16.00	Benzene, 1,3,5-trimethyl	120/105/91/77	0.97	0.92
A1	17.54	Benzene, 2-ethyl-1,4-dimethyl	134/119/105/91	0.31	0.29
A1	18.14	Benzene, 1-methyl-4-(1-	132/117/91	0.49	0.44

		methylethenyl)			
A1	18.32	Benzene, (2-methyl-1-propenyl)	132/117/105/91	0.46	0.83
A1	18.75	Benzene, 1-ethyl-2,3-dimethyl	134/119/105/91	0.58	0.52
A1	19.74	Benzene, 1-methyl-4-(2-propenyl)	132/117/105/91	1.19	1.11
A1	20.19	Benzene, 2-ethenyl-1,4-dimethyl	132/117/105/91	0.49	0.44
A1	29.25	Benzene, 1,3,5-trimethyl-2-(1,2-propadienyl)	158/143/128/115	0.51	0.49
			total	**25.47**	**22.42**
A2	25.20	Naphthalene, 1,2-dihydro-6-methyl	144/129/115	0.53	1.41
A2	26.34	Naphthalene, 1-methyl	142/115	0.40	0.57
A2	27.12	Naphthalene, 2-methyl	142/115	0.40	0.66
A2	30.06	Naphthalene, 2,7-dimethyl	156/141/128/115	0.25	0.71
A2	30.87	Naphthalene, 1,6-dimethyl	156/141/128/115	0.51	0.49
A2	33.84	Naphthalene, 1,2-dihydro-2,5,8-trimethyl	172/157/142/128/115	0.25	0.26
			total	**2.34**	**4.10**
	17.80	UNKNOWN	122/107/96/81	**1.94**	**2.25**

9.2.3 Treatment at 500°C

The pyrograms obtained at 500°C (**Table 18**) revealed that this condition was not optimal for the treatment of betulinol. It was clearly difficult to identify the peaks due to very noisy base line and low intensity of the response (ten times lower than the previous ones). The total amount of identified compounds represented less than 35% of the total peaks area. At the beginning of the pyrograms it was possible to notice the same products as those detected in the previous conditions (isoprene, xylene, and trimethylbenzene) but the dominant product was the peak at RT 17.72 min. Benzene dicarboxylic acid was recognizable in both pyrograms at around RT 65 min.

Table 18. Identified compounds from pyrolysis of betulinol at 500°C (for X, I, A1, and A2, see Chapter 8)

Type	**RT (min)**	**Compound**	**m/z**	**20 s**	**5s**
X	2.45	1,3-Butadiene, 2-methyl or 1,3-pentadiene or cyclopropane, ethylidene.	67/53	10.66	13.55
X	3.31	2,4-Hexadiene	82/67/53	13.61	-
X	4.71	2,4-Hexadiene, 3-methyl	96/81/67/55	-	8.10
X	14.90	Cyclohexene, 1-methyl-4-(1-methylethenyl)		-	0.88
			total	**24.27**	**22.53**
A1	10.15	Benzene, 1,3-dimethyl	106/91/77	3.89	1.41
A1	14.77	Benzene, 1,3,5-trimethyl	120/105/91	1.60	-
A1	16.00	Benzene, 1,2,4-trimethyl	120/105/91/77	1.09	1.42
A1	27.34	Phenol, 4-ethenyl-2-methoxy		2.02	2.70

A1	64.81	Benzene, 1,2-dicarboxylic acid	279/167/149	0.65	1.28
			total	**9.25**	**6.81**
	17.72	UNKNOWN	122/107/96/81	**3.44**	**7.14**

As a conclusion, the interpretation of betulinol pyrograms was more complicated than that of abietic acid and no direct comparison of the betulinol products was possible due to the scarcity of similar pyrolytic studies in literature. A study on birch wood conducted by Fagernäs *et al.* (2012)[72] showed similar type of aromatic hydrocarbons as the main products of tar and aqueous phase, although there were differences to take into account since the afore mentioned study was conducted on slow pyrolysis regime and not fast pyrolysis as in the present case.

9.2.4 Summary

The distribution of the product groups and the overall influence of temperature and time on them are summarized in **Table 19** and visualized graphically in **Figure 27**. In most cases, it seemed that higher temperature and prolonged pyrolysis time promoted the formation of the detected compounds. The peak area obtained for the peak at RT 17.7 min was added to the sum of identified compounds to show the increase in its presence influenced by the decreasing of pyrolysis temperature.

Table 19. Betulinol products distribution at different pyrolysis condition (peak area %) (for X, I, A1, and A2, see Chapter 8)

		Betulinol					
Temperature (°C)	**Time (s)**	**X**	**I**	**A1**	**A2**	**?**	**Total identified (%)**
700	20	8.49	7.49	41.19	10.85	(1.14)	68.02*
	5	8.31	6.37	39.72	9.87	(1.36)	64.27*
600	20	17.61	3.46	25.47	2.34	(1.94)	48.88*
	5	13.58	4.99	22.42	4.10	(2.25)	45.09*
500	20	24.27	-	9.25	-	(3.44)	33.52*
	5	22.53	-	6.81	-	(7.14)	29.34*

*The peak area % of the unknown (?) has not been included in the total % of identified compounds.

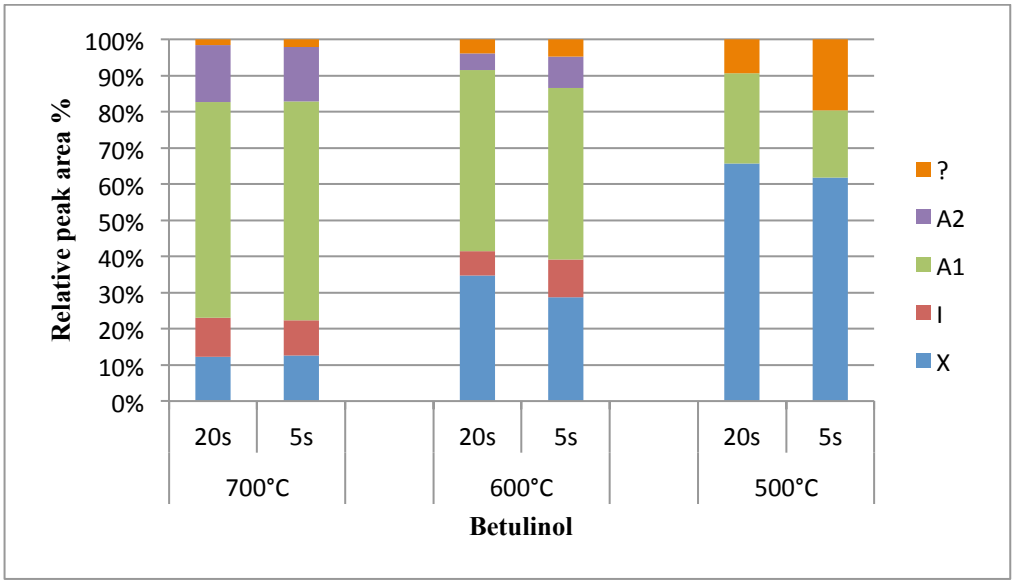

Figure 27. Effect of pyrolysis temperature and time on betulinol product composition (relative area %).

