Chapter

Chemical Characterization of Lignocellulosic Materials by Analytical Pyrolysis

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Abstract

Analytical pyrolysis is used to chemically study complex molecular materials and is applied in a wide range of fields. Pyrolysis is a thermochemical process associated to the breaking of chemical bonds using thermal energy, transforming a nonvolatile compound into a volatile degradation mixture. This chapter refers to analytical pyrolysis of lignocellulosic materials, i.e., when pyrolysis is used for chemical characterization, applied to samples with small particle sizes, at 500–650°C, and with short residence times. The reactions that occur during pyrolysis of the structural components are discussed regarding the mechanisms and the pyrolysis products obtained from cellulose, hemicelluloses, and lignin. A compilation of data is made on the characterization of lignocellulosic materials using Py-GC/FID(MS) or Py-GC/MS as analytical tools including woods and barks of several species. The pyrogram profiles and important parameters on lignin chemical composition such as the H:G:S relation and the S/G ratio are summarized. Analytical pyrolysis is a versatile methodology that may be applied to characterize the lignin directly on the lignocellulosic material or after isolation from the cell wall matrix (e.g., as MWL or dioxane lignin) or from pulps or spent liquors. It is therefore an excellent tool to study lignin compositional variability in different materials and along various processing pathways.

Keywords: Py-GC/MS, wood, barks, lignin, cellulose, H:G:S relation, S/G ratio

1. Introduction

Analytical pyrolysis has been used to study complex molecular materials covering a wide range of fields. A search in *Scopus*® for "analytical pyrolysis" found a total of 756 publications within the subject areas of chemistry, chemical engineering, environmental science, agricultural and biological sciences, materials science, earth and planetary sciences, energy, and engineering. This clearly shows the amplitude of application of this analytical technique, highlighting its importance for the scientific community.

Pyrolysis may be defined based on the occurring chemical reactions, e.g., "the transformation of a nonvolatile compound into a volatile degradation mixture by heat, in the absence of oxygen" [1] or "the breaking of chemical bonds using thermal energy" [2], as well as on its potential applications, e.g., "the basic thermochemical process for converting biomass to a more useful fuel" [3].

The word pyrolysis is derived from *pyro* = fire and *lysis* = separation and is inherently associated with reaction pathways of combustion and coal formation. The production of wood charcoal was the first application example of pyrolysis under controlled conditions, followed by wood distillation to produce methanol, and later by the petrochemical industry where heavy crude oil fractions are transformed into light fuels.

During pyrolysis, the biomass is heated at temperatures of 400–1000°C, in an atmosphere without oxygen, for a short period of time (0.5 s to 5 min), generating bio-oil (liquid), charcoal (solid), and fuel gas products [4–6]. When pyrolysis is used for the chemical characterization of complex polymers, it is denominated *analytical pyrolysis*. This chapter only refers to procedures of analytical pyrolysis, where the sample has small particle sizes (<1 mm or <0.5 mm) and is heated at temperatures from 500 to 650°C with short residence times (10 s to 1 min).

The analysis is performed in a pyrolysis unit linked to an analytical instrument for the separation and measurement of the pyrolysis products, usually a gas chromatograph (GC). The pyrolysis unit comprises a controller (that provides the electrical energy for heating) and the pyrolyzer itself (e.g., a coil) that is heated at high temperatures. The pyrolysis units can be of several types, depending on the heating technique: (i) microfurnaces that provide constant heating, and the samples are introduced by a syringe or a small cup; (ii) Curie-point pyrolyzers, in which the sample is rapidly heated by magnetic induction; or (iii) filament style pyrolyzers that use a resistant metal for filament construction, usually platinum, that is heated following a temperature program, with the sample placed in a quartz boat if using a coil probe or placed directly into a ribbon probe [7]. Other possibilities include laser and plasma pyrolyzers [4]: the laser pyrolyzer allows the analysis directly on the solid matter with no need for sample preparation or pretreatment; the plasma pyrolyzer has a high gas productivity but is seldom used since it requires considerable electrical power consumption [4].

Pyrolysis linked to GC is a powerful combination for the characterization of complex materials: pyrolysis produces a mixture of volatile compounds that flows through a capillary column carried by an inert gas (usually helium) where the compounds are separated due to different retention times and are subsequently identified by mass spectrometry (MS) or/and quantified by a flame ionization detector (FID). An MS detector is frequently used associated with pyrolysis due to advantages in relation to speed, specificity, and sensitivity: the pyrolysis product is identified based on the selective fragmentation by electron impact and, even if a molecular ion is not found, the fragmentation pattern together with the retention time on the GC column and comparison with spectra in data bases can identify the compound [4]. The FID detector is sensitive and reliable giving nearly the same response for different organic compounds and therefore is preferred for quantification once the compounds have been identified [8].

The advantage of pyrolysis is that a wide range of macromolecules and materials (from plant materials to textiles, synthetic polymers, and many others) may be studied since they are thermally fragmented into volatile compounds that can be subsequently separated, identified, and quantified. The reactions that occur during pyrolysis of the structural components of plants—cellulose, hemicelluloses, and lignin—will be discussed in the following subsection.

The aim of this chapter is to present a compilation of data regarding the characterization of lignocellulosic materials using Py-GC/FID(MS) or Py-GC/MS as analytical tools.

1.1 Broad features of pyrolysis reactions

During pyrolysis, the molecules are degraded by the breaking of chemical bonds through homolitic scissions with formation of free radicals that further react by recombination, rearrangements, or elimination of radicals and hydrogen [2]. Any radical is instable and will react as soon as possible with other radicals or molecules. The pyrolysate composition will depend on the stability of the produced radicals or molecules, e.g., a tertiary radical is more stable than a secondary radical and is consequently produced in higher proportion.

The pyrolysis products depend on the original chemical composition of the raw material. Therefore, the pyrolysis of lignocellulosic materials will produce pyrolysis products from their main components: cellulose, hemicelluloses, and lignin. **Figure 1** presents a pyrogram of *Eucalyptus globulus* wood as an example of the complex mixture of volatile compounds that is obtained. The peaks corresponding to the fragmentation of lignin and polysaccharides are numerous, and most may be assigned as derivatives from either carbohydrates or lignin, including differentiation between the monomeric moieties of lignin.

Pyrolysis of the lignocellulosic components involves complex reactions and mechanisms that depend on pyrolysis conditions (heating rate, pressure, and temperature) and on biomass particle size [5]. The study of the thermolytic breakdown of model compounds helps to explain the global mechanisms of pyrolysis, while kinetic models are helpful to characterize the degradation steps and to predict product distribution [9–12].

