



Original Article

Lignin – an alternative precursor for sustainable and cost-effective automotive carbon fiber



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ABSTRACT

Lightweight design is an essential part of the overall Volkswagen strategy for reducing the CO₂ emission. The use of carbon fiber reinforced polymers (CFRP) offers an enormous lightweight potential in comparison to aluminum, enabling a weight reduction, if a load-adapted (unidirectional) CFRP-design is used, of up to 60% in automobile parts without a degradation of the functionalities. Today, the use of CFRP is limited in mass series applications of the automotive industry by the cost of the conventional carbon fiber precursor Poly-Acrylic-Nitrile (PAN). Fifty percent of the cost of a conventional carbon fiber already belongs to the cost of the PAN precursor.

The analysis of lignin as an alternative precursor shows clearly a significant reduction in the cost of CFRP and reduction of CO₂ emission during carbon fiber production. This fact is essential to make carbon fibers ready for a mainstream use within the automotive industry. Key aspects are: the examination and quantification of lignin as an alternative precursor, the optimization of the manufacturing processes, the characterization and quantification of the properties of the novel carbon fibers within an established material pre-validation process and a final economic efficiency and sustainability analysis.

Furthermore, the process ability and demonstrators as well as the suitability for high volume production of the developed processes are main issues for successful implementation in future lightweight vehicle concepts.

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1. Background and Introduction

New emission standards provided for the automotive industry particular challenges in the coming years. A significant reduction in emission of carbon dioxide is needed to achieve the political stated emission targets.

The average emission of the cars produced by the brand Volkswagen was 130 gCO₂/km in 2012. The example of the German CO₂ emission standards shows, how much CO₂ needs to be reduced in the coming years (Fig. 1).

The emission standards have already been set by politics for 2020 in the European Union by 95 gCO₂/km, the United States by 114 gCO₂/km and Japan by 113 gCO₂/km (Table 1).

It is clear that these emission standards will not be achieved by improvements in the efficient engines and drive technology alone. Other factors for better CO₂ efficiency are the aerodynamic design (Cd value) and the vehicle weight.

One of the deciding factors for achieving the emission targets will be the vehicle weight. Unfortunately the weight of cars has been rising in the last decades. Higher safety standards, better quality, more interior and convenience has led to a higher weight of the vehicle (Fig. 2). Almost every car generation got a higher weight. Stronger body adjustments for safety reasons lead for example to heavier high performance chassis. To archive the same dynamic performance of the car heavier high performance engines with higher gas consumption are necessary, which leads to bigger heavier tanks. This chain could be continued and leads to the e principle of the “weight spiral” shown in Fig. 2 [4].

Lightweight construction is one fundamental key for achieving the emission standards for the year 2020. However, weight reductions of 50% or more in some components of the car will be necessary to achieve the goals of the new emission standards. Such enormous weight reductions will not be

achieved with lightweight designs based on steel (compare Volkswagen Golf) or aluminum (compare Audi A8) construction [4]. Fig. 3 shows the potential of lightweight construction carbon fiber reinforced plastics in structural applications and the related cost factors, which would be realized by substitution of a steel component by carbon fiber reinforced plastics [4].

One possible solution for the challenge weight reduction is carbon fiber reinforced plastic (CFRP). Carbon fiber reinforced plastics offer the opportunity to reduce the component weight by up to 60% with the same functionality [5]. The reversing of the “weight spiral” is finally necessary to reach the future emission standards. How the reversing of the “weight spiral” could work is shown in Fig. 4 [4]. Lighter body adjustment leads to lightweight chassis and a combination of downsizing of the engine with reduced tank volume leads to lighter cars. The weight spiral is reversing (Fig. 4).

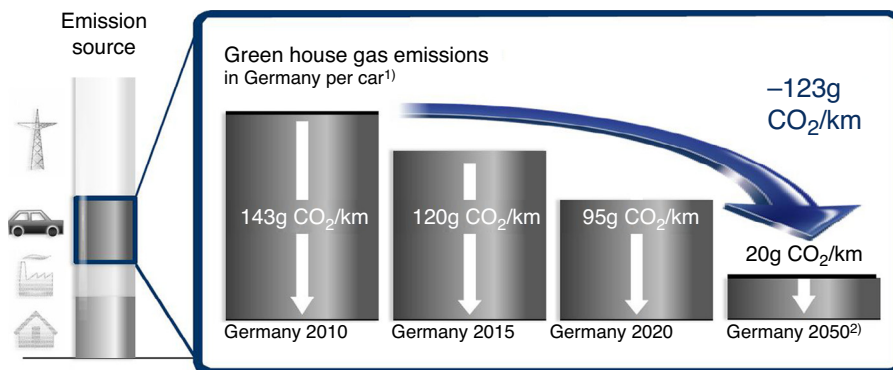
For customers of the automotive industry lightweight construction has enormous benefits. In context the reduction of fuel consumption, the increase of the range, as well as a better driving dynamics of the vehicle are the main benefits of lightweight construction using carbon fiber reinforced plastics. In summary the lightweight construction effects by reducing the weight of a car by 100 kg means for the standard engine a reduction in fuel consumption of 0.3l/100 km or for an electric engine drive a range increase of 100 km [6,7].

