

Chapter 2

Qualitative and Quantitative Analysis of Lignins from Different Sources and Isolation Methods for an Application as a Biobased Chemical Resource and Polymeric Material

Basma El Khaldi-Hansen, Margit Schulze, and Birgit Kamm

Abstract Lignins in general have been extensively studied, though the relation between source, isolation method and application is rarely described. In the present work, lignin from different sources (wheat straw and beech wood) and isolation methods (steam explosion, Organosolv) has been characterized regarding their application as a chemical resource and polymeric material. A range of analytical methods were applied including elemental analysis, FT-IR, ^{31}P NMR, SEC, Py-GC-MS and HPLC to gain information about establish the purity, structure, molecular weight, thermal behavior and to determine carbohydrate residues according to the NREL protocol. TGA and DSC were used to study the thermal behavior of the isolated lignins and showed relatively low glass transition temperatures around 120 °C and decomposition temperatures between 340 and 380 °C. NREL analysis presented a carbohydrate-free lignin fraction derived from beech wood via Organosolv process which has not been achieved to date. The finding of this work supports Organosolv as an efficient method to isolate pure lignin fractions from beech wood with practical value in industry, in particular for application in polyurethanes and phenolic resins.

Keywords Lignin • Organosolv process • Beech wood • Analytics • Chemical resource • Biobased polymeric material

Dedicated to Michael Kamm, Founder of biorefinery.de GmbH.

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2.1 Introduction and Research Question

The application and use of renewable raw materials for the production of base and fine chemicals is becoming increasingly significant. Although the petroleum prices plunged in 2014, the more significant need is to reduce the vast CO₂ emissions which are responsible for global warming (Hoglund 2015). The use and/or processing of fossil-based raw materials must be reduced. This can only happen by substituting fossil fuels with alternative energy sources such as rapeseed oil, bioethanol or wind energy. Another means of reducing CO₂ emissions is the production of energy and of base and fine chemicals from renewable raw materials such as biomass that contains lignocellulose (Kamm et al. 2006). Obtaining chemicals used industrially from renewable raw materials would lessen dependency on crude oil. Interest in researching lignocellulose-containing biomass has greatly increased in the last decade, since it definitely has potential as a source of raw materials for base chemicals. In Western Europe, approx. 40.5 million metric tons of ethylene and propylene are required every year. Today, the global production of base and fine chemicals including polymers is at more than 500 million metric tons (VdCI 2004). This illustrates the major requirement in quantity terms for renewable raw materials.

Worldwide, nature offers us approx. 170 billion metric tons of plant biomass annually, but currently only approx. 3 % ($1.8\text{--}2 \times 10^{11}$ t) of this is used worldwide in production annually in the “non-food” sector as, among other things, fuels (methanol, heating oil, biodiesel), bio-based chemicals (phenols, furfurals, fatty acids) and biopolymers (in paints, varnishes, cleaning agents, additives) (RBACAS 2004; Froböse 2004).

The principle of sustainability was introduced in 1992 in the Rio Declaration and Agenda 21 at the United Nations Conference on Environment and Development (R.o.t.U.N.C.o.E.a. 1992). For the implementation of sustainable development, the American chemical industry, for example, decided upon the Vision 2020 programme which described recommendations for attaining specific sustainability goals. One recommendation alludes to the use of renewable raw materials as a source of chemicals, specifically cellulose and carbohydrates (TUCI 1992).

The EU, too, is aiming to obtain 30 % of chemicals sustainably from renewable raw materials by 2025 (ETPSC 2005). One possible approach for achieving this is the construction of lignocellulose biorefineries (Kamm et al. 2007). Figure 1.1 shows the schematic structure and the product tree of a lignocellulose biorefinery. Lignocellulose-containing biomass contains cellulose (40–50 %), lignin (16–33 %), hemicelluloses (15–30 %) and extractive constituents (1–10 %). Cellulose is an unbranched glucose polymer which, by virtue of the linked structure of the linear β -1,4-glycosidic bonds, forms microfibrils which bundle to form crystalline macrofibrils (Krässig 1993). These fibrils link up with one another through hemicelluloses, which produces the “backbone” of plant cell walls (Jayme and Hunger 1957).

Hemicellulose is an amorphous, branched heteropolymer. This association of cellulose and hemicellulose is surrounded by lignin, a three-dimensional network of phenylpropane units (Fengel and Wegener 1989). Lignin constitutes approx. 20 % of terrestrial biomass and is therefore quantitatively the second largest organic material (Blazei 1979). Currently it is still primarily used as a fuel, but structurally has major

potential for replacing fossil-based sources of carbon (Tomani and Axegard 2011). The US Department of Energy estimates that approx. 1.3 billion metric tons of biomass are available in the USA alone for use in biorefineries (Perlack and Wright 2005). The utilization of these quantities in turn generates approx. 225 million metric tons of lignin, which is then available for further use. Assuming that 20 % of this biorefinery lignin (approx. 45 million metric tons) was used for processing into BTX chemicals and hydrocarbons, this would mean a substitution of approx. 10 % of fossil-based with bio-based base chemicals (Holladay et al. 2007). Translating crude oil refinery systems to biorefineries requires the complete separation of the biomass into its precursors, carbohydrates, lignin, proteins and fats.

Figure 2.1 shows, in diagram form, a lignocellulose feedstock (LCF) biorefinery and the resulting products. Promising, among other things, is the extraction of furfural, which is used as a starting material for the production of nylon-6 and nylon-6,6 and also the manufacture of (bio)ethanol by means of hydrolysis reactions (Kamm and Kamm 2007). Current utilization of the lignin polymer is aimed at its use as a fuel or adhesive or filler. This utilization is not satisfactory, since the structure of lignin has monoaromatic compounds which, viewed on their own, constitute an important foundation for the production of base chemicals (e.g. phenols) (Ringfeil 2002). It is known that the lignin structure varies depending on the plant source, but above all is altered by the particular digestion process. Currently, 60 million metric tons of lignin accumulate per year as a

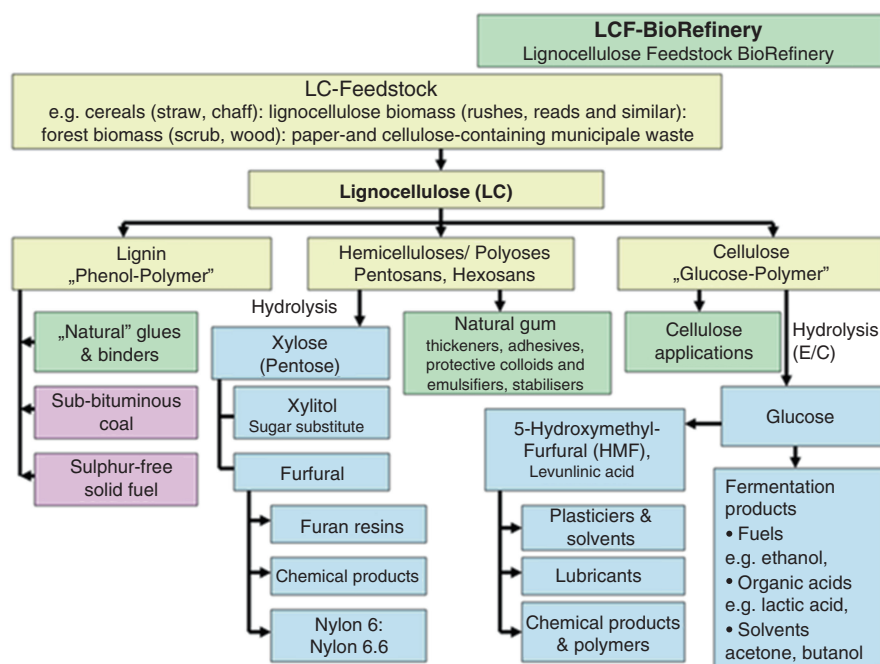


Fig. 2.1 Diagram of a LCF biorefinery (Kamm et al. 2006)

by-product in the waste lyes from the cellulose industries (Lora 2010). Enhancing the value of this accumulating lignin is desirable. Although research has been taking place into lignins for over 100 years, detailed characterization of the heterogeneous lignin structure still constitutes a major challenge.