1.1.1 Lignin

The lignin polymer undergoes a number of degradation reactions that include depolymerization, hydrolysis, oxidation, dehydration, and decarboxylation [13]. The thermal decomposition of the lignin polymer starts with the cleavage of the weak bonds (α-ether and β-ether bonds), releasing a mixture of phenol-, guaiacyl-, and syringyl-type derivatives, which maintain their substituents in the aromatic ring [10, 11, 14]. This enables making their correspondence with the original lignin moieties of *p*-hydroxyphenyl, guaiacyl, and syringyl moieties [1, 15]. **Figure 2** shows a few of the compounds formed during lignin pyrolysis that can be assigned to specific original moieties: H units (phenol (1) and 4-methylphenol (*p*-cresol, 4)), G units (guaiacol (2) and 4-methylguaiacol (5)), and S units (syringol (3) and 4-methylsyringol (6)).

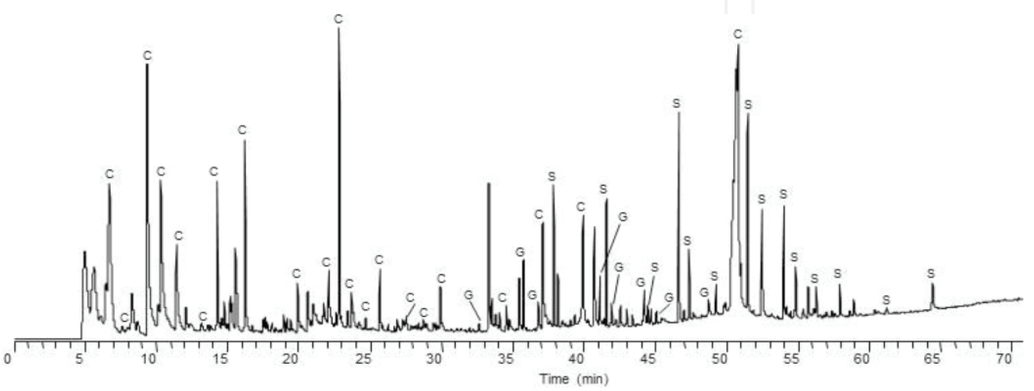

Figure 1.
Pyrogram of Eucalyptus globulus wood obtained by Py-GC/FID. The peaks are assigned to carbohydrates (C) and from lignin, distinguished in guaiacyl (G) and syringyl moieties (S).

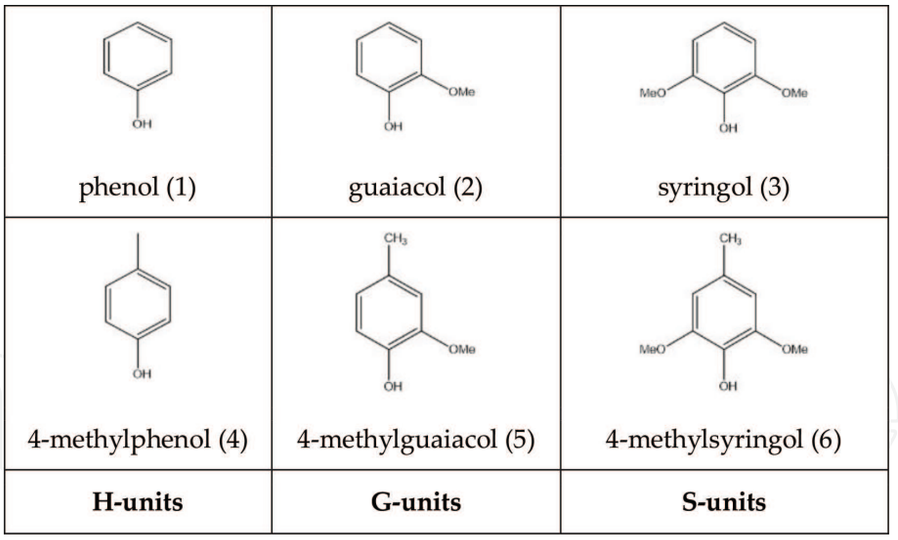

Figure 2.
Some examples of the compounds obtained from lignin pyrolysis.

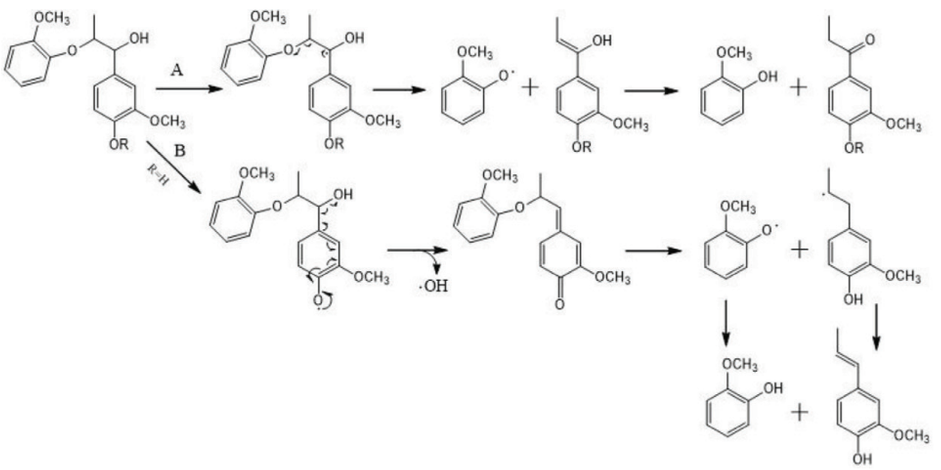

Figure 3.
Proposed radical mechanism for the formation of guaiacol (redrawn from Kawamoto [17]).

In the case of softwoods, more guaiacyl units are released during pyrolysis, while hardwoods will produce both types of compounds, in relation with the original monomeric composition of lignin [16]. Kawamoto [17] proposed two pathways for the degradation of lignin by the cleavage of ether bonds and formation of guaiacol (**Figure 3**). *Pathway A* starts with the formation of C_α radical by the liberation of hydrogen from C_α-H, followed by the cleavage of the β-ether bonds, forming $C_\alpha{=}O$ monomers and guaiacol. *Pathway B* starts with the formation of phenoxy radicals through the liberation of the phenolic OH, followed by the homolytic cleavage of the β-ether bond in the quinone methide intermediate.