However, the weight benefits are up to now restricted by high production cost of the carbon fibers. Today the precursor Poly-Acrylic-Nitrile (PAN) is used for carbon fiber production. When considering the cost of carbon fibers it becomes clear that more than 50% of the cost relate to the production of the precursor, 15% related to the oxidation process and 23% related to the carbonization process (Fig. 5) [8]. Fig. 3 demonstrates schematically the cost factors which are connected to the different materials (blue line in Fig. 3). The cost factors are not to be disregarded and one possibility to reduce the cost of carbon fiber is the change of the precursor for carbon fiber production.

The alternative precursors with the highest potential for the automotive industry are polyethylene and lignin. If lignin is compared to polyacrylonitrile as a precursor for carbon fiber the ability to reduce the cost of manufacturing is by more than

Table 1 – Emission standards for 2020 [1–3].

Limit value for carbon dioxide emission in 2020	
EU	95 gCO ₂ /km
USA	114 gCO ₂ /km
Japan	113 gCO ₂ /km



1) Source: McKinsey & company, ministry of environment

2) Memorandum of understanding, e.g. EU-and G8+5-staates, part of Copenhagen accord 2009

Fig. 1 – CO₂ emission standards in Germany [4].

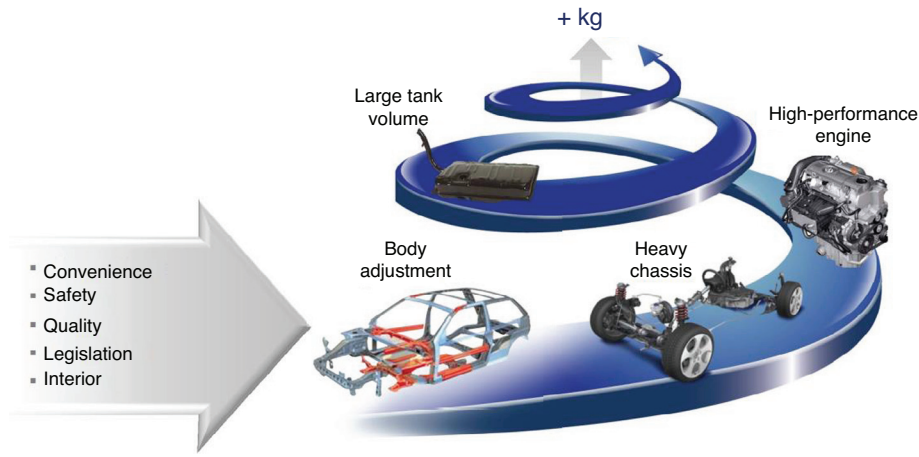


Fig. 2 – Principle of “weight spiral” [4].

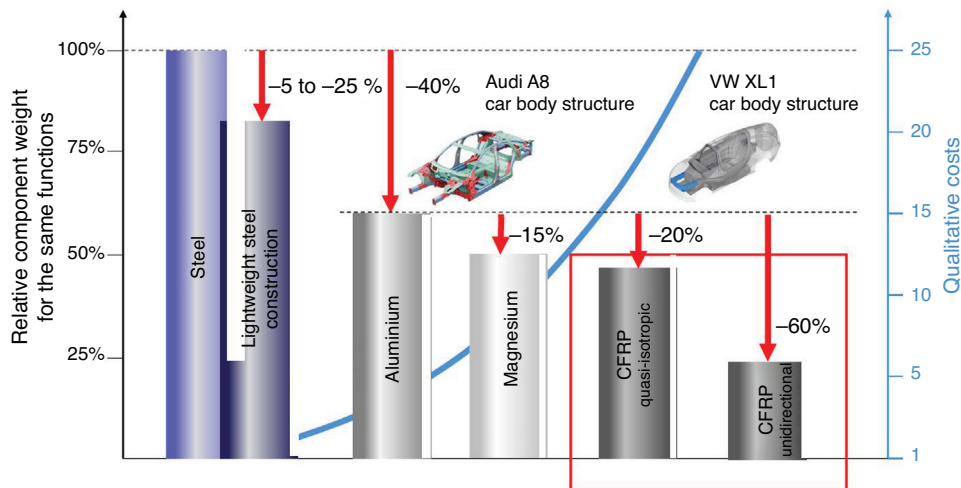


Fig. 3 – Potential of lightweight construction – material substitution in structural applications [4].