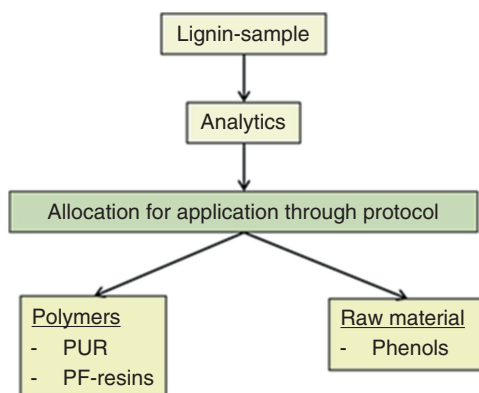
2.2 The Understanding of the Lignin Structure

Today, lignin accumulates in significant quantities as a by-product and has major structural potential for generating platform chemicals. A prerequisite for material utilization is detailed and comprehensive knowledge of the structure and properties of the corresponding lignins. The following results show investigated lignins from beech wood, isolated by different conditions during Organosolv process. Analytical processes are used which provide a very comprehensive picture of the isolated fractions. The results should enable an estimation as to which method combining the source quality is suitable for the material utilization of lignin. The characterization of the lignin fractions comprises purity analyses in accordance with the NREL protocol, chromatographic (pyrolysis-GC/MS, GPC), thermal (TGA, DSC), spectroscopic (UV-Vis, FT-IR, ^{31}P -NMR) and additional methods, including the testing of solubility behaviour, water content and elementary analyses.

The results constitute a basis for making lignin marketable. The main focus here is on its use as a source of raw materials for the generation of base chemicals, comparable to the products which at the moment are still produced by the petroleum industry. The focus of the decomposition products lies primarily on the generation of phenolic products. The results shall also be considered in relation to use as a polymeric material. Knowledge of the thermal behaviour in particular is necessary for this.

The objective of the chapter is to produce instructions concerning steps and/or analytical methods to be carried out, firstly in the case of use as a raw material, secondly as a polymeric material as you can see in Fig. 2.2. A generally applicable protocol is to be derived for this.

Fig. 2.2 Work scheme



2.3 Current Level of Research

2.3.1 Lignin

Lignin is by definition a polymeric natural product which is generated through enzymatically initiated dehydration polymerization of three primary precursors: *p*-coumaryl, coniferyl and sinapyl alcohol (Lai and Sarkanen 1971; Bunzel and Steinhart 2003; Bunzel et al. 2005). These monomer units, also called main monolignols, are divided into **guaiacyl**, **syringyl** and ***p*-hydroxybenzaldehyde** types. The monomeric building blocks of lignin are derived from the *p*-hydroxycinnamyl alcohols (Nimz et al. 1981). Figure 2.3 shows the chemical relationship of the *p*-hydroxycinnamyl alcohols generated from biosynthesis to the monolignols. Lignins from conifers (gymnosperms) differ from lignins from deciduous trees and shrubs (dicotyledons) and grasses in respect of the ratio of these three phenylpropane units and are differentiated accordingly into: guaiacyl lignins (G lignins), guaiacyl-syringyl lignins (GS lignins) and guaiacyl-syringyl-*p*-hydroxybenzaldehyde lignins (GSH lignins). Lignins from conifers have a G/S/H ratio of 90/2/8; here, coniferyl alcohol is the predominant monomeric subunit. These lignins belong to the G lignins. Lignins from deciduous trees and shrubs are classed among the GS lignins. Unlike with the gymnosperms, more sinapyl alcohols units are introduced during polymerization. The monomer composition in the lignins of the monocotyledons likewise differs from the other categories; they have an increased proportion of *p*-hydroxybenzaldehyde (H units) (30 % and over) (Adler 1977).

These monomeric subunits are phenylpropanoids, i.e. phenols with a propenol group in the *para* position. In nature, the macromolecular structure of the lignin is generated from the oxidation of the *p*-hydroxycinnamyl alcohols to phenoxy radicals (Freudenberg 1965). Through the dehydrogenation of the alcohols, the phenoxy radicals are produced; these are present in five mesomeric formulae illustrated in Fig. 2.4 using the example of coniferyl alcohol.

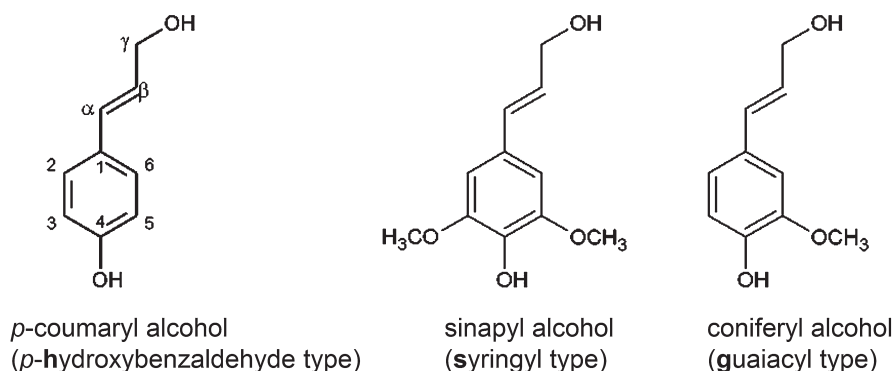


Fig. 2.3 Monomeric units of the lignin structure

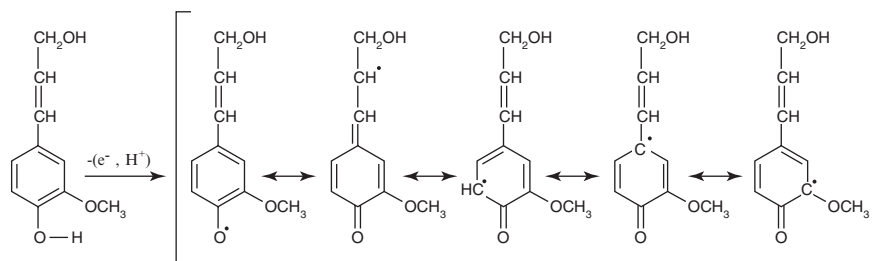


Fig. 2.4 Mesomeric formulae of the phenoxy radical

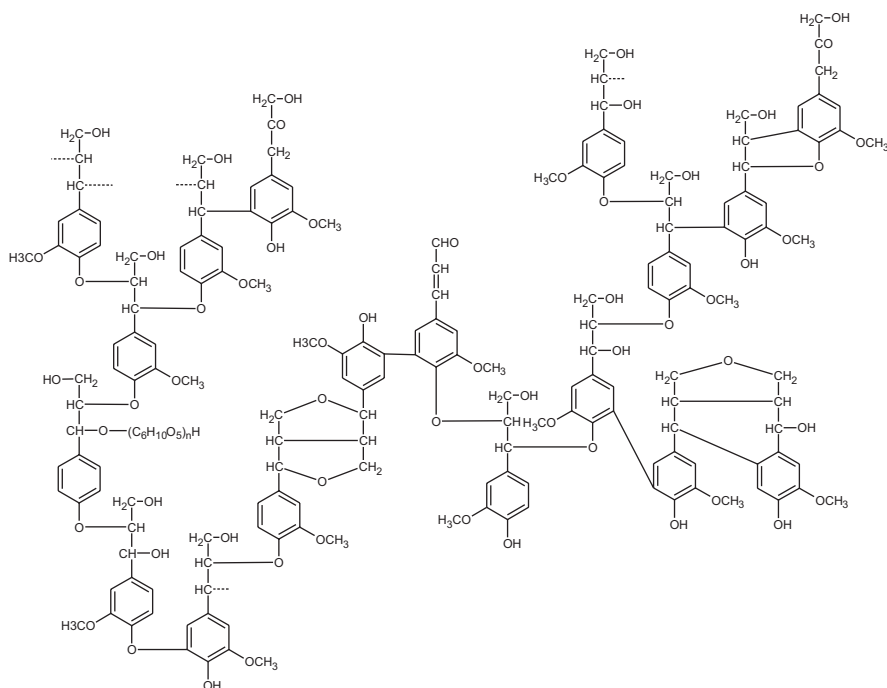


Fig. 2.5 Lignin structure referring to Freudenberg and Neish (1968)

Figure 2.5 shows the structure of lignin which was postulated by Freudenberg (Freudenberg and Neish 1968). The most frequently occurring bonds are aryl ether linkages (α -O-4 and β -O-4); they occur, with a frequency of approx. 50–65 %, as the most important linkages in the lignin structures (Glasser 1980). Lignins from deciduous wood have, as a result of the high proportion of aryl ether bonds, only a few free phenolic hydroxyl groups. The S units also form β -O-4 bonds more frequently than G units. In spruce lignin hardly any S units

occur; consequently the proportion of β -O-4 bonds is significantly lower. Alongside these ether bonds, one also encounters C-C linkages in the lignin structure such as the β -1 bond which occurs in beech lignin at 15 % and leads to 1,2-diaryl compounds. Glasser and Adler were able to show that spruce lignins contain 10 % β -5, 5-5 and α - β bonds (Nimz 1974; Glasser 1981).

2.3.2 Recovery of Lignin

The chemical pulping processes provide every year about 70 million tons of lignin (Römpf 1995). The various industrial processes serve as the selective isolation of cellulose from the cell wall matrices. Lignin is produced as a by-product. The macromolecular structure of lignin is fragmented with cleavage of α -O-4 and β -O-4-bonds.