The liberated compounds will further react by two possible ways: homolytic cleavage of the O-CH_3-producing catechols and pyrogallols or by radical rearrangement reactions producing cresols and xylenols [18, 19]. Recently, Kawamoto [17] presented an update on the state of art of the pathways and mechanisms involved in the lignin pyrolysis and focused upon the influence of temperature on the pyrolysis products. Pyrolysis primary reactions occur at 200–400°C, leading to the formation of 4-substituted guaiacols and 4-substituted syringols (in case of SG lignin), with the main side chains constituted by unsaturated alkyl groups and, in less extent, saturated alkyls groups [17]. The increase of temperature leads to secondary reactions, and guaiacols/syringols are degraded to catechols and cresols [17].

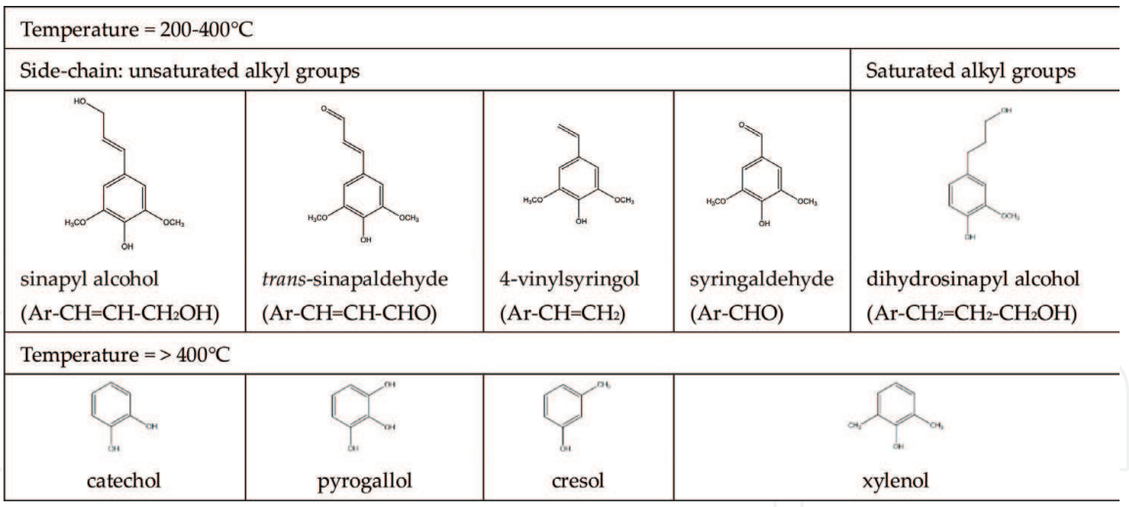

Figure 4.
Influence of the pyrolysis temperature on the aromatic side chain of an S type lignin.

Figure 4 shows the lignin degradative products from S units that are produced during the primary and secondary reactions.

Other compounds with low molecular mass are also produced during pyrolysis, such as formaldehyde, methanol, acetic acid, acetaldehyde, and water as well as gases (CO, CO_2, and CH_4) that are assumed to be liberated from the methoxy group [20, 21].

1.1.2 Carbohydrates

The degradation of cellulose and hemicelluloses by pyrolysis occurs by heterolytic cleavage of the glycosidic C-O bonds [17] and involves complex reactions and several pathways [22]. First, cellulose breaks into lower molecular mass compounds and forms the so-called "activated cellulose" that can be decomposed by two competitive reactions, generating volatiles (anhydrosugars) or char and gases [3]. Volatiles are composed by the cellulose monomeric units including levoglucosan (7, **Figure 5**), levoglucosenone, and 1,4:3,6-dianhydro-α-D-glucopyranose [23, 24]. Levoglucosan is produced by the cleavage of the 1,4-glycosidic linkages followed by dehydration (**Figure 6**) [25]. The yield is influenced by the cellulose characteristics (purity and physical properties), by the pyrolysis conditions [22, 26], and also by the presence of inorganic compounds [27].

Cellulose pyrolysis produces also some compounds with low molecular mass (**Figure 5**), such as hydroxyacetaldehyde (8), 1-hydroxypropan-2-one (9), 1-hydroxybutan-2-one, and 2-furaldehyde (10) [3]. Hydroxyacetaldehyde is obtained by cleavage of a C-C linkage followed by ring opening, while 1-hydroxy-2-propan-2-one is formed by dehydration and decarboxylation reactions [28], where both compounds compete with levoglucosan formation [29].

The degradation of hemicelluloses involves pathways that are similar to those of cellulose and produces the same type of compounds [30]. For instance, xylan pyrolysis produces 1,4-anhydroxylopyranose, 1,5-anhydro-4-deoxy-pent-1-en-3-ulose [31], 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one (11, **Figure 5**), a xylan marker [32], and 2-furaldehyde [28, 31], but not levoglucosan [30].

Other compounds, such as 2-furaldehyde and acetic acid, can be produced by either hemicelluloses or cellulose [28]. For instance, two chemical pathways lead to formation of 2-furaldehyde from xylan: (i) depolymerization of xylan by cleavage of the hemiacetal bond (between C1 and oxygen on the pyran ring) with ring opening, followed by dehydration between OH in C2 and C5 positions; (ii) cleavage of the 1,2-glycosidic bond between the 4-O-methyl-glucuronic acid unit and the xylan

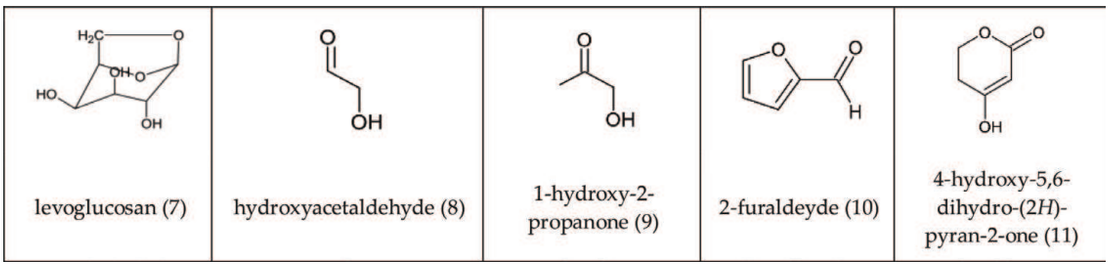

Figure 5.
Compounds obtained by the pyrolysis of carbohydrates.