It is possible to see in **Figure 27** that similar pyrolysis products were obtained at 700 and 600°C, with the former having the higher percentages of identified aromatic and indene-types of compounds. Fewer compounds could be identified at 500°C, but it was possible to notice an increase in the lower-molar-mass compounds, the lack of naphthalene and indene groups, and a significant increase in the unknown compound at RT 17.7, which was labeled with a question mark.

In a similar way as for abietic acid, **Figure 28** shows an estimation of the product distribution of the total integrated area, based on a general analysis of the MS spectra of both identified and unidentified compounds. Even in this case, indene derivatives have been considered together with the one benzene ring (A1) group, in order to simplify the classification process.

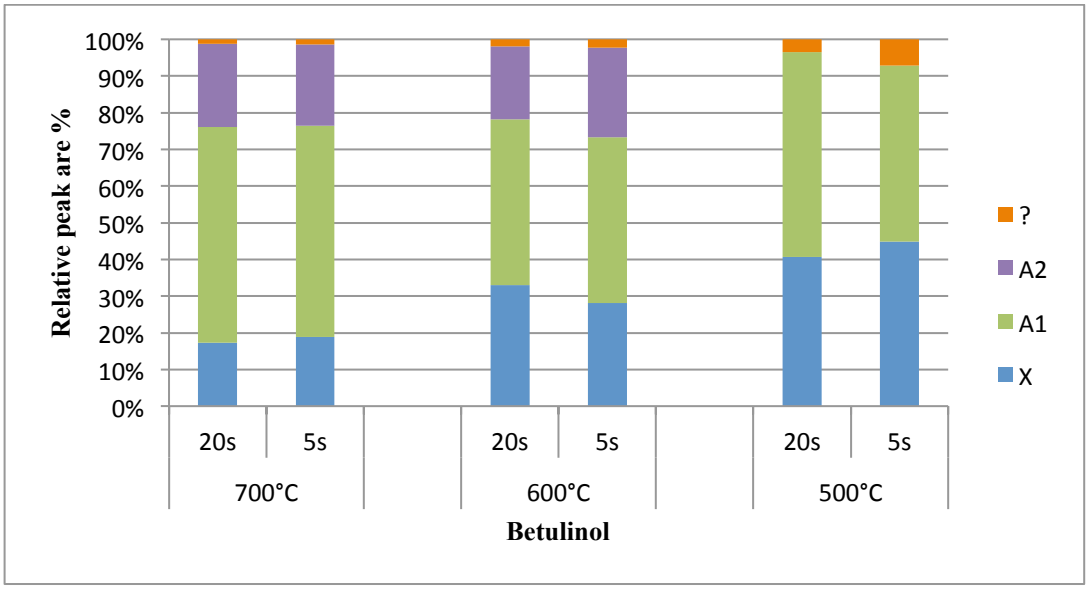

Figure 28. Estimation of the product distribution calculated on the total integrated area.

It can be stated that **Figure 28** resembles the product distribution obtained in **Figure 27**, with one benzene ring aromatics as dominant products, and two benzene rings present only for the higher temperatures (700 and 600°C).

10 Concluding remarks

10.1 General discussion

Two model compounds representing the class of tricyclic diterpenes and tetracyclic triterpenes were investigated experimentally by Py-GC/MS. It has been demonstrated that Py-GC/MS allows the detection of a wider range of compounds than simple GC/MS, especially with high boiling point and polarity.[57] Moreover, its high sensitivity and low limit of detection are also among the reasons why this technique is widely used in modern biomass pyrolysis investigations.[57,64,66-68] Despite its intrinsic limitations, Py-GC/MS proved to be suitable mean for the qualification of pyrolysis products and for studying the influence of pyrolysis conditions. At times the multiplicity of products and complexity of reaction taking place during pyrolytic conditions made the process of products identification quite challenging. These challenges could come from chromatographic aspects as the difficulty of achieving perfect chromatographic separation, base line drift, and changes in peak shapes.[64,73] Furthermore, the confidence level on products identification could be reduced by the absence of molecular ion, possible in the EI mode.[64] On the other hand, EI mode is also a useful tool since allows comparison with established spectral library, which speeds considerably the result interpretation process.

In this study, it was observed during pyrolysis experiments that the position of the sample with respect to the platinum filament coil influenced the yield of pyrolysis products and the success of pyrolysis experiments. Considerable attention was used for placing the sample in a systematic way in order to enhance repeatability and achieve the most uniform pyrolysis temperature, usually in the middle of the filament coil.[45,74] The most uniform condition of temperature was found to be slightly towards the bottom side of the coil, due to minor shape changes of the filament with usage. Therefore, when analyzing the product pyrograms, it should be kept in mind the fact that manual sample preparation and placement could be a possible source of error. In particular, when the sample amount utilized is quite small, sample size variation errors are unavoidable.

Observing the pyrograms of both abietic acid and betulinol (**Appendices 1** and **2**), it was intuitively possible to notice changes in the yields of the main pyrolytic products along with changes in pyrolysis temperature. On the contrary, the pyrolysis residence

time seemed to be a less influential factor than temperature. The nature of pyrolysis products obtained at higher temperatures appeared to be the same in different experimental conditions, whereas their relative abundances were the main difference. At the lower temperature the formation of aromatic products did not seem favorable, while different fragmentation products of the original molecule were present. In most cases, those fragments, especially at lower temperature, could not be identified due to an increase in the base line and/or a decrease in the response.