Digestions in aqueous media require insertion of hydrophilic sulphuric or sulphonic acid groups at the decomposed lignin products to enhance their solubility. These hydrophilization steps do not apply to processes employing organic solvents. The most important method is the sulphate digestion (kraft cooking) with about 76 % share (Sjöström 1981), followed by the sulphite process with about 8 % (Ullman's Enzyklopädie 1979).

The search for alternative methods is becoming more important as the processes mentioned are very harmful to the environment. There are a number of alternative special pulping processes; they are primarily aimed at the production of high-quality pulps (about 16 % share).

2.3.2.1 Organosolv Process

The Organosolv process is as a pulping process with a use of organic solvents to improve lignin solubility (Alcell process: ethanol/water mixtures (Nimz 1986)).

The solvent (or solvent mixture) must be able to dissolve the lignin completely and should have a low boiling point, so that a slight recovery is possible.

Due to the improved solubility a hydrophilization of the lignin in contrast to sulphite processes are not necessary. El Hage (2009) were able to show that in this process preferably β -O-4 bonds are cleaved. Advantages of this method are the sulphur-free treatment and hemicellulose-free products. A disadvantage is that during the cooking process a lot of phenolic and aliphatic hydroxyl groups are etherified, which impedes a subsequent application as a component for polycondensation processes. Another drawback is that not all types of wood can be pulped, including woods with high syringyl content due to the blocking of ortho positions. Preference should be given grasses with high *p*-hydroxybenzaldehyde units.

2.3.2.2 Steam Explosion

This procedure is one of the pretreatments of wood species for the enzymatic hydrolysis (Lindorfer et al. 2010). To be treated, shredded material is pulped with saturated steam under pressure and subsequent relaxation. By steaming the lignocellulose structure is digested, the hemicellulose hydrolyzed and lignin depolymerized. The process temperature is about 200 °C. Pretreatment proceeds without catalyst, only an addition of acid is enough to release the monomeric sugars of the hemicellulose. After washing with distilled water and subsequent precipitation by addition of sodium hydroxide solution, the lignin may be recovered in pure form. Li et al. (2009) showed that under the steam explosion mainly β -O-4 bonds are cleaved. In addition, a high percentage of phenolic OH groups could be detected.

2.3.3 Use of Lignins

Lignin is a versatile product that can be used for lots of different applications. The possibilities and challenges relating specifically to biorefinery lignins have been described in a detailed study by Holladay et al. (2007). This shows the diversity of lignin for potential applications, which are subdivided into three groups:

1. Energy, fuel, synthesis gas.
2. Macromolecules.
3. Aromatic compounds.

In group 1, the lignin is used as a source of carbon for energy production and/or for reprocessing as a synthesis gas. The second group makes use of the natural macromolecular structure of the lignin. The lignin can be used in major application areas such as binders, carbon fibres or polyurethane foams. The third group requires technologies for the degradation of the macromolecular structure to obtain monomeric units while retaining the aromatic structure. This is a prerequisite for the production of the polymer building blocks benzene, toluene and xylene (BTX), phenols and vanillin.

Table 2.1 shows areas of research concerning the use of lignins. It is noticeable that until now, prior characterization of the lignin fractions has not always been carried out; industrially accumulating fractions are used among other things for the manufacture of epoxy and phenol formaldehyde resins. One focuses on the differences in the finished polymer product and observes the mechanical properties such as strength and notched impact strength. Khan et al. (2004) investigated bagasse lignins for use as adhesives following characterization carried out during FT-IR and/or UV spectroscopy and thermal analyses. It should be noted that the results of the end products in the case of the studies by Wang et al. (1992) show that polymers with improved mechanical properties can be obtained if phenol is substituted with lignin. A prerequisite for use in resins is good solubility and the associated optimum distribution in an unhardened resin system. Cazacu et al.

Table 2.1 Use of lignins

Source/pulping process	Use	Lignin analytics	Tested parameters final product	Comment	Literature
Lignin (bagasse)	Wood adhesive	IR UV DSC TGA CHN	Adhesive strength IS 851-1978, shearing behavior ASTM D 2339-94A, IR, Tg	Comparable stability regarding commercial resins when substitution of phenol through lignin (50 %), structure of lignin resins similar to the commercial resins	Khan et al. (2004)
Kraft (hardwood)	Epoxide resins	IR NMR TGA solubility	Strength (E-Modul), impact strength	Improved mechanical properties at good solubility in uncured resin system	Wang et al. (1992)
Lignosulphonate	Polyolefins (blend polymers)	CHN solubility	DSC, TGA, IR, breaking elongation	Improved mechanical properties	Cazacu et al. (2004)
Lignosulphonate	Phenol formaldehyde resins	No	Viscosity Curing time	Higher viscosities and curing times	Peng and Riedl (1994)
Lignosulphonates (from softwood), Kraft	Vanillin	UV IR NMR	–	–	Araújo et al. (2010)
Organosolv	Phenol formaldehyde resins	No	Strength, curing time, density	Improved curing time, unchanged density compared to commercial resins	Cetin and Özmen (2002)
Organosolv	Epoxide resins	No	Glass transition, dielectrical constant	Higher glass transition temp., unchanged dielectric constant	Kosbar et al. (2001)
Organosolv/Kraft	Carbon fibre	1H-NMR DSC TGA SEM	Strength	Unchanged strength	Kadla et al. (2002)

(2004) were also able to show similar results. Here, lignosulphonates were used as a blend material. Beforehand attention was, here too, devoted chiefly to the solubility. The end product exhibits improved mechanical properties (here, elongation at break was tested). In the USA there are already several patented phenolic resin systems on the basis of lignin. Here the attempt was made to substitute lignins for phenols. Peng and Riedl (1994) found that using up to 40 % w/w lignosulphonates, the hardening times increase *vis-à-vis* conventional phenol formaldehyde systems and the viscosities increase with a greater lignin proportion. The main field of use of lignin-based phenolic resins is the glueing of chipboard; polyurethane-lignin systems are also a possible option for this application. Another research field which is not mentioned in the list below is the field of lignin-polyurethane chemistry, research groups led by Feldman (Feldman 1994; Feldman and Lacasse 1989; Feldman and Lacasse 1994; Feldman et al. 1988; Glasser et al. 1982; Toffey and Glasser 1997; Kelley et al. 1988, 1989a, b; Saraf et al. 1985) and Hirose and Hatakeyama (Hirose et al. 1989; Yoshida et al. 1990) have carried out many investigations. By Hatakeyama, polyurethanes were synthesized from a kraft lignin and different polyethylene glycols using up to 40 % w/w lignin. The end products were soft-elastic to hard.

Polyurethane systems with up to 20 % w/w kraft lignin were investigated by Feldman. The rigidity values increased with higher lignin content. The materials had the best mechanical properties at a lignin content of 5 % w/w (Reimann et al. 1990).

Use is made mainly of lignosulphonates for application in industrial products. Owing to their viscosity behaviour, lignosulphonates have high cohesive force and adhesive power (Windeisen and Wegener 2012). By occupying with hydrophilic sulphonic acid groups, the solubility of the native lignin changes considerably. Today, up to 200,000 metric tons of lignosulphonates are sold annually as a cement additive. They contribute to the deagglomeration of the cement particles and liquefy the mortar by reducing the viscosity. In the petroleum industry, too, lignosulphonates are used as flow improvers for water-oil emulsions (Booregard Lignotech 2015). The use of technical lignins permits significantly lower water quantities and facilitates the recovery of drilling water.

2.3.4 Lignin Analytics

Lignins from a variety of plant sources and digestion processes are often characterized in wood and lignin research. Admittedly, the analysis is frequently aimed at the direct application. One example of this is the research field of Methacanon et al. (2010); here, kraft lignins were investigated in relation to their direct use in phenol formaldehyde resins (PF resins). The techniques employed were IR spectroscopy, GPC, TGA and DSC. Mansouri et al. (2006), in addition to investigating kraft lignins, also investigated lignosulphonates and organosolv lignins. Here, too, the investigation aimed at the use of lignins in PF resins. Alongside the analysis of the proportions of sugar and ash, GPC was used for the

determination of the molecular weight, and ^1H -NMR to investigate the bond types in the lignin. The focus of characterization is on the detection of the hydroxyl groups. Here is a priority list of the features that lignins ought to have for use in PF resins: (1) Presence of phenolic hydroxyl groups, (2) Presence of aliphatic hydroxyl groups, (3) Structures that can form quinone methide intermediates, (4) Non-substituted 3- or 5-positions on phenolic C_9 units, (5) Low molar masses (M_w).