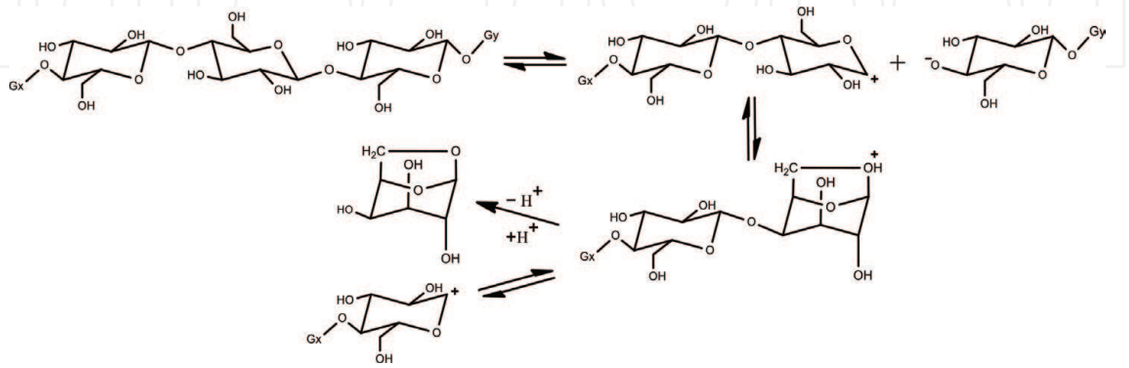

Figure 6.
Mechanism of levoglucosan formation (redrawn from Patwardhan et al. [24]).

unit, followed by ring opening and rearrangement of the 4-O-methyl-glucuronic acid after elimination of the methanol and CO_2 [33]. Acetic acid may also be formed by two possible pathways: (i) by elimination of acetyl groups linked to C2 in the xylan chain and (ii) elimination of the carbonyl and O-methyl groups [33].

Thus, the pyrolysis of polysaccharides has a particular aspect that is the production of the same compounds by thermal degradation of both cellulose and hemicelluloses, e.g., furans and pyrans have distinct molecular ions, but both can be obtained either from cellulose (hexose-based) or from hemicelluloses (hexose- and pentose-based) [34]. This fact contributes for the difficulty of distinguishing the origin of a polysaccharide-derived pyrolysis compound. Overall, carbohydrate-derived pyrolysis products are considerably more difficult to identify by mass spectrometry when compared to lignin-derived products for several reasons [35]: (i) the mass spectra of the carbohydrates are less specific since they are easily fragmented; (ii) there are several structural isomers with identical mass spectra; and (iii) the presence of inorganic compounds has a catalytic effect on the pyrolytic degradation of polysaccharides. Analytical pyrolysis is therefore less suitable for the determination of carbohydrates composition, e.g., the quantification of pentoses and hexoses.

1.2 Factors affecting pyrolysis reactions

Pyrolysis yields and product composition can be influenced by several factors:

i. The feedstock and its chemical composition, where different materials will produce, by pyrolysis, different types of compounds [3, 36].

ii. The presence of inorganic salts increases the formation of small molecules [37, 38], thereby reducing the proportion of large molecules that provide better structural information [39], and contributes for the production of levoglucosan [38].

iii. The sample components can interact during pyrolysis, e.g., the interaction between cellulose and hemicelluloses promotes the formation of furans and inhibits the formation of levoglucosan [40], while the presence of pyrolysis vapors from cellulose and lignin induces the secondary degradation of levoglucosan [41].

iv. The particle size influences the heating rate of the material: if the sample is composed of fine particles, the heating rate is uniform, and less interaction will occur between the produced primary compounds, thereby limiting secondary reactions [42].

v. The operating temperature influences the compounds produced [9, 43]: increase of temperature rises the yield of smaller products and gases, while it induces more secondary reactions. For example, the formation of levoglucosan occurs above 260°C, but in the range from 450 to 500°C, degradation products such as hydroxyacetaldehyde start to be formed [9]. Also, to degrade suberin (a cell wall polymer of barks) into volatiles, higher temperatures (above 650°C) are required as discussed by Marques and Pereira [44].

1.3 Advantages and disadvantages of analytical pyrolysis

Pyrolysis can be used to study complex molecular structures, covering wide and diversified fields: fibers and textiles, forensic materials, wood and paper, art materials, synthetic polymers [2]. Analytical pyrolysis presents some advantages over other chemical techniques to characterize lignocellulosic materials:

i. It is a rapid technique when compared with others, as it involves a simple sample preparation (extraction and milling), and data acquisition only takes from a few minutes to 1.5 h [1].

ii. It requires only a small sample size (1–100 μg) [45].

iii. It presents good reproducibility [46], provided that the sample is consistent in size [4] and distribution, for example, in a quartz boat.

iv. It does not require pre-isolation of the compounds to be studied [1]; for example, the lignin content in the sample can be determined without isolation as required in wet chemistry procedures.

v. The lignin and phenolic acid compounds are easily identified by mass spectrometry [15], because they maintain the ring substitution patterns from the lignin polymer and therefore can be identified as being derived from the *p*-hydroxyphenyl (H), guaiacyl (G), or syringyl (S) units of lignin [1].

vi. It provides information about S, G, and H lignin units [1, 47], enabling the calculation of the S/G ratio; this is a valuable parameter, for example, to determine the quality of pulpwood materials.

Nevertheless, pyrolysis also presents a few disadvantages:

i. It has limitations when analyzing samples constituted of carbohydrates, since during pyrolysis, their derivatives can originate either from hexoses or pentoses [34].

ii. The pyrolysis results are highly influenced by the methodology used, i.e., the conditions applied, such as time, temperature, and type of GC column, which can result in discrepancies when comparing results obtained by different authors.

iii. Attention must be paid when analyzing barks rich in suberin, for which the adequate temperature range to determine the H:G:S relation is 550–600°C, and higher temperatures should be applied if suberin composition is the target of the analysis [48].

2. Characterization of lignocellulosic materials

Analytical pyrolysis is an important tool for the chemical characterization of several lignocellulosic materials such as wood (softwoods and hardwoods), barks, pulps, and lignins and is an essential instrument to support the objective of potentiating their use as raw materials for different applications.

Table 1 makes a synthesis of results obtained by analytical pyrolysis for different lignocellulosic materials. Most wood species were studied due to their economic importance as pulping raw materials such as spruce and pine (softwoods) and birch and eucalypt (hardwoods), while herbaceous species are increasingly considered as fiber and energy sources. In addition, barks are important industrial residues with potential for added-value products under the biorefinery context in a circular economy.