Among the pyrolytic products, benzene, indene, naphthalene, and their derivatives, mainly methylated, were the main products common to both model compounds. Phenanthrene derivatives were only found from pyrolysis of abietic acid, due to the stability of the phenanthrene skeleton, which is a characteristic of tricyclic resin acids. These products were obtained always at 700 and 600°C temperature for both model compounds, while they could not be clearly identified for betulinol at 500°C. In fact, pyrolysis temperature showed to be a more crucial parameter compared to pyrolysis time. A general trend could be seen in higher pyrolysis temperature and longer time enhancing the formation of the detected compounds.

The scarcity in literature of a similar work specifically focused on terpenoid model compounds made the comparison of the results quite difficult. Nevertheless, the fact that the main products obtained were mostly aromatics was in line with what expected from previous studies on resin and rosin products.[45,63,69,70]

The reaction temperature normally used for biomass pyrolysis on a large-scale reactor is around 500°C with the purpose of maximizing the liquid product.[21,75] Considering that the presence of aromatics is undesirable when bio-oils are meant for the production of fuels and fuel additives, terpenoic substrate does not seem appropriate for this purpose.[45] Therefore, the interest should be shifted towards obtaining more valuable products, for example, chemicals that are traditionally derived from petroleum feedstock.[44]

The relevance of this type of research relies on the fact that investigating individual biomass components under varying pyrolytic conditions can support the understanding of the whole biomass behavior during pyrolysis. Specifically, through model compounds it is possible to identify the influence of a particular compound or molecular

group on the whole biomass.[59] Thus, studies devoted to the understanding of lignocellulosic material behavior under different conditions have a primal role in evaluating the feasibility of certain fuels and chemicals and the ability to maximize the desired products.[66] As a conclusion, this work can be interpreted as an informative database of fragmentation products obtainable when the feedstock to be pyrolyzed contains one of the two model compounds studied.

10.2 Improvements and future researches

Strictly related to this work, many improvements could be made. Observing betulinol pyrograms is noticeable that a different chromatographic oven temperature program could be elaborate in order to better separate the pyrolysis products, since all the main products were already eluted within the first 40 minutes.

Moreover, in order to ensure reproducibility of the results, the analyses should have been performed at least twice for each sample. Unfortunately it was not possible due to lack of time and technical problems with the equipment, which paralyzed the experimental analysis for a certain period of time. The majority of the samples have been analyzed twice but not all of them; this is why duplicates have not been taken into account when presenting the area percentages of the identified compounds. Averaged values obtained from duplicates and their standard deviations would make the results of this study more reliable. Furthermore, actual quantification of the most significant compounds could be done through calibration curves with internal standards. It could have also been interesting to compare the behavior of the studied model compounds in a real biomass matrix, for example, in birch bark for betulinol, since comparative data were harder to find.

During pyrolysis conditions, feedstock may undertake different reactions: decarboxylation, dehydration or different transformation by rearrangements and cyclization reactions.[57] Taking into account the product distribution and the effects of different pyrolysis conditions, it could have been possible to hypothesize the pyrolytic pathways that led to the formation of the main products. In addition, more advanced studies could be made on abietic acid and betulinol as model compounds, in order to explore their pyrolytic reaction mechanisms. In-depth studies can clarify the

intermediate processes taking place during pyrolysis and bring forward the investigation on biomass pyrolysis mechanisms.[68]

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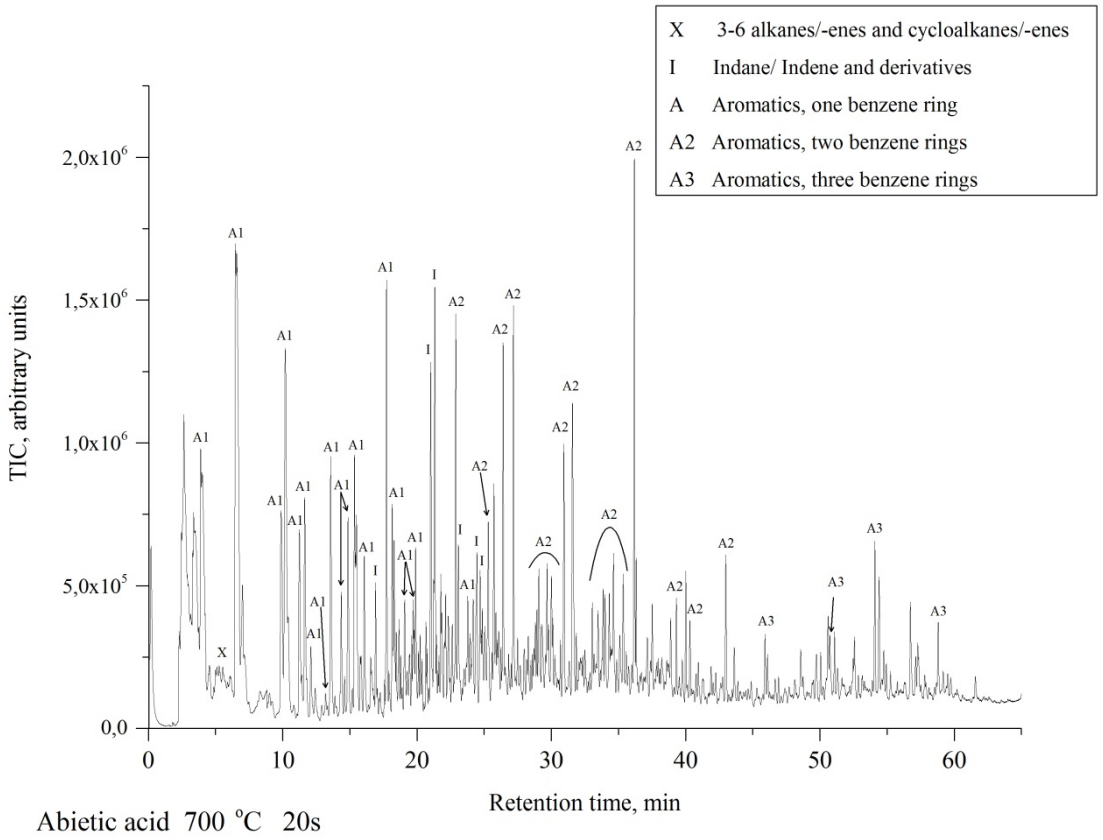
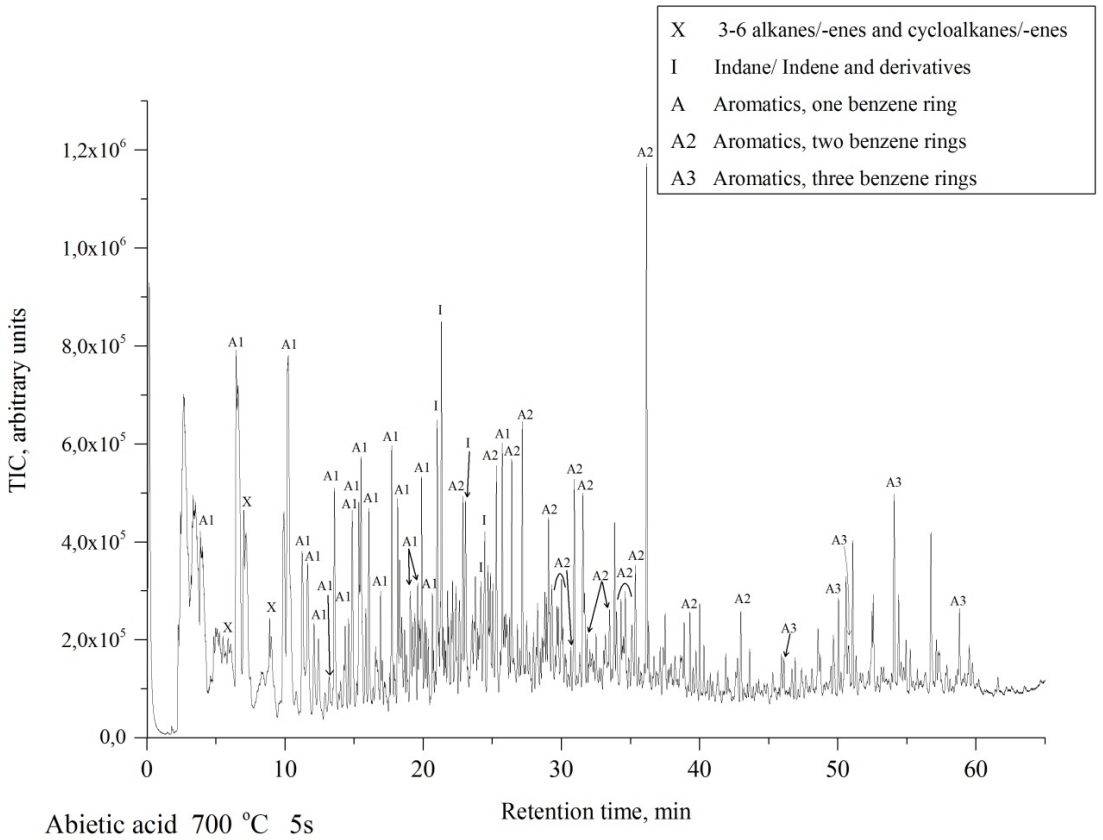
Appendices