In recent years a number of different lignins have been analyzed from various pulping processes and were characterized. Focus of this work is the development of a reliable, reproducible procedure for lignin characterization and the adaptation of established methods on the lignins from the applied isolation methods. Among the most important parameters to be determined are the molecular weight (M_w and M_n) and its distribution (MWD), as well as the thermal behavior, in particular the glass transition temperature (T_g). These parameters affect the later processing in a significant way. The melting behavior is important for the technical processing and application. The melting range and the glass transition temperature are dependent on the type of pulping conditions and the content of impurities or the (remaining) water content of the sample.

The analytical methods can be divided into two categories: the analysis of the chemical structure of lignin and the characterization of its physico-chemical properties, see Fig. 2.6.

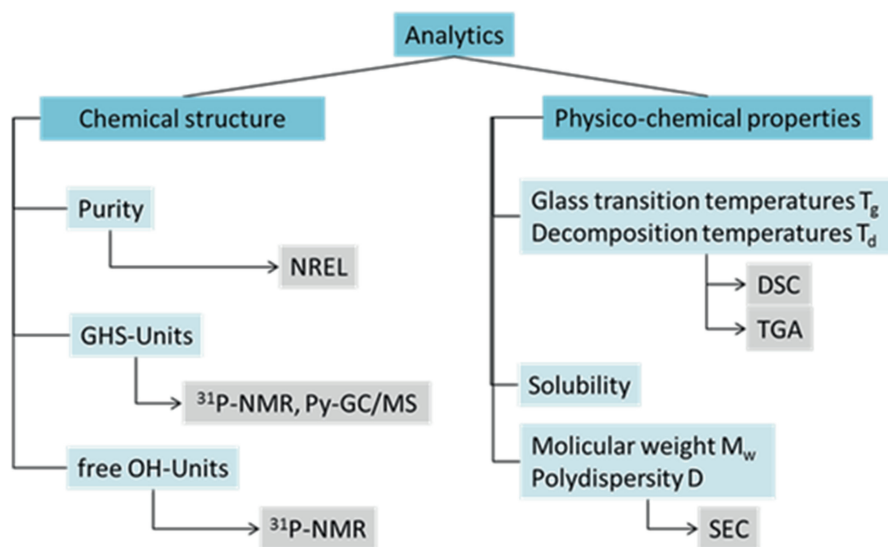


Fig. 2.6 Analytical methods of lignin fractions

2.3.5 Prerequisites for Lignin Properties from Literature Values, for Use in Polyurethanes (Thermoplastic/Thermosetting)

For the purpose of the approach of this chapter described above, a specific use is to be derived for the lignin-containing samples investigated using detailed characterizing analyses. Use as a polymeric material is made more specific in the form of thermoplastic and thermosetting polyurethanes and phenolic resins. The extraction of phenols from the lignins considered is contemplated as a second important use. Current applications have been researched for this specific data. In the case of thermoplastic polyurethane, Alcell lignin was successfully processed into thermoplastic polyurethanes at a level of up to 65 % w/w by Saito et al. Here, lignin is considered the “hard segment”, which significantly influences the mechanical strength. The polybutadiene is hence the “soft segment” component and responsible for the rubber-like property in the polymer overall. For this, the lignin must initially be pretreated with formaldehyde in order to keep the molecular weight and the glass transition temperature controllable. In this specific example, the setting of the molecular weight M_w at over 800,000 g mol⁻¹ and a glass transition temperature of T_g : 150 °C were ideal for the resulting mechanical properties. The DSC analyses of the finished polymer showed a two-phase morphology as is typical of thermoplastic copolymers (Saito et al. 2013).

Glasser and Leitheiser (1984) were able to produce polyether adducts following a reaction of lignin with epoxides. This reaction is initiated by a base attacking the phenolic hydroxyl groups of the lignin, so that phenoxides are generated. Through the alkoxylation of the lignin, physical properties of the molecule change: the glass transition temperature is lowered. This results in a low viscosity in all temperature ranges. The alkoxylation reaction is a very important step for the manufacture of thermosetting polyurethanes with isocyanates. The modification of the lignin delivers primary alcohols which are chemically more reactive than phenolic hydroxyl groups. In addition, through the necessary lowering of the glass transition temperature the lignin becomes liquid at relatively low temperatures. A reaction condition for the polymerization to polyurethanes is the use of liquid reactants at temperatures around 60 °C. The lignin modified through the alkoxylation consequently constitutes the liquid polyol component of the reaction, which can be processed using injection moulding. If one now observes the structure of the lignin, it becomes clear that such alkoxylation reactions can only take place sterically unimpeded, hence the reaction is more successful if the basic structure of the isolated lignin has few syringyl units.

2.3.6 *Prerequisites for Lignin Properties from Literature Values, for Use in PF Resins*

If the lignin is considered for possible use as a phenol substitute in phenol formaldehyde resins, the lignin batch must contain certain physical and chemical properties. The main use of lignin-based PF resins is currently the glueing of chipboards. With this application, the phenol component is substituted completely or partially with lignin. In order to achieve comparable quality in the end product, the raw material used must be free from accompanying substances. Flidner and van Herwijnen (2011) were able to substitute 30 % of the phenol quantity through the use of lignin as a component. The resulting resins were tested on the basis of their mechanical properties using standard methods (DIN EN 319, DIN EN 312, DIN EN 314, DIN EN 310). The results compare well with the conventionally manufactured PF resins. Here too, the reaction with formaldehyde requires a lignin structure where H/G units dominate. Syringyl units act as a steric hindrance. Tejado et al. (2007) were able to achieve good results for the manufacture of lignin-based PF resins, with lignin input values with molecular weights up to 8000 g mol^{-1} and glass transition temperatures of up to 150°C and decomposition temperatures of between 300 and 400°C . The physico-chemical requirements on lignins of this study are summarized in Table 2.2.

2.4 Analytical Data

Investigated lignins:

The investigated Organosolv lignin fractions are products from a biorefinery pilot plant in Leuna, Germany using beech wood as the feedstock material. The pulping process parameters for OBL_1 are a 50/50 ethanol/water mixture, a reaction temperature of 170°C , a reaction time of 120 min and sulphuric acid as a catalyst with 0.94 % w/w. OBL_2 is a result of isolating beech wood with a 50/50 ethanol/water mixture at a temperature of 180°C and a reaction time of 240 min. The fraction of LigSteam results from an acid steam explosion process using wheat straw as raw material. The applied process parameters cannot be published.

Table 2.2 Requirements on lignins

Analytics	Lignin for PF resins	Lignin for polyurethanes (thermoplastic)
Solubility	Good solubility in polar-protic organic solvents	Good solubility in polar-protic organic solvents
Ligningehalt [%]	From 90	From 90
M_w [g mol^{-1}]	Between 600 and 8000	Up to 4000
T_d [$^\circ\text{C}$]	>200	>200
T_g [$^\circ\text{C}$]	–	100–150
G/H/S	Dominant G/H-units	Dominant G/H-units

2.4.1 Purity and Fractional Yield of Lignin: LigSteam vs OBL_1 and OBL_2

The results of moisture, ash, elemental sugars, Klason (AIL) and acid-soluble (ASL) lignin contents (w/w %) are summarized in Table 2.3. The results show highly pure lignin fractions for isolated beech wood lignin (91.4-94.0 %). The sugar content is under the quantification limit (<0.1 ppm). The fraction of the isolated wheat straw lignin via steam explosion show less purity with high contents of sugars (<21 %).

In comparison to other studies these results of Organosolv samples are unique. El Mansouri and Salvadó (2006) investigated lignosulphonates, Kraft, soda-anthraquinone, Organosolv and ethanol process lignins for the industrial production of adhesives. The results of these lignins also show high contents of total lignin yield but all considered lignins exhibit carbohydrates contents. Erdocia et al. (2014) studied different Organosolv conditions on olive wood. They used the Acetosolv, Formosolv and a mixture of both processes at a temperature of 130 °C and a reaction time of 90 min. The resulting lignin fractions had contents of Klason lignin between 69.05 and 79.01 % w/w. The sugar contents were between 1.88 and 5.87 w/w %.

2.4.2 Solubility

It is known that lignins have limited solubility in organic solvents due to the heterogeneous three-dimensional molecular structures. Therefore it is essential to find appropriate solvents, especially for detailed structural analysis using spectroscopic or chromatographic methods. Lignins are generally insoluble in water and

Table 2.3 Analysis of moisture, ash, lignin and carbohydrates

	OBL_1 [% w/w on dry matter]	OBL_2 [% w/w on dry matter]	LigSteam [% w/w on dry matter]
Moisture content	3.48	3.81	4.92
Ash content	0.22	0.47	16.95
Total lignin ^a	94.32	91.71	51.95
Klason lignin (AIL)	92.71	87.77	51.75
Acid-soluble lignin (ASL)	1.61	3.95	0.2
Carbohydrate	NF ^b	NF	21.14
<i>Carbohydrate composition</i>			
Glucose	NF	NF	17.68
Arabinose	NF	NF	3.46
Galactose	NF	NF	NF
Mannose	NF	NF	NF

^aAIL acid insoluble lignin, ASL acid soluble lignin

^bNF not found

most of the organic solvents, with the exception of Organosolv-processed lignins which show a higher solubility in organic solvents than industrial lignins. In this study, the solubility of OBL and LigSteam was examined in a variety of nonpolar to polar solvents and corresponding mixtures (Table 2.4) as classified by Reichardt (2010). The solvents are mainly divided in terms of their polarity and protic behaviour. Organosolv lignin and LigSteam lignin show insolubilities in water.