An analysis of the available information regarding determination of lignin composition and content by analytical pyrolysis is made subsequently. Some studies applied analytical pyrolysis directly to the extractive-free material, while others studied isolated lignins, e.g., as MWL. This will be specified for each case.

2.1 Wood from gymnosperms

2.1.1 Picea abies

Lignin content in spruce determined by analytical pyrolysis was near the values obtained by wet chemical analysis as Klason lignin (21.6–25.7% of extractive-free dry wood) [49, 50]. Spruce presented more G lignin units (21.9% of identified compounds) and less H units (1.0%). The main pyrolysis products derived from G units were 4-vinylguaiacol (2.5%), 4-methylguaiacol (2.6%), coniferyl aldehyde (2.4%), and guaiacol (1.6%), while only phenol and cresol isomers were derived from H lignin [49]. The carbohydrates represented around 77% (of identified compounds), where levoglucosan was 11.1%, followed by hydroxyacetaldehyde (13.1%), and propanal-2-one (7.3%). The ratio between carbohydrates and lignin (C/L) was 3.4 [49]. The pyrolysis of spruce milled wood lignin (MWL) with addition of TMAH (tetramethylammonium hydroxide) and under different temperatures (310–710°C) showed that the lowest temperature (310°C) produced the highest yield of lignin monomers with intact propane side chain and minimized the production of unmethylated lignin monomers such as phenols and methoxyphenols [51].

2.1.2 Pinus pinaster

The lignin content of maritime pine wood determined by pyrolysis was well correlated with the Klason values determined by wet chemical analysis (23.0–29.6%

Species	Component	Lignin content (%)*	S/G	H/G	H:G:S	C/L	Ref.
SOFTWOODS							
Pinus pinaster	Wood	23.0-29.6	-	0.041-0.113	1:16:0	2.95	[49, 50]
Picea abies	Wood	21.6-25.7	-	0.034-0.118	1:23:0	3.36	[49, 50]
Pseudotsuga menziesii	Cork	-	0.1	-	1:7:0.8	-	[80]
HARDWOODS							
Eucalyptus globulus	Wood Pulps	23.0/23.7 ** 2.2/2.3**	1.9-5.4 0.58/ 0.51*	- -	1:8:29/ 1:11:39** 1:2:1**	3.2/ 3.1** 2.7-44.3	[55, 56]
Paulownia fortunei	Wood***	-	0.67	-	1:59:40	-	[67]
Tectona grandis	Sapwood Heartwood Bark	35.4 37.3 28.0	0.7 0.8 0.8	- - -	1:34:24 1:29:23 1:11:9	0.89 0.85 0.91	[69]
Quercus suber	Wood*** Phloem*** Cork***	- - -	1.2 0.7 0.1; 0.03	- - -	- - 1:11:0.3	- - -	[68, 75]
Quercus cerris	Wood Cork	- -	0.71 0.01	- -	1:52:37 1:38:1	- -	[48]
Betula pendula	Wood Cork	- -	1.5 0.14	- -	1:26:40 1:36:5	- -	[48]
MONOCOTYLEDONS							
Ensete ventricosum	Fibers Stalks	6.1 4.6	1.1 0.5	- -	1:0.7:0.8 1:0.4:0.2	11.0 13.4	[77]
Saccharum ssp.	Straw*** Bagasse***	- -	0.4 1.6	- -	1:17:7 1:19:30	- -	[76]

**% of lignin-derived peaks in the total chromatographic area;*
***sapwood and heartwood respectively;*
*****Björkman lignin.*

Table 1.
Chemical characterization by analytical pyrolysis of lignin in biomass components of different species.

of extractive-free dry wood) [49, 50]. Lignin was constituted predominantly by G units (23.7% of identified area) and less H units (1.6%) in accordance with softwood lignin literature compositional data [52]. The main compounds obtained were 4-vinylguaiacol (2.9%), 4-methylguaiacol (2.7%), coniferyl aldehyde (2.5%), and guaiacol (2.1%) [49]. The pyrolysis compounds derived from carbohydrates represented 75% (of the total identified compounds), where levoglucosan was the main compound (12.5%) followed by hydroxyacetaldehyde (11.6%) and propanal-2-one (7.4%). The C/L ratio was 2.9 [49]. Alves et al. [53] showed that analytical pyrolysis conjugated with PCA analysis may be a potent tool for lignin origin discrimination, e.g., pine, spruce, and larch wood samples could be separated and, in the case of maritime pine, it was also possible to separate samples from two sites and between reaction wood and normal wood.

2.1.3 Pinus sylvestris

Scots pine wood pyrolysis produced a high amount of lignin-derived products from guaiacyl units (vanillin, homovanillin, acetaldehyde, coniferyl aldehyde, and coniferyl alcohols), and the highest peaks from carbohydrate-derived products were 5-hydroxymethyl-2-tetraydrofuraldehyde-3-one, 5-hydroxymethyl-2-furaldehyde, and levoglucosan [54].

2.2 Wood from angiosperms

2.2.1 Eucalyptus globulus

Sapwood and heartwood samples were characterized by a similar content in lignin, respectively, 23.0 and 23.7%, in extractive-free base [55, 56]. The main lignin products were 4-vinylsyringol (12.0 *vs*. 11.4% of total area), 4-propenylsyringol (10.3 *vs*. 10.4%), syringol (10.0 *vs*. 7.0%), syringaldehyde (7.5 *vs*. 7.4%), 4-methylsyringol (5.4 *vs*. 6.5%), and 4-allysyringol (4.0 *vs*. 3.8%). Sapwood presented the highest value of S/G ratio comparatively to heartwood (3.63 *vs*. 3.45), with an H:G:S relation of 1:8:29 and 1:11:39 [55]. Carbohydrates represented 49.2% (sapwood) and 43.3% (heartwood) of total chromatographic area, and their pyrolysis produced mainly levoglucosan (22.7 *vs*. 27.5%), hydroxyacetaldehyde (12.7 *vs*. 12.4%), oxo-propanal (10.5 *vs*. 10.1%), acetic acid (9.3 *vs*. 8.0%), and in minor amounts 4-hydroxy-5,6-dihydro-2H-pyran-2-one, 2-furaldehyde, and 3-hydroxypropanal in percentages between 5.1 and 2.5%. No great differences were attained between the carbohydrate-to-lignin ratio (C/L) with values of 3.2 and 3.1 [56].