Appendix 1: Pyrolysis of abietic acid (3 pages)

Appendix 2: Pyrolysis of betulinol (3 pages)



Abietic acid 700 °C 20s



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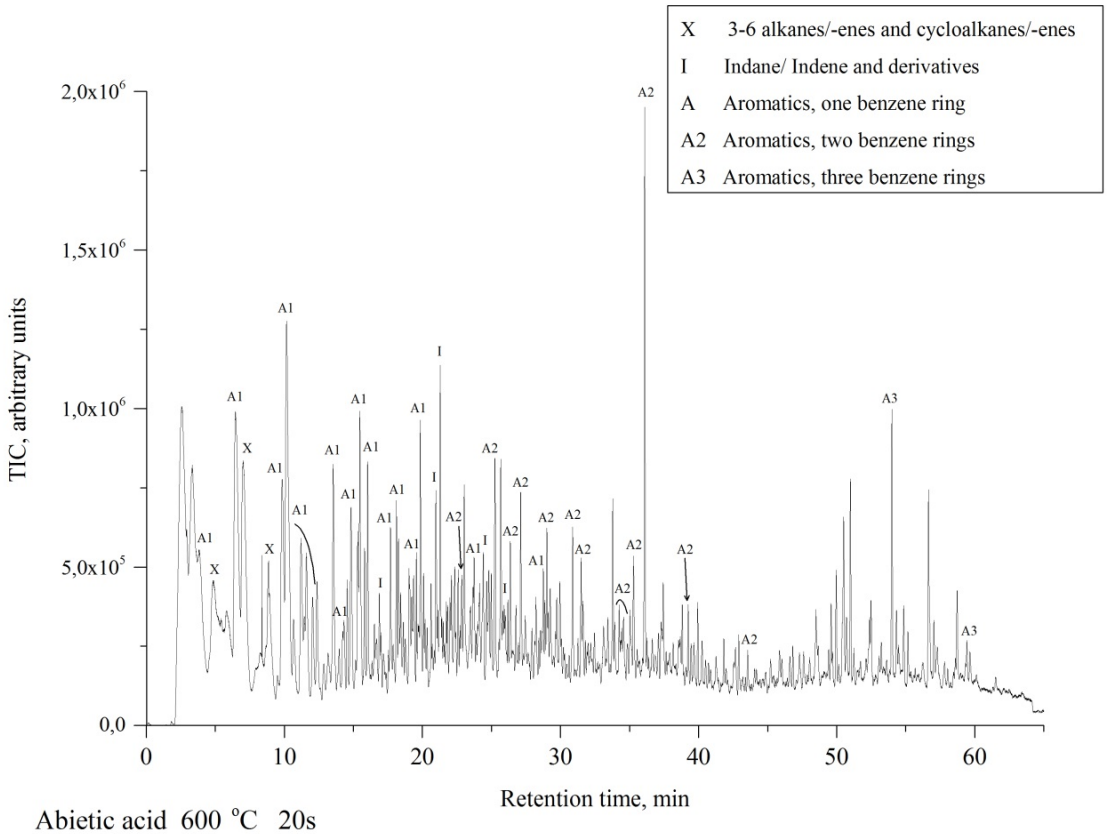