OBL_1 and OBL_2 fractions show good solubility in protic polar solvents such as methanol and ethanol and aprotic polar solvents like acetonitrile and acetone. The highest solubilities for these fractions were observed in dioxane, tetrahydrofuran and pyridine which belong to the classes of aprotic apolar, protic polar and aprotic dipolar solvents, respectively.

In general, there are few studies on solubility characteristics of lignins.

Cybulska et al. (2012) investigated the solubility of Organosolv lignins derived from cord grass, switch grass and corn stover in DMSO, dioxane, methanol, ethanol, ethyl acetate and methyl isobutyl ketone MIBK. The results show best solubility values in methanol as protic polar solvent and dioxane as aprotic apolar solvent and rather poor solubility in DMSO, ethyl acetate and MIBK as aprotic polar solvents in particular for cord grass lignin. Lignin from steam explosion processes show slightly solubility in all applied solvents. This is due to the less purity and the high contents of sugars. Modification methods are required (e.g. acetylation) to enhance the solubility in organic matters.

2.4.3 Physico-chemical Characteristics of Organosolv Derived Lignin

2.4.3.1 Fourier Transform Infrared (FT-IR) Spectroscopy

FTIR-spectra of Organosolv lignins and LigSteam lignin are given in Fig. 2.7; the corresponding assignments and references are summarized in Table 2.5. According to former studies, the network of hardwood lignin like beech wood is mainly composed by GS units. Wheat straw lignin is composed by GHS units.

Table 2.4 Solubility behaviour of OBL and LigSteam

Solvent ^a	Classification ^b	OBL_1 [% w/w]	OBL_2 [% w/w]	LigSteam [% w/w]
Water	HBSA	25	27	27
Methanol	HB	72	73	50
Ethanol	HB	60	60	50
Tetrahydrofuran	HB	96	97	46
Pyridine	AHD	97	98	45
Acetone	AD	71	73	30
Acetonitrile	AD	58	60	34
Dioxane	EPD	97	98	40

^a $C_{M\%} = 2$; $T = 25\text{ }^{\circ}\text{C}$ in ultrasonic bath for 30 min

^bClassification according to Reichardt ^[12] *HBSA* hydrogen bonding, strongly associated, *HB* hydrogen bonding, *AHD* aprotic, highly dipolar, *AD* aprotic, dipolar, *EPD* electron pair donor

The broad absorption band at 3430 cm^{-1} is assigned to aromatic and aliphatic OH groups, bands at 2940 , 2840 and 1460 cm^{-1} are related to C-H vibration of CH_2 and CH_3 groups, absorptions at 1600 , 1515 and 1425 cm^{-1} are related to aromatic ring vibrations of the phenyl propane skeleton. The absorption at 1700 cm^{-1} can be attributed to non-conjugated carbonyl groups. Phenolic OH groups are shown by absorption bands at 1330 and 1365 cm^{-1} , whereas the one at 1030 cm^{-1} is related to primary alcohols. Absorptions at 1330 , 1220 and 834 cm^{-1} are assigned to the syringyl units, while small shoulders at 1270 , 1120 and 1153 cm^{-1} can be attributed to the guaiacyl units. The Organosolv process results in cleavage of the β -O-4-linkages which are mainly present in beech wood lignin generating both phenolic hydroxyl (1365 cm^{-1}) and carbonyl groups (1700 cm^{-1}) (Nimz 1974).

2.4.3.2 ^{31}P NMR Spectroscopy

The lignin samples were first phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane and analyzed via quantitative ^{31}P NMR spectroscopy (with endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide as internal standard) according to the method described by Granata and Argyropoulos (1995). The obtained spectrum (Fig. 2.8) provides information about the concentration of each hydroxyl group calculated in reference to the hydroxyl content (mmol g^{-1}) of the internal standard.

According to the results obtained from ^{31}P NMR spectra, Organosolv-isolated lignin samples exhibit considerable quantities of G and H units and rather low amounts of S units (see Table 2.6). It shows the presence of aliphatic hydroxyl groups (δ 146 – 149 ppm , 0.38 mmol g^{-1}), amounts of syringyl units (δ 143 – 144 ppm , 0.12 mmol g^{-1}), guaiacyl units (δ 142 – 143 ppm , 0.25 mmol g^{-1}), hydroxyphenyl units (δ 139 – 140 ppm , 0.27 mmol g^{-1}) and low amounts of carboxylic acid (δ

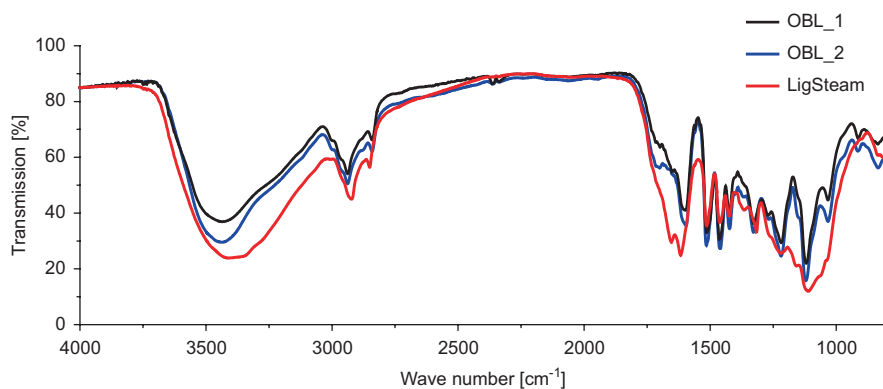


Fig. 2.7 FT-IR spectra Organosolv lignin and LigSteam

Table 2.5 FT-IR bands assignment

Band [cm ⁻¹]	Assignment	Vibration ^a
3435	Phenolic OH + aliphatic OH	st O-H
2938	CH ₃ + CH ₂	st C-H
2841	CH ₃	st C-H
1699	Non-conjugated C=O	st C=O
1595	Aromatic skeleton (S>G)	st C-C
1514	Aromatic skeleton (S<G)	st C-C
1459	CH ₃ + CH ₂	δ _{asymmetric} C-H
1423	Aromatic skeleton	st C-C
1369	Phenolic OH	δ _{ip} O-H
1327	Aromatic skeleton (S)	st C-O
1268	Guaiacyl unit	st C-O
1218	Phenolic OH	st C-O (H)
1152	Aromatic ether	st C-O-C
1120	Guaiacyl unit	δ _{ip} Ar C-H
1032	First order aliphatic OH	st C-O (H)
970	CH=CH	δ _{op} C-C
914	Aromatic ring	δ _{op} C-H
834	Aromatic ring (S)	δ _{op} C-H

^ast stretching vibration, δ_{ip} in-plane deformation vibration, δ_{op} out-of-plane deformation vibration

135 ppm, 0.02 mmol g⁻¹). The high amount of guaiacyl hydroxyl units in OBL is a consequence of cleavages of β-O-4 linkages. The resulting ratios of monomeric units (H/G/S) were 32/49/19 for OBL_1 and 43/40/17 for OBL_2. The beech wood lignin data obtained by Faix et al. (1987) show monomeric ratios of beech milled wood lignin of 4/56/40. El Hage (2009) investigated Organosolv lignin from Miscanthus and found hydroxyl amounts: aliphatic 1.19 mmol g⁻¹, syringyl 0.13 mmol g⁻¹, guaiacyl 1.33 mmol g⁻¹ and hydroxyphenyl 0.61 mmol g⁻¹. Regarding the results of Faix et al. (1987) our beech wood lignins show higher amounts of hydroxyphenyl units arising from Organosolv isolation method cleaving mainly the β-O-4 bonds. The spectra of steam exploded wheat straw lignin LigSteam shows presence of GHS units with 42/13/45. References give a GHS ratio of 49/5/46 (Lapierre 1993). These results were also confirmed by pyrolysis gas chromatography (Fig. 2.9).