Eucalypt wood was characterized by different authors in relation to the syringyl-to-guaiacyl (S/G) ratio, and a large variation range was observed: 5.4 [57], 4.3 [58], 4.1 [59], and 1.9–2.3 [60]. Such differences may derive from the tree origin [61] and the lignin heterogeneity as discussed by Yokoi et al. [62]. Eucalypt MWL isolated by the Björkman method had an S/G ratio of 3.0 [63], while eucalypt dioxane lignin was characterized with an S/G ratio of 5.6 and an H:G:S relation of 1:30:169 [64].

Other eucalypts, such as *Eucalyptus camaldulensis* trees presented S/G ratios ranging from 1.5 to 2.2 depending on the seed origin. The pyrograms profile regarding the distribution of the lignin-derived compounds showed a similar tendency: vinylsyringol, syringol, guaiacol, trans-coniferyl alcohol, and *trans*-sinapyl alcohol were the main pyrolyzates [62].

2.2.2 Fagus sylvatica

Beech MWL had a monomeric composition with more syringyl units (56.8% of the total lignin-derived compounds) over guaiacyl units (37.2%) and phenol groups (1.2–1.8%) showing that beech wood has an SG type of lignin. The lignin pyrogram showed a predominance of alcohol compounds such as coniferyl alcohol (13%) and sinapyl alcohol (10%), and less guaiacol (4.7%) and syringol lignin units (9.0%) [65]. Choi et al. [66] observed in the pyrograms of beech MWL other synapyl-derived compounds such as sinapaldehyde (12.4%), followed by syringol, 4-vinylsyringol, and syringaldehyde with 8.7%, and 4-methylsyringol (7.7%), and guaiacyl-derived compounds such as 4-vinylguaiacol (6.0%), guaiacol (4.6%), and 4-methylguaiacol (4.2%).

2.2.3 Paulownia fortune

The MWL pyrograms presented a predominance of guaiacyl over syringyl units and only small amounts of *p*-hydroxycinnamyl units (~1%), corresponding to an

H:G:S relation of 1:59:40 and an S/G ratio of 0.7 [67]. The main lignin-derived compounds released during pyrolysis were in molar % of the total peaks: guaiacol (9.0%), 4-vinylguaiacol (8.3%), 4-methylguaiacol (6.8%), syringaldehyde (5.3%), syringol (7.5%), vanillin (4.8%), *trans*-isoeugenol (4.8%), *trans*-coniferaldehyde (4.7%) *trans*-coniferyl alcohol (4.3%), 4-vinylsyringol (4.2%), 4-methylsyringol (4.1%), *trans*-4-propenylsyringol (3.0%), and *trans*-sinapaldehyde (4.0%) [67].

2.2.4 Quercus suber

Lourenço et al. [68] recently studied the wood from cork oak trees. The milled wood lignin was characterized with more syringyl lignin units, where the pyrolysis products were mainly 4-methylsyringol (15.9 *vs*. 8.9% in relative molar %), syringol (14 *vs*. 12.3%), 4-methylsyringol (10.0 *vs*. 15.8%), 4-vinylsyringol (4.5 *vs*. 11.6%), and guaiacol (7.3 *vs*. 13.1%). Marques and Pereira [48] reported for wood lignin a H:G:S relation of 1:25:24 and an S/G ratio of 0.9.

2.2.5 Tectona grandis

Teak sapwood and heartwood presented a similar lignin content of, respectively, 35.4 and 37.3% (extractive-free material), with a composition predominantly of guaiacyl units (57.6 and 54.4% of total lignin units), lower syringyl units (40.6 and 43.8%), and only 1.8% of *p*-hydroxyphenyl units [69]. The main lignin-derived compounds in the pyrolysis products were 4-vinylsyringol (6.3 and 6.9% of total chromatographic area), *trans*-coniferyl alcohol (4.5 and 4.4%), coniferaldehyde (2.0% in both), 4-vinylguaiacol (1.6%), 4-methylguaiacol (1.6%), and vanillin (1.5%). Therefore, teakwood lignin is a GS type of lignin with an H:G:S relation of 1:34:24 (sapwood) and 1:29:23 (heartwood) and an S/G ratio of 0.7 and 0.8, respectively. Carbohydrates represented 31.6% in sapwood and 31.6% in heartwood (% of total area), with a predominance of levoglucosan (15.2 and 14.4%), 2-hydroxymethyl-5-hydroxy-2,3-dihydro-4H-pyran-4-one (3.6%), and around 1.5% of furfural, 4-hydroxy-5,6-dihydro-2H-pyran-2-one and 5-hydroxymethyl-2-furaldehyde. The carbohydrate-to-lignin ratio was 0.89 and 0.85 in, respectively, sapwood and heartwood [69].

2.2.6 Betula pendula

Birch wood lignin has a monomeric composition with an H:G:S relation of 1:26:40 and an S/G ratio of 1.5 [48]. Ghalibaf et al. [70] studied untreated and treated (with hot-water-extracted) birch samples by Py-GC/MS under different temperatures (500–700°C) and reported an enhanced production of furan derivatives at 500°C and an increase of aromatic compounds when the temperature rises from 500 to 700°C. The carbohydrates-to-lignin ratio was 2.2 (untreated) and 1.4 (treated).

2.2.7 Cynara cardunculus

Cardoon stalks were separated in pith and depithed samples and characterized by Py-GC/MS(FID). The lignin content in stalks was in average 22.9%, ranged in pith from 18.8 to 24.6% and in depithed stalks from 22.7 to 25.5% [71]. The monomeric composition was slightly different between pith and depithed stalks: guaiacyl units predominated in depithed stalks (40 *vs*. 29% of total chromatographic area), syringyl units were predominant in pith (64 *vs*. 53%), and the same amount of H units was found in both (7%). The distribution of the main lignin products of cardoon pyrolysis

was: 4-vinylsyringol (in average 2.9% of total area), 4-propenylsyringol (2.0%), sinapinaldehyde (1.4%), *trans*-sinapyl alcohol (1.3%), syringol (1.0%), and *trans*-coniferyl alcohol (1.0%). In lower amounts (ca. 1%) were obtained: 4-methylguaiacol (0.9%), syringaldehyde (0.9%), 4-propylguaiacol (0.8%), and 4-vinylguaiacol (0.7%). The lignin monomeric composition presented an H:G:S relation of 1:4:9 (pith) and 1:6:8 (depithed), corresponding to an S/G ratio of 2.2 and 1.3 [71]. Cardoon lignin is an SG type of lignin, with more syringyl units compared to guaiacyl and less content of hydroxyphenyl units. Carbohydrates represented in average 21.8% in pith and 23.9% in depithed stalks (% of total chromatographic area). The carbohydrate pyrolysis products were levoglucosan as the main compound (7.6%), followed by 4-hydroxy-5,6-dihydro-2H-pyran-2-one (3.6%), furfural (2.3%), 2-hydroxymethyl-5-hydroxy-2,3-dihydro-4H-pyran-4-one (1.5%), and 3H-pyran-2,6-dione (1.3%).