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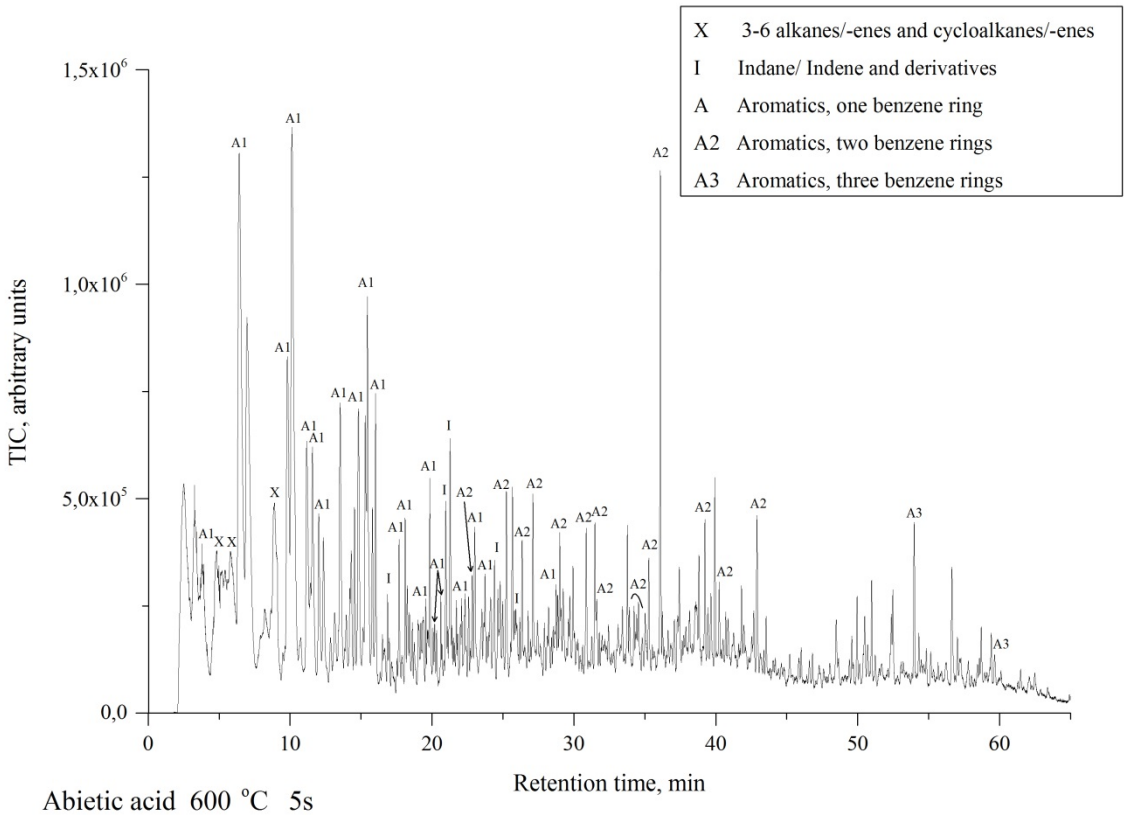

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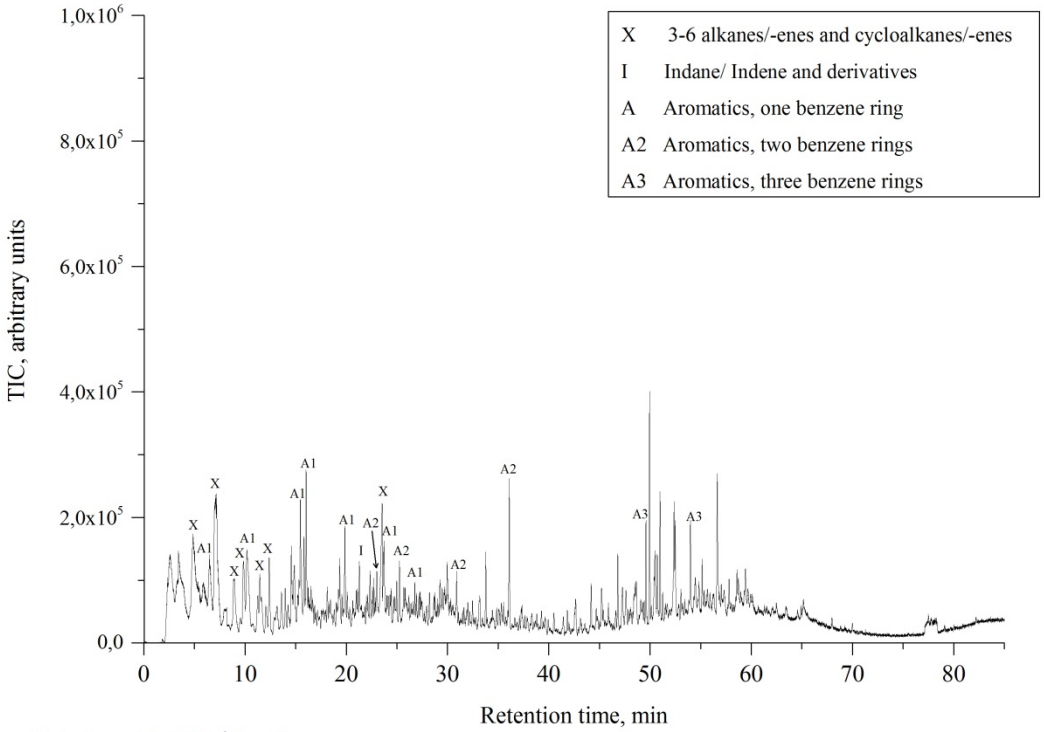