2.4.3.3 Thermogravimetric Analysis (TGA)

Thermal analysis of lignins determined their thermal behavior which was based by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermograms of Organosolv beech wood lignin and LigSteam (Fig. 2.9) show that the thermal degradation of lignin occurs in a broad temperature range (100–700 °C). This is due to the complex structure of lignin consisting of phenolic hydroxyl,

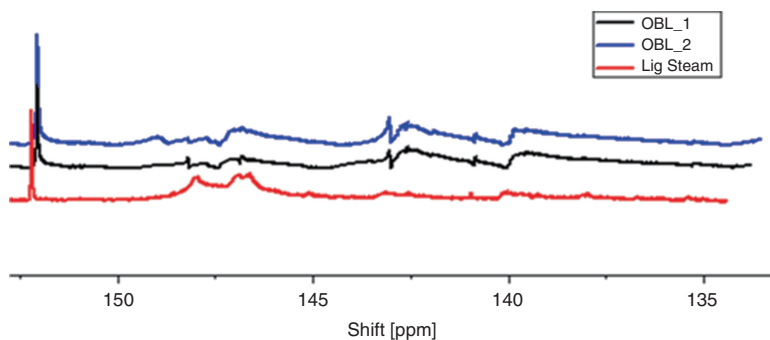


Fig. 2.8 ^{31}P NMR spectra of OBL_1, OBL_2 and LigSteam

Table 2.6 Signal assignment for ^{31}P NMR spectroscopy of OBL and LigSteam

Chemical shift range $\delta^{31}\text{P-NMR}$ [ppm]	Assignment	OBL_1 [mmol g $^{-1}$]	OBL_2 [mmol g $^{-1}$]	LigSteam
146.5–150	Aliphatic OH	0.50	0.38	2.85
152	e-HNDI (IS)			
143	Syringyl OH	0.14	0.10	0.48
142–143	Guaiacyl OH	0.38	0.24	0.44
139–140	<i>p</i> -hydroxyphenyl OH	0.25	0.26	0.14
135	Carboxylic acid	0.02	0.01	0.02

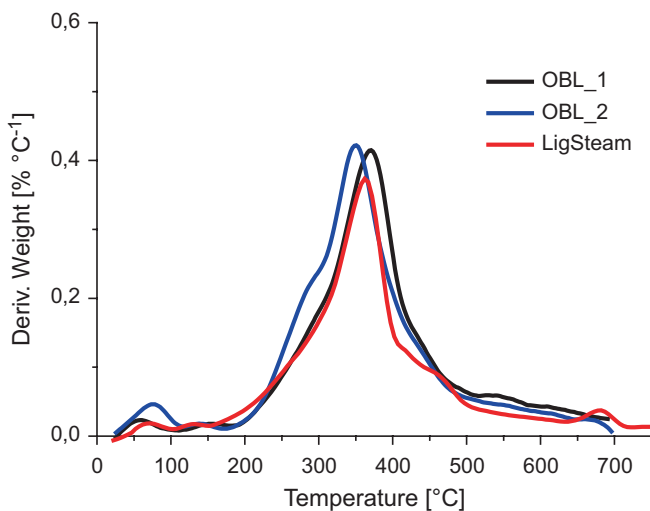


Fig. 2.9 DTG of Organosolv lignins and LigSteam

carbonyl and benzylic hydroxyl functionalities. Several stages of weight-loss can be observed in the TG curves. Initially, the decrease in loss of weight was attributable to moisture present in the lignin sample and to the release of volatile products such as carbon dioxide and carbon monoxide up to 200 °C (Domínguez et al. 2008). According to Wittkowski et al. (1992), the degradation of propanoid side chains of lignin occurs between 230 and 260 °C with formation of methyl, ethyl and vinyl guaiacol derivatives. Aryl ether bonds can be cleaved at temperatures below 310 °C due to their low thermal stability. According to the studies of Nimz, more than 65 % of the monomer units of beech wood lignin are connected by β -O-4 linkages (Nimz 1974). The major degradation occurs between 200 and 600 °C. The first derivative of the TG curves leads to the DTG curve which shows the corresponding rate of weight-loss. The curves are presented in Fig. 2.10 and show maximal values at 381 and 346 °C (DTG_{max}), respectively, with a weight-loss value of 0.4 % °C⁻¹. The sample of LigSteam presents a decomposition temperature of 367 °C and a weight-loss 0.37 %. In general, DTG_{max} values vary between 350 and 425 °C for softwood and hardwood lignins (Tejado et al. 2007). The decomposition temperature strongly depends on the molecular structure of lignin. Lignins with high contents of G units exhibit higher molecular weights caused by intermolecular C-C bonds, which have a high stability and are not cleaved during the pulping processes (El-Saied and Nada 1993). Domínguez et al. (2008) investigated the thermal stability of Organosolv lignins from *Eucalyptus* and found average DTG_{max} values of 340 °C. Nitsos et al. (2013) performed a systematic investigation of the hydrothermal pretreatment of beech wood. Amongst other characterizations they used TGA to compare the DTG curves of untreated biomass and samples pretreated by hydrothermal processes. The

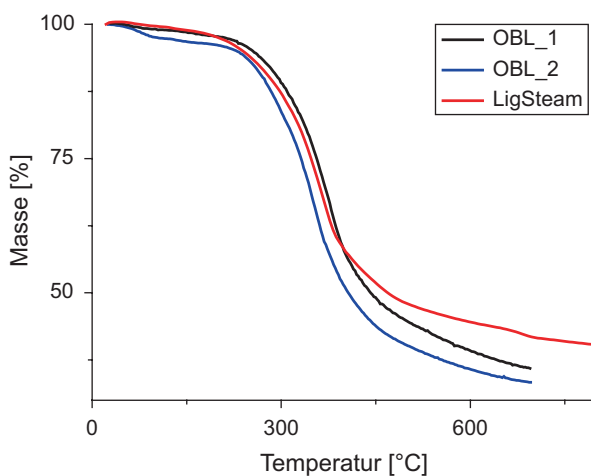


Fig. 2.10 Thermograms of OBL_1, OBL_2 and LigSteam

isolated beech wood lignin shows a DTG_{max} of 375 °C. Monteil-Rivera et al. (2013) performed thermal analysis on wheat straw lignins and flax lignins. They observed degradation temperatures of 375 °C.

2.4.3.4 Differential Scanning Calorimetry (DSC)

DSC is the most common method to determine thermal behavior and glass transition temperatures (T_g) of polymers, also used for various lignins (Glasser 2000). The glass transition is a reversible phenomenon; it is correlated to the viscoelastic behavior of amorphous polymers. At temperatures below the glass transition viscoelastic materials are stiff and glassy. This stiffness decreases in the transition region; a rubber-like elasticity is shown by the material resulting from chain entanglements (Kaelbe 1971; Aklonis et al. 1972). Glass transitions are correlated local rotational or translational flowings of chain-segments of the molecules at increasing temperature. Thermal expansion increases the free volume allowing these motions to take place. Visthal reported glass transitions for Organosolv lignin with T_g value of 97 °C; these studies were performed in order to study lignins as components in polymer blends (Vishtal and Kraslawski 2011). Softwood Kraft lignins show higher T_g values than Organosolv lignins derived from hardwoods (Glasser and Jain 1993). The studied Organosolv beech wood lignin samples also show relative low T_g values of 123 °C (see Figs. 2.11 and 2.12). There are no documented studies on DSC analysis from steam exploded wheat straw samples. LigSteam exhibits a glass transition temperature of 75 °C (see Fig. 2.13). The studies of Sameni et al. (2014) present glass transitions for steam exploded hardwood lignins at temperatures about 149 °C.