The lignin present in the whole stalks was studied after isolation by the Björkman method (MCyL) and characterized by Py-GC/MS [72]. In general, there was a similar distribution of the lignin-derived compounds formed during pyrolysis of MCyL comparatively to depithed and pith samples pyrolysis, and the G units were released in higher abundances than the respective S units, attaining an S/G molar ratio 0.3.

2.2.8 Linum usitatissimum

Flax fibers and shives were studied regarding its lignin composition, after isolation by Björkman procedure [73]. The lignin-derived compounds released by pyrolysis were guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-vinylguaiacol, vanillin, syringol, *trans*-isoeugenol, and 4-methylsyringol. Flax shive lignin also released high amounts of *trans*-coniferaldehyde and *trans*-coniferyl alcohol contrasting to the minor compounds produced by flax fiber lignin. Milled lignins presented significant differences in respect to H:G:S molar ratio of 1:6:1 (fibers) and 1:17:2 (shives), and the values of the S/G ratios were low in both lignins, with a ratio of 0.2 (fibers) and 0.1 (shives).

2.3 Monocotyledons

2.3.1 Miscanthus

Py-GC/MS was used to examine genotype and harvest influence upon the chemical composition [74]. The most abundant compounds were acetic acid, 4-ethenylphenol, and levoglucosenone. The effect of harvest time upon the relative amount of pyrolysis compounds was small, but the samples collected during February produced higher amounts of 2-propenoic acid methyl ester, 3-hydroxypropanal, (2H)-furan-3-one, 2-hydroxy-3-oxobutanal, and 1,5-anhydro-β-D-xylofuranose.

2.3.2 Bamboo

Milled lignin presented a lignin composition rich in G units (68% of identified lignin compounds), followed by S units (21%), and H units (11%) and included *p*-coumaric acids as degradation products [75]. Therefore, the correspondent H:G:S relation was 1:6:2 and the S/G ratio 0.3.

2.3.3 Saccharum ssp.

Sugarcane straw and bagasse presented differences regarding lignin composition. The isolated lignin from bagasse is rich in syringyl units, with an H:G:S

relation of 1:19:30 and an S/G ratio of 1.6. Straw lignin is rich in guaiacyl units, with an H:G:S relation 1:17:7 and an S/G ratio of 0.4 [76].

2.3.4 Ensete ventricosum

Enset or false banana fibers and inflorescence stalks were characterized by Py-GC/MS by a low amount of lignin (6 and 5% of total pyrogram area). The fibers presented a similar content in H units, but more G and S units when compared to stalks. Therefore, the H:G:S relation was 1:0.7:0.8 and 1:0.4:0.2,respectively. The S/G ratio values were 1.1 (fibers) and 0.5 (stalks). The fibers and the stalks presented a great amount of carbohydrates (67 *vs*. 62% of total pyrogram area), where levoglucosan was the main compound (17.1 *vs*. 5.4%), followed by 2-hydroxy-2-cyclopenten-1-one (1.4 *vs*. 3.1%), 2-hydroxymethyl-5-hydroxy-2,3-dihydro-(4H)-pyran-4-one (1.1 *vs*. 0.7%), and 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one (1.2 *vs*. 0.3%) [77].

2.4 Barks

Barks are structurally heterogeneous and include phloem and periderm, and often a rhytidome with several superposed periderms [78]. Periderm contains cork (phellem), a tissue that differs chemically from wood and phloem by the presence of suberin as one of the cell wall structural polymers. The extent of cork proportion varies between species and some have cork-rich barks [79]. When chemically characterizing barks, it is therefore important to specify if the whole bark is analyzed or if the components are separated, i.e., in cork and phloem, for instance.

2.4.1 Pseudotsuga menziesii

Douglas-fir cork was separated from the whole bark and used for analysis. Cork was constituted by a lignin content of 60% (% total pyrogram) and carbohydrates content of 40% [80]. Cork pyrolysis products were mainly G units (~81% of lignin units): 4-vinylguaiacol (13%), 4-methylguaiacol (9%), guaiacol (6%), vanillin (5%), and eugenol, while the H units represented 11%, with phenol and dimethylphenol isomers as main derivatives, respectively, 1 and 4%. The S units were minority (~9%), mainly represented by syringol (2%) and 4-methylsyringol (2%) [80]. The H:G:S was 1:7:0.8 and the S/G ratio was 0.1. Some differences were found when Björkman lignin was isolated from saponified cork: the H:G:S relation was 1:40:1, while the S/G ratio was 0.02, revealing an enrichment of guaiacyl units and a decrease in H units with the isolation.

2.4.2 Quercus suber

The cork lignin represented 60.7%, with a predominance of guaiacyl units (84.7% of total lignin units), followed by *p*-hydroxyphenyl units (12.8%), and with a minor percentage of S units (2.5%); thus the H:G:S was 1:6.6:0.2 and the S/G ratio was 0.02 [75]. The prevalent degradation products from the G moieties in lignin were guaiacol, 4-methylguaiacol, 4-vinylguaiacol, isoeugenol, vanillin, and coniferyl alcohol and those from the S units were syringol and 4-methylsyringol [48, 75]. Cork pyrolysis produced a total carbohydrate of 39.3%, where hexoses represented 57% and pentoses 43% [75]. Björkman lignin was isolated from cork, and the results showed a predominance of guaiacyl units (~90% of lignin units), a decrease of H and S units, contributing for an H:G:S relation of 1:11:0.3 and an S/G ratio of 0.03 [75]. The milled lignin isolated from phloem tissue presented an S/G ratio of 0.62 [68].

2.4.3 Quercus cerris

The cork of *Q. cerris* was manually separated from bark and characterized by Py-GC/MS(FID). Cork presented a lignin content of 31.8% (% of total area), 8.5% of carbohydrates, with aliphatic compounds derived from suberin representing 18.4%. Lignin had a monomeric composition largely of G units (93.7%), with a low proportion of S and H units, respectively, 2.7 and 3.6%, which corresponds to an S/G ratio of 0.01 [48].