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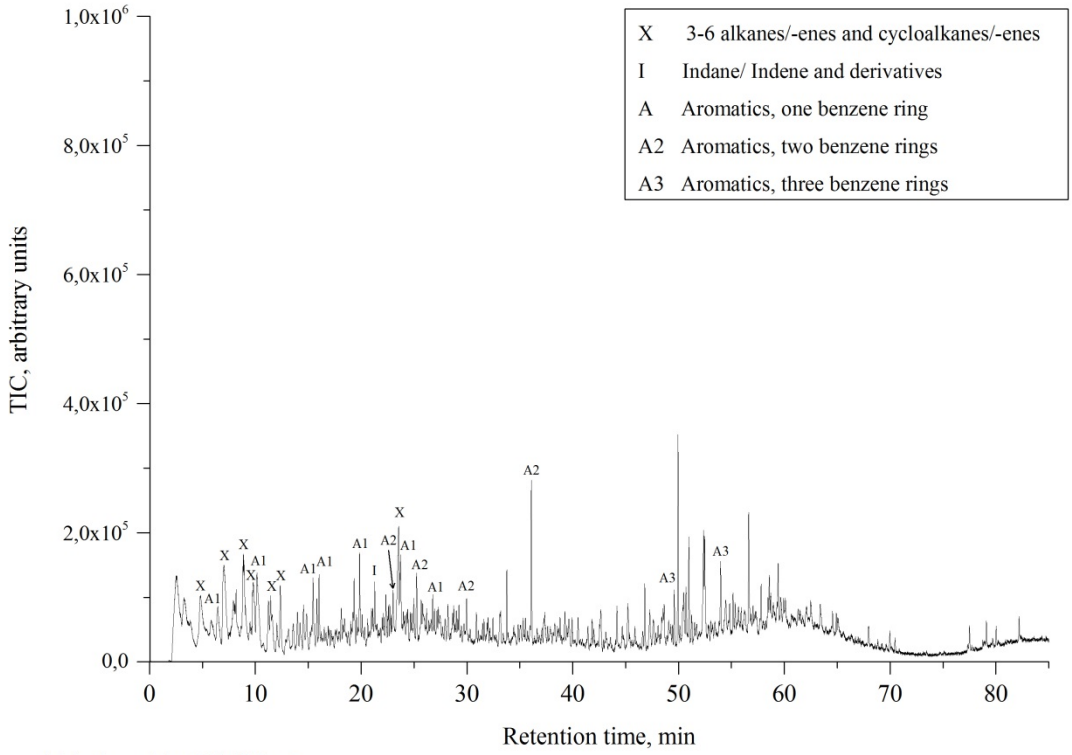

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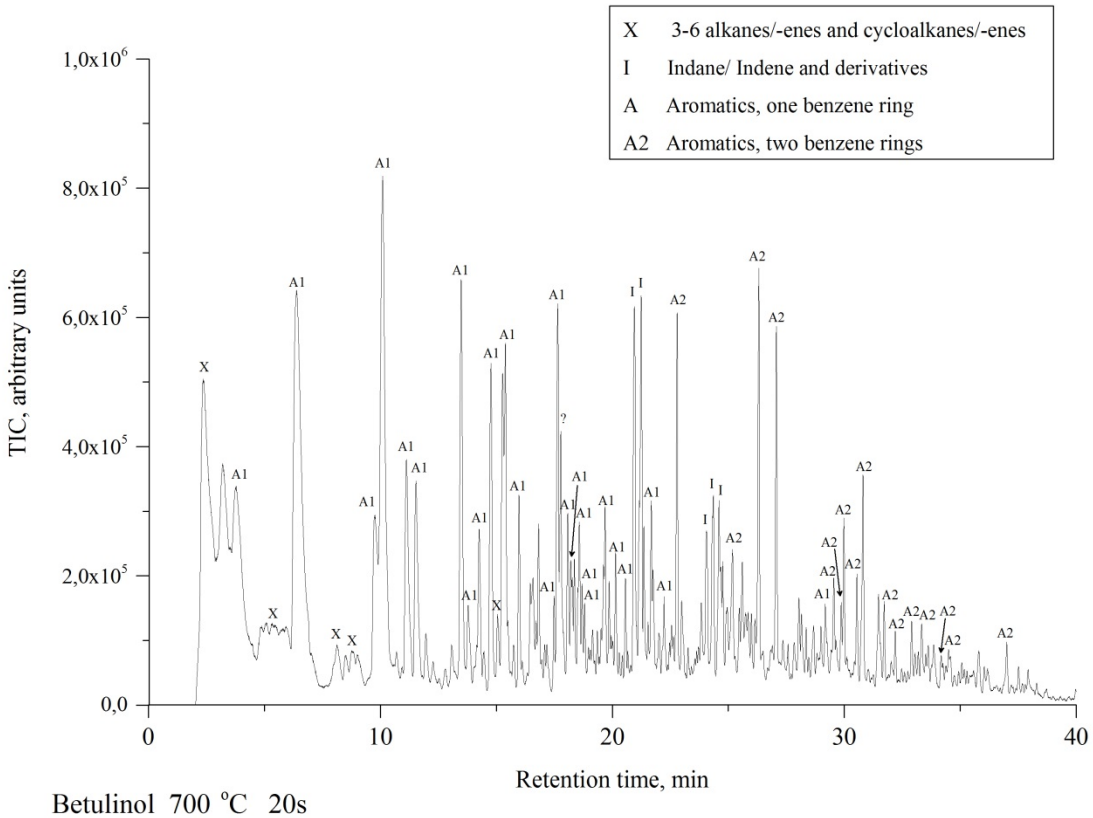
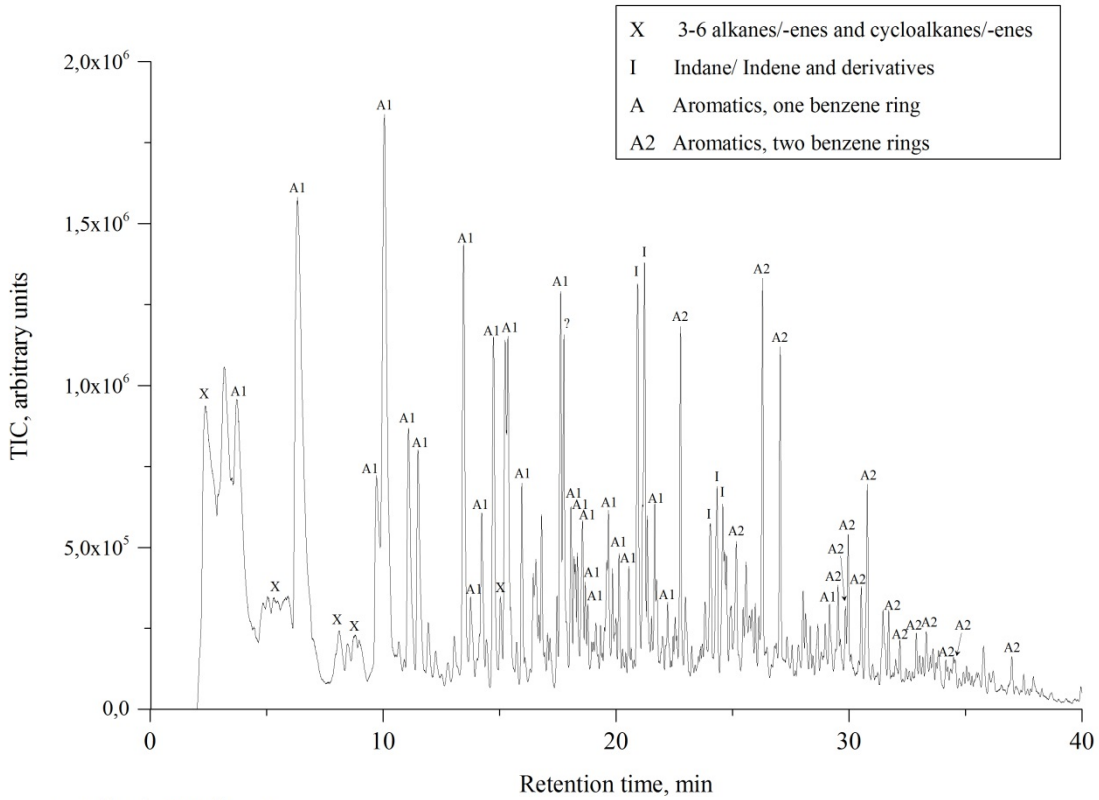