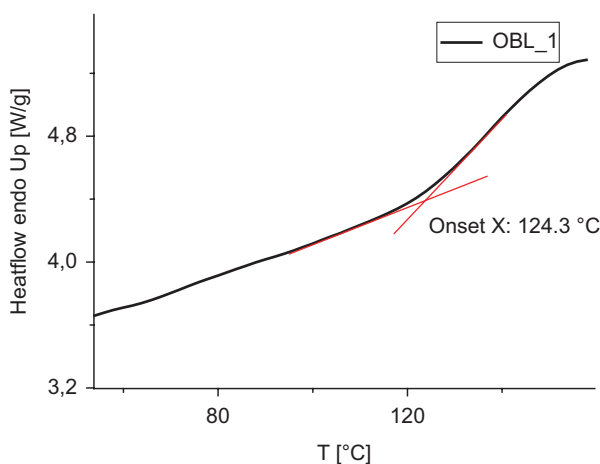


Fig. 2.11 DSC curve of OBL_1

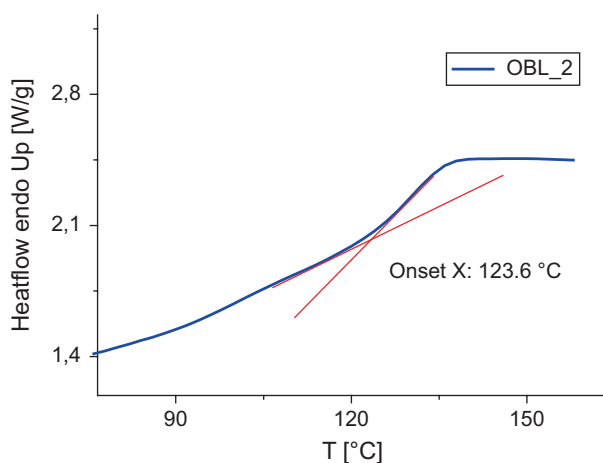


Fig. 2.12 DSC curve of OBL_2

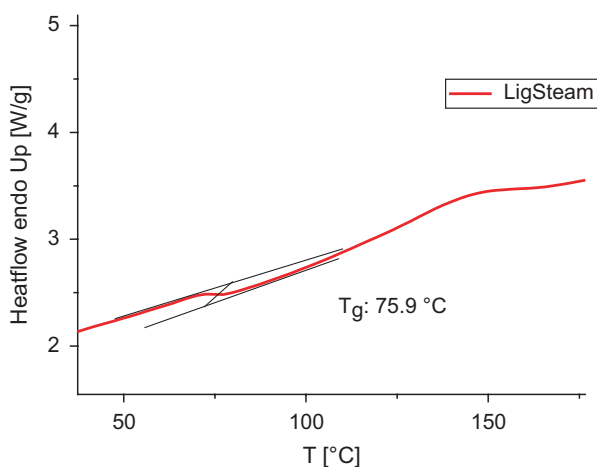


Fig. 2.13 DSC curve of LigSteam

2.4.3.5 Size Exclusion Chromatography (SEC)

The molecular weight and the molecular weight distribution of lignin has been analyzed through THF-eluted SEC. Due to polystyrene calibration standards the obtained data are discussed in comparison to literature studies performed under the same calibration conditions. Tejado et al. (2007) have investigated Kraft softwood lignins, Soda softwood lignins and Organosolv hardwood lignins. Technical Kraft lignins showed a weight average of 8700 g mol^{-1} , Organosolv lignins from hardwood (tamarind) exhibited a molecular weight of 3100 g mol^{-1} . Results of Kim et al. (2013) show molecular weights of 4168 g mol^{-1} for Organosolv-treated poplar wood using an alkaline catalyst.

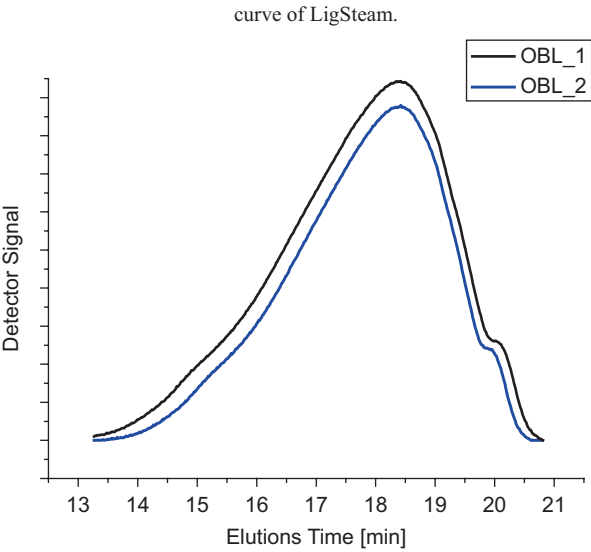


Fig. 2.14 SEC Elugram of OBL_1 and OBL_2

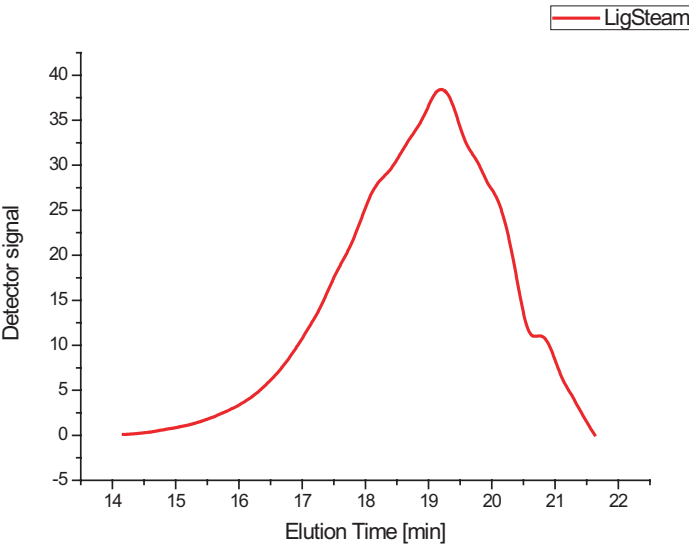


Fig. 2.15 SEC Elugram of LigSteam

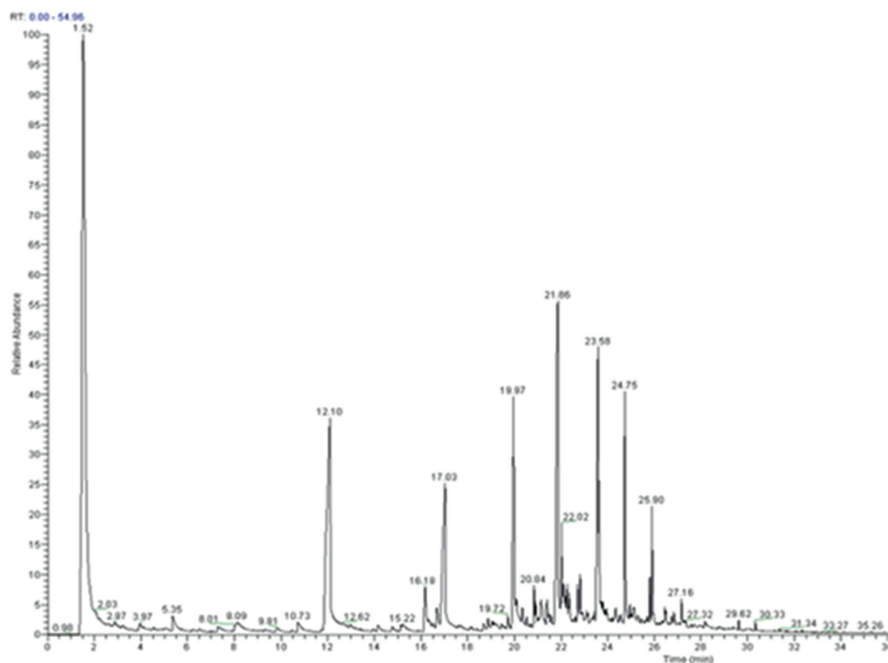


Fig. 2.16 Chromatogram of OBL_1

As confirmed by solubility tests a previous acetylation was necessary for the LigSteam sample. Figure 2.14 shows the chromatogram for the Organosolv-treated and steam-exploded lignin samples. LigSteam show higher molecular weights, this is an indication of less degradation during the process (see Fig. 2.15).

2.4.3.6 Pyrolysis GC/MS

Among the different degradation techniques, pyrolysis in combination with gas chromatography and mass spectrometry detection (Py-GC-MS) allows an online degradation and fragment analysis of the samples. Today, Py-GC-MS is an established technique to determine decomposition characteristics and monomeric contents. Pyrolysis decomposes a sample in the absence of oxygen into molecules of lower mass which can be detected by GC or MS. That results in a pool of fragments, a fingerprint, which is characteristic for each sample. There are basically two methods which are applied in pyrolysis research studies: the continuous mode and the pulse mode. In the continuous mode the sample is placed into a furnace and the temperature is kept fixed during the pyrolysis procedure. The pulse mode requires an introduction of the sample on a cold pyrolysis probe, which is then rapidly heated to the desired pyrolysis temperature (mainly applied: Curie-point pyrolysis). Curie-point pyrolysis of beech milled wood lignin has been investigated by Faix et al. (1987).