2.4.4 Betula pendula

The cork from birch bark is constituted predominantly by guaiacyl units (85.7% of total lignin) with a minor proportion of syringyl units (11.9%) and *p*-hydroxyphenyl (2.4%), corresponding to an H:G:S relation of 1:36:5 and an S/G of 0.14 [48].

2.4.5 Tectona grandis

The whole teak bark was characterized with a lignin content of 28.0% determined by analytical pyrolysis (PY-GC/MS(FID)) [69]. The main pyrolysis compounds were 4-vinylsyringol and *trans*-coniferyl alcohol with, respectively, 1.4 and 2.7%. Teak bark has a GS type of lignin, with G units reaching 53.3% of the total lignin units, followed by S units with 42.1%, and a minor amount of H units (4.6%). The relation H:G:S was 1:11:9, and the S/G ratio was 0.8 [69].

3. Characterization of cellulosic pulps and isolated lignins

3.1 Cellulosic pulps

The lignin monomeric composition evaluated by the S/G ratio is a valuable parameter to estimate the aptitude of a raw material for pulping by predicting the ability of the material for delignification, the chemical consumption, and in some cases pulp yield, given the different reactivity of the lignin moieties in the pulping liquor. Some works used analytical pyrolysis to characterize the pulps in respect to lignin and, in some cases, to carbohydrates.

Ohra-aho and coworkers [81] characterized kraft pulps from *Pinus sylvestris* wood before and after bleaching. The hydroxyphenyl lignin units (phenol, 2-methylphenol, and 4-methylphenol) were highly enriched in the unbleached and bleached pulps: the proportion of hydroxyphenyl structures in the fully bleached pulp was threefold in comparison to the unbleached pulp, while in wood chips the proportion of hydroxyphenyl structures was less than 1%. This enrichment in hydroxyphenyl structures is a documented fact, but the reason for the phenomenon has been unclear.

As regards *Eucalyptus globulus* wood, a correlation between pulp yield and the lignin monomeric composition of the starting material was shown, with woods with high S/G ratios (4.0–6.4) producing kraft pulps with higher pulp yields (46.6–59.6%) [46]. Lourenço et al. [55, 56] studied the kraft pulping behavior of sapwood and heartwood of eucalypt wood along delignification (from 1 to 180 min) and at different temperatures (130, 150, and 170°C). The residual lignin in the pulps was different from that of the initial wood and differed with time, i.e., the pulps were enriched in G and H units along delignification. The kinetics of the process showed that only small differences were found between S and G units reactivity during the bulk phase, while the higher reactivity of S over G units was better expressed in the later pulping stage. The S/G ratio ranged between 3 and 4.5 when the pulp residual

lignin was higher than 10% but decreased rapidly to less than 1 in the more delignified pulps [82]. The C/L values were the same in heartwood and sapwood (3.2) and remained constant during the first pulping times until a loss of 60% in lignin and 15–25% in carbohydrates occurred; after that, the ratio increased severely until 44, corresponding to the removal of 95% of lignin and 25–35% of carbohydrates [56].

3.2 Isolated lignin from cellulosic pulps and liquors

Residual lignin from *Picea abies* pulps was isolated and characterized by pyrolysis. The lignins presented an H:G relation of 1:47, 1:17, 1:12, and 1:42, respectively, for the kraft, sulfite, ASAM, and soda/AQ/MeOH pulps [66]. Overall, the main lignin-derived compounds were the same in all the isolated lignins but were produced in different percentages depending on the pulp. For example, guaiacol was the major lignin-derived pyrolysis product from kraft and soda/AQ/MeOH pulps (23.8 and 23.6% of the total lignin peaks), while 4-vinylguaiacol was the main lignin-derived compound in the lignin from ASAM pulp (22.6%) [66].

Ibarra and coworkers [63] isolated the lignin from the pulping liquor and from the pulp of *Eucalyptus globulus*: (i) after acidic precipitation from the kraft liquors and (ii) after enzymatic hydrolysis of the kraft pulps (unbleached, delignified with oxygen, and bleached with peroxide). Kraft lignin recovered from the liquor was characterized mainly with syringol (23.7 molar relative abundance), 4-methylsyringol (16.7), 4-vinylsyringol (10.5), guaiacol (6.1), 4-vinylguaiacol (6.2), *trans*-isoeugenol (3.3), and the S/G ratio reported was 5.2, showing a preferential solubility of syringyl units during pulping, as discussed by Lourenço et al. [82]. In the case of the lignin isolated from the pulps, the main compounds produced were the same mentioned for kraft lignin but were formed in minor amounts as shown by the S/G of 3.0, 3.0, and 3.9, respectively, for unbleached, bleached with oxygen, and bleached with peroxide [63]. These values are closer to the reported for eucalypt MWL, indicating that the lignin modified during pulping was released to the liquor and the pulps retained a residual lignin with features near to those of native lignin.

The lignins isolated enzymatically from pulps produced with beech wood (*Fagus sylvatica*), with different delignification processes, were characterized by an H:G:S relation of 1:20:14, 1:7:6, 1:78:88, and 1:20:13 for, respectively, kraft, sulfite, ASAM, and soda/AQ/MeOH pulps, while the corresponding S/G ratio values were 0.68, 0.77, 1.12, and 0.66 [66]. The main lignin-derived compounds produced by pyrolysis were 4-vinylsyringol (17.5% of total lignin) in lignin from sulfite pulp, and syringol (16.8, 17.4, and 21.5%) in, respectively, ASAM, kraft, and soda/AQ/MeOH pulps.

4. Concluding remarks

Analytical pyrolysis has proved to be an important tool for chemical characterization of lignocellulosic materials, including woods and barks, in particular to evaluate the lignin monomeric composition and its composition during delignification and bleaching process for the production of cellulosic pulps. Analytical pyrolysis is a versatile methodology that may be applied to characterize the lignin directly on the lignocellulosic material or after isolation from the cell wall matrix (e.g., as MWL or dioxane lignin) or from spent liquors.

Pyrolysis presents several advantages, such as the small sample size, easy preparation, and is a rapid technique with good reproducibility, although it has constraints regarding the influence that the analysis conditions have on the obtained

pyrolysis products and the little information given regarding carbohydrates profile. It is, however, an excellent methodology with a high potential to study lignin compositional variability in different materials and along various processing pathways.

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