Betulinol 700 °C 20s



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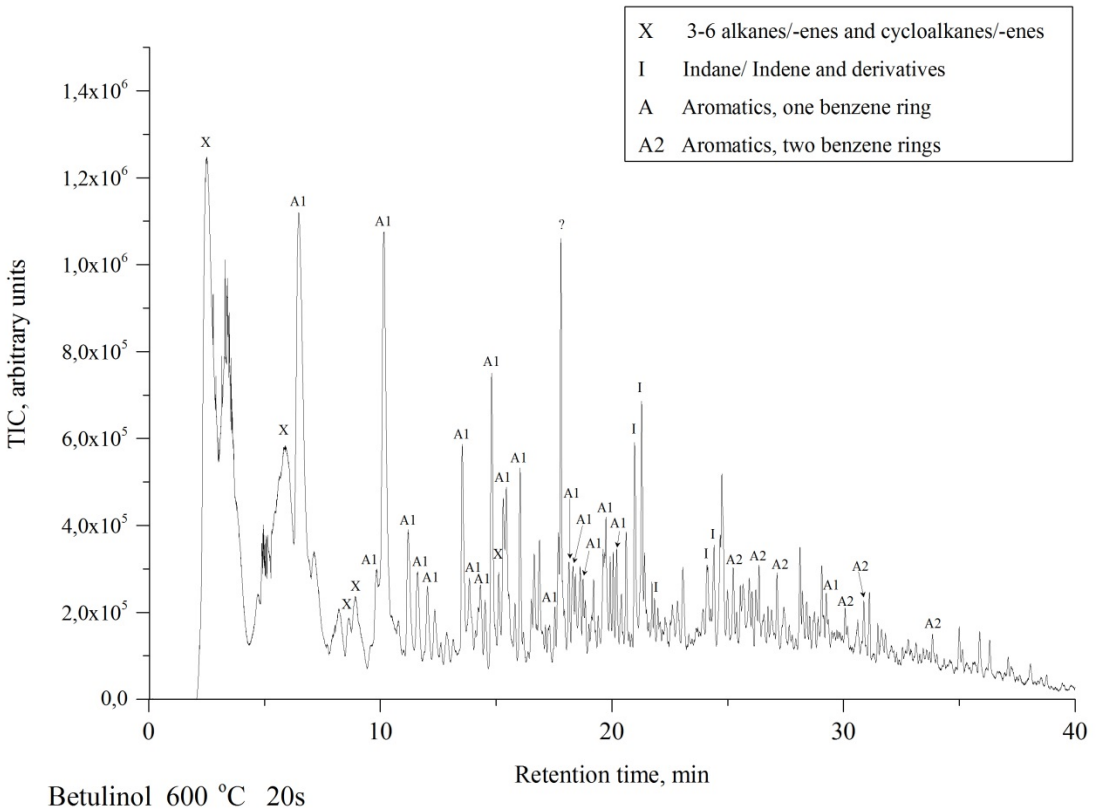

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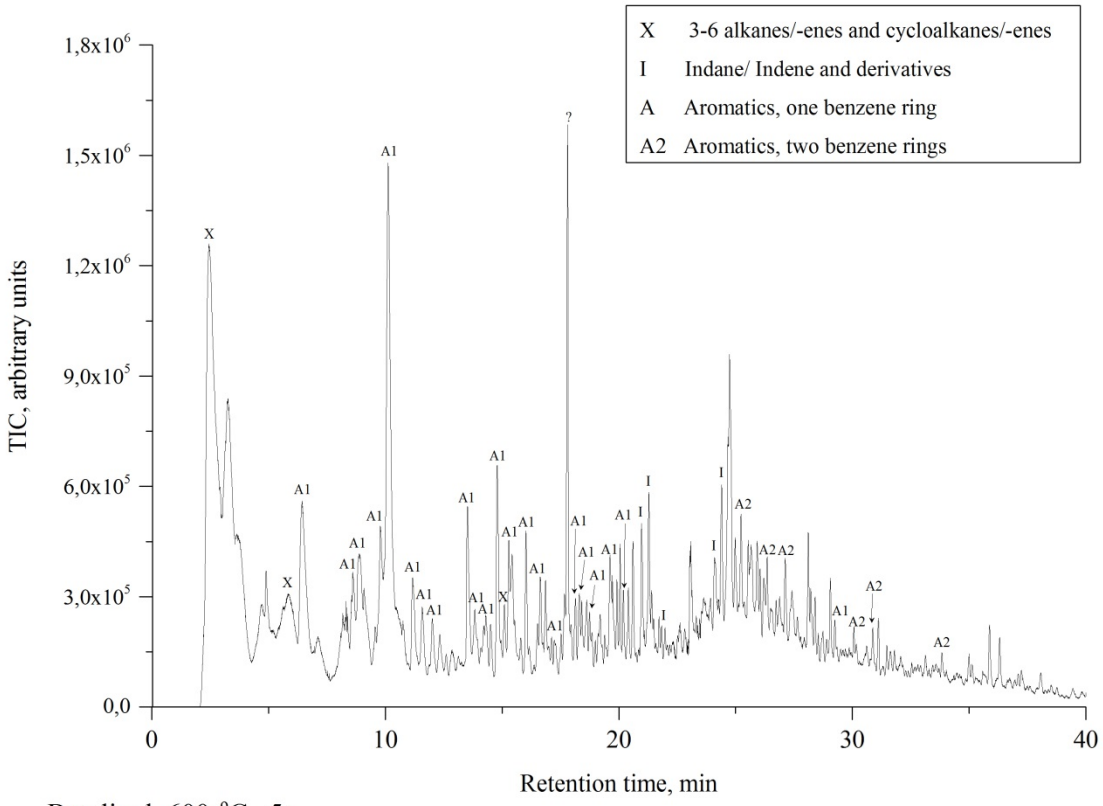