Table 2.7 Compounds identified by Py-GC-MS from lignin fragments of OBL_1

Compound	Molecular weight [g mol ⁻¹]	Origin
CO ₂	44	
2-Methyl 2-cyclopenten-1-one	96	C
2,3-dimethylphenol	96	C
4-ethyl-2-methylphenol	124	H
Phenol	94	H
2-methoxy-4-methylphenol (4-methylguaiacol)	138	G
4-ethyl-2-methoxyphenol	122	H
2,3-dimethoxybenzyl alcohol	138	G
2,3-dimethylhydroquinone	138	G
2-methylphenol	108	H
4-ethylphenol	108	H
4-ethylcatechol	138	H
2,3-dimethylhydroquinone	138	H
2-methoxy-4-propenyl-phenol (isoeugenol)	164	G
Phenol, 2-methoxy-4-propyl-(4-propylguaiacol)	138	H
Phenol, 2-methoxy-4-(1-propenyl)-	138	H
3-methoxy-5-methylphenol	164	G
Phenol, 4-(3-hydroxy-1-propenyl)-2-methoxy-	164	G
Phenol, 2,6-dimethoxy-4-(2-propenyl)-(4-allyl syringol)	194	S
Benzene, 1,2,4-trimethoxy-5-(1-propenyl)-, (Z)-	208	S
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	194	S
Ethanone, 1-(2,6-dihydroxy-4-methoxyphenyl)-	182	G
1,2-dimethoxy-4- <i>n</i> -propylbenzene	180	S
2,6-dimethoxyphenol (syringol)	154	S
1,2-dimethoxy-4- <i>n</i> -propylbenzene	180	S

Their results specifically show fragments of syringyl (S), guaiacyl (G) and *p*-hydroxyphenyl units (H) which is in line with the estimated SGH ratio on the basis of chemical degradation by Nimz (1974). The pyrogram also reveals fragments derived from carbohydrates. Lignin and polysaccharides are connected through covalent bonds to lignin carbohydrate complexes (LCC) (Jung and Deetz 1993). Carbohydrates, which are not completely removed, can be detected by Py-GC-MS. So, pyrolysis coupled to GC-MS gives valuable information about the relative amounts of lignin and carbohydrates. The pyrogram of Organosolv lignin OBL_1 is shown in Fig. 2.16. The nature and molecular weight of the released compounds after pyrolysis at a temperature of 550 °C are listed in Tables 2.7 and 2.8. Besides the fragments of GHS units there are small quantities of fragments originating from carbohydrate residues. Here, we found these small quantities of carbohydrates due to the lower detection limit of 1 ppb. The detection limit of HPLC is 10 ppb, so carbohydrates were not found. NMR results show a higher content of H and G units for OBL_2. These results are confirmed by Py-GC-MS fragment analysis.

Table 2.8 Compounds identified by Py-GC-MS from lignin fragments of OBL_2

Component	Molecular weight [g mol ⁻¹]	Origin
CO ₂	44	
Benzene	78	C
Toluene	92	C
Ethylbenzene	106	C
p-xylene	106	C
5-methyl-2-furalaldehyde	110	C
Phenol	94	H
2-propenylbenzene	118	H
2-methylphenol (<i>o</i> -cresol)	108	H
3-methylphenol	108	H
Mequinol	124	G
2,4-dimethylphenol	122	H
3-ethyl-5-methyl-phenol	136	G
2-methoxy-4-methylphenol (4-methylguaicol)	138	G
1,2-dihydroxybenzene (pyrocatechol)	110	H
3-methoxypyrocatechol	140	H
p-ethylguaicol	152	G
4-allylphenol	134	H
2-methoxy-4-vinylphenol (4-vinylguaicol)	150	G
2,6-dimethoxyphenol (syringol)	154	S
4-ethylcatechol	138	H
Vanillic acid	168	G
2-methoxy-4-propenyl-phenol (isoeugenol)	164	G
4-ethylsyringol	182	S
4-vinylsyringol	180	S
2,6-dimethoxy-4-allylphenol	194	S
Syringaldehyde	182	S

LigSteam shows degradation products which can be correlated to a molecular structure consisting GHS units which are typical for wheat straw. The fragments of pyrolyzed Lig Steam are listed in Table 2.9.

2.5 Summary

Beech wood lignin isolated via Organosolv treatment and wheat straw lignin isolated via Steam explosion have been characterized. Organosolv lignins of different process parameters mainly result in different molecular weights and decomposition temperatures. OBL_1 has been isolated using sulphuric acid as catalyst, whereas OBL_2 has been extracted without catalyst but at double

Table 2.9 Compounds identified by Py-GC-MS from lignin fragments of LigSteam

Component	Molecular weight [g mol ⁻¹]	Origin
CO ₂	44	
Benzene	78	C
Toluene	92	C
Ethylbenzene	106	C
<i>p</i> -xylene	106	C
5-methyl-2-furalaldehyde	110	C
Phenol	94	H
2-propenylbenzene	118	H
2-methylphenol (<i>o</i> -cresol)	108	H
3-methylphenol	108	H
Mequinol	124	G
2,4-dimethylphenol	122	H
3-ethyl-5-methyl-phenol	136	G
2-methoxy-4-methylphenol (4-methylguaicol)	138	G
1,2-dihydroxybenzene (pyrocatechol)	110	H
3-methoxypyrocatechol	140	H
<i>p</i> -ethylguaicol	152	G
4-allylphenol	134	H
2-methoxy-4-vinylphenol (4-vinylguaicol)	150	G
2,6-dimethoxyphenol (syringol)	154	S
4-ethylcatechol	138	H
Vanillic acid	168	G
2-methoxy-4-propenyl-phenol (isoeugenol)	164	G
4-ethylsyringol	182	S
4-vinylsyringol	180	S
2,6-dimethoxy-4-allylphenol	194	S
Syringaldehyde	182	S

process duration time. The fractionated lignins are found to be highly pure without carbohydrate residues. This enables conclusions to the pulping and isolation processes and the corresponding bond cleavages between lignin and carbohydrates. NMR studies revealed a GHS ratio of 49/32/19 for OBL_1 and 40/43/17 for OBL_2. Furthermore, the lignin showed a high solubility in the applied solvents like THF, pyridine and 1,4 dioxane. Concerning the three dimensional macromolecular structure, the samples exhibit a rather low molecular weight and polydispersity. Thermal analysis studies using TGA and DSC demonstrated typical thermal behavior for Organosolv-fractionated lignins. Organosolv-treated beech wood lignin samples exhibit decomposition temperatures (T_d) of 381 and 348 °C and glass transition temperatures (T_g) of 123 and 124 °C. Pyrolysis studies presented an individual pyrogram with fragments that originated from GHS units which are in agreement with NMR analyses. Lignin isolated via steam explosion

show impurities with high content of carbohydrates. As a result of solubility tests, a modification, in particular an acetylation, was required to enhance the solubility in organic solvents. LigSteam lignin exhibits a lower glass transition temperature (75 °C) compared to Organosolv lignins. The molecular weight of this fraction is higher than Organosolv lignin which means less depolymerization during the isolation process. The monomeric GHS composition of the fraction has been detected by ^{31}P NMR analysis and pyrolysis. The results can be compared with the literature values for wheat straw lignins.

In summary, the Organosolv process seems to be an efficient method to isolate pure lignin fractions. Resulting molecular weights are dependent on reaction time and catalysts used for lignin isolation. Thus, the presented data provides beneficial information for the utilization of beech wood lignin for chemical synthesis and material development. Referring to Table 3.2 OBL lignins meet the requirements for use as a component in phenol formaldehyde resin and polyurethane systems.

2.6 Analytical Methods

2.6.1 Purity, Ash and Sugar Contents

The chemical composition (% w/w) was performed according to National Renewable Energy Laboratory's (NREL) standard analytical procedure (Sluiter et al. 2008). A Macherey-Nagel HPLC was used with a flow rate of 0.4 mL/min, a column (300 × 7.8 mm) of Macherey-Nagel at a temperature of 90 °C. This analysis was kindly performed by the biorefinery.de GmbH.

2.6.2 Solubility

Solutions were prepared in 5 mL volumetric flasks, using 0.1 g of lignin sample. The solutions were kept for 30 min in an ultrasonic bath and then filtered through a paper filter. The solid residue was dried and weighed. Comparison of the initial sample weight and the remaining solid residue after filtration is the percent solubility value.

2.6.3 FT-IR Spectroscopy

FT-IR spectra of the lignin samples were recorded on a Jasco FT/IR 410 spectrometer in the range of 4000–400 cm^{-1} using a KBr disc containing 1 % finely ground samples. The spectrum recorded over 30 scans with a resolution of 4 cm^{-1} .

2.6.4 ^{31}P NMR Spectroscopy

Quantitative ^{31}P NMR spectra were performed on a Bruker DRX-400 spectrometer using pyridine- d_5/CDCl_3 (1.6:1 v/v) as the solvent, endo-*N*-hydroxy-5-norbornene-2,3-dicarboxiimide as the internal standard, chromium acetylacetonate as the relaxation reagent, and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxapholane as the phosphorylation reagent.

2.6.5 SEC

The lignin sample was completely dissolved in THF (1 mg mL^{-1}) at room temperature with gentle stirring at room temperature. Size exclusion was performed at room temperature with THF as the mobile phase (flow rate 1.0 mL min^{-1}) and a UV detector (280 nm) using an Agilent 1100 instrument. Calibration was performed with polystyrene standards (PSS Standards).

2.6.6 TGA

TGA was performed with about 10 mg of lignin using a Netzsch TGA 209F1 with a heating rate of 20 $^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere. The temperature ranged from ambient to 800 $^{\circ}\text{C}$.

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