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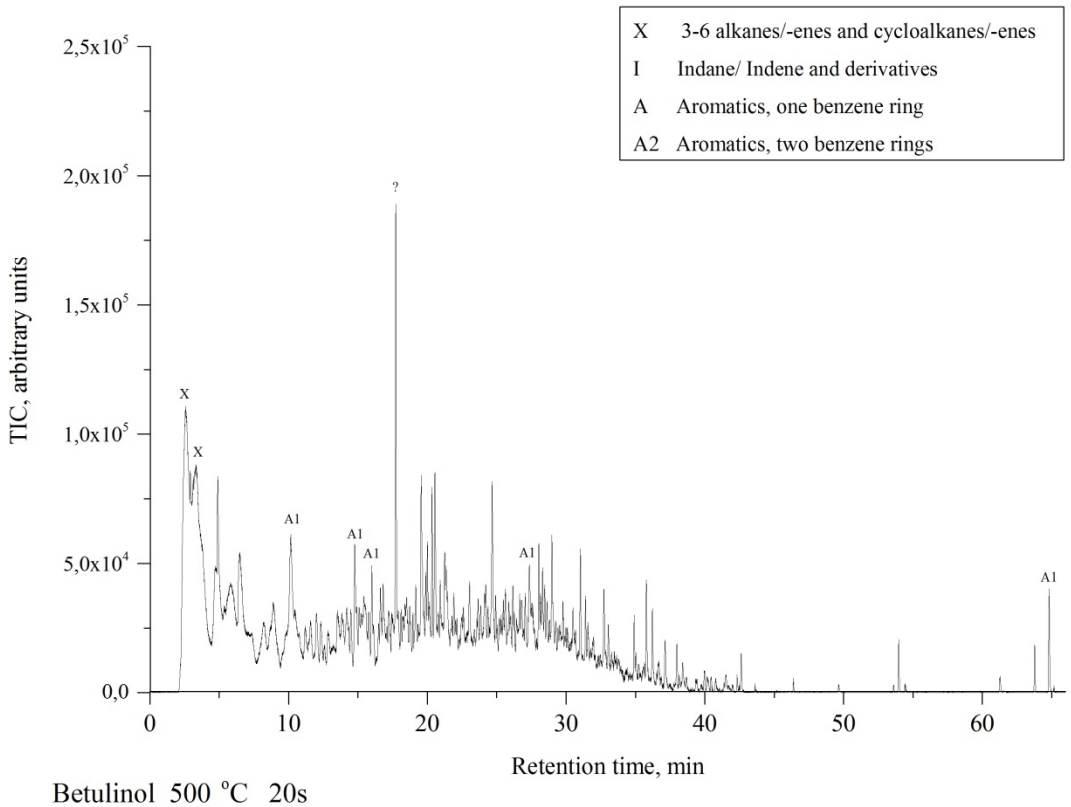

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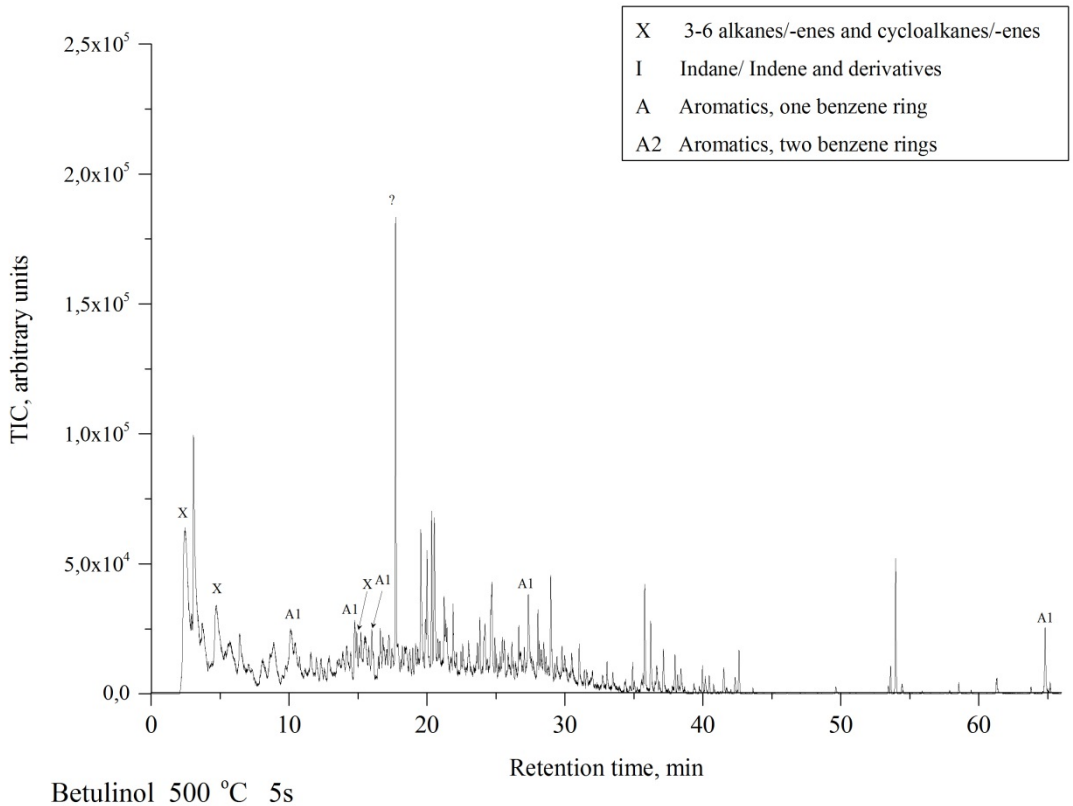

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