50% [9]. That is the reason for the investigation in lignin based carbon fibers in the research of the Volkswagen Group. Hardwood Lignin is as a waste product of the paper mill cheap in huge amounts available. For this reason Hardwood Lignin

as a precursor will especially be considered as an alternative for the production of carbon fibers. Hardwood Lignin is also a sustainable, renewable resource. The use of Hardwood Lignin offers significant cost savings potential in the production of

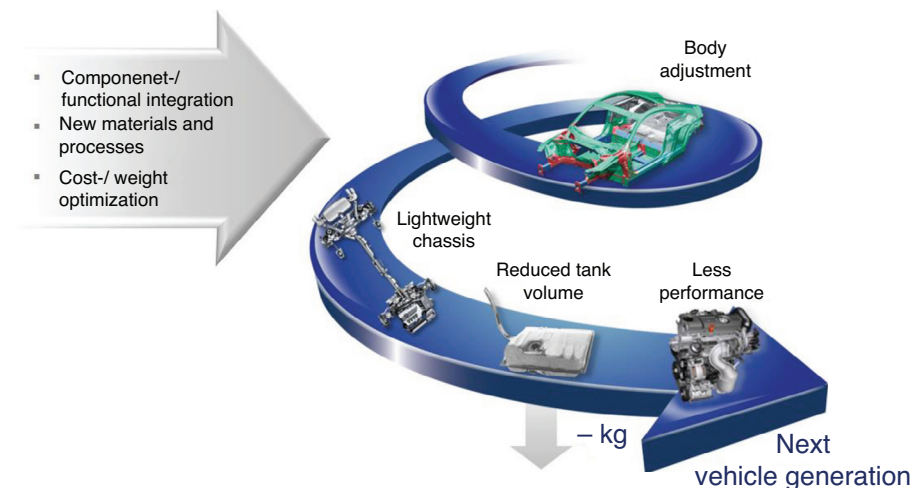


Fig. 4 – Reversing of “weight spiral” [4].

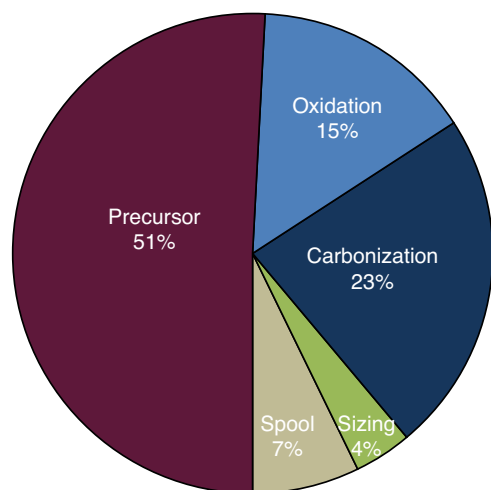


Fig. 5 – Cost distribution for the production of PAN based carbon fiber [4].

carbon fiber and it makes it possible to produce a carbon fiber based on renewable resources.

2. Characterization of Hardwood Lignin as a precursor for carbon fiber

For qualifying lignin as a precursor for carbon fiber for automotive mass production a detailed chemical characterization of this new material is necessary. Therefore elementary analyses, nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy are used.

2.1. Elementary analysis

The elementary analysis is a technique for the determination of the weight percent of chemical elements in organic components. From this data it is possible knowing the molar mass determination to investigate the empirical formula and this way the stoichiometry of an organic compound like Hardwood Lignin. Through further physical analysis it is also possible to find the structure formula [10]. The most common form of elementary analysis, CHN analysis, is accomplished by combustion analysis. In this technique the sample is exactly weighted and then catalytically burned at high temperatures (up to 1800 °C by using of exothermic reactions) with pure oxygen. Then the gases from combustion (oxidation products) with the aid of an inert carrier gas (in most cases helium) are transferred to a catalytic bed made from copper or tungsten. Nitrogen oxides will be reduced over this catalytic bed to pure nitrogen at temperatures of 600–900 °C. After that the gases from combustion (CO₂, H₂O, SO₂ and N₂) are separated in separation column (adsorption and desorption separation column) and quantitative detected by thermal conductivity detector (TCD) and infrared detectors. The masses of these combustion products can be used to calculate the composition of the unknown sample [11].

Table 2 – Results of the elemental analysis of the used Hardwood Lignin powder.

Analyzing Tool	Element	Content	RSD
CHN628	C	61.73%	0.423
	H	6.1%	0.668
	N	0.12%	14.19
Ma 45	H ₂ O	4.5%	0.886
CS 230	S	3.2%	0.927

2.1.1. Experimental

The investigations of the contained elements in the used Hardwood Lignin for carbon fiber production are done with the Vario ELcube CHNS from Elementar. The sulfur-carbon-analyzer CS230 and the CHN-analyzer from LECO were used. All measurements were repeated at least three times and the average of the results is shown.

2.1.2. Results and discussion

For the Hardwood Lignin powder a detailed elementary analyze was made (Table 2). The moisture of 4.5% can be reduced before fiber spinning by drying of the powder.

With the assumption that the lignin monomer is assembled only from the elements carbon, hydrogen and oxygen, the oxygen ratio was estimated as the difference to 100%. From this data the C₉-unit was calculated with: C₉H_{10.8}O_{3.56}. The Formulae C₉ contains complete information about the lignin monomer structure (Fig. 6).

The elementary analysis shows, that the used Hardwood Lignin for making carbon fiber has a carbon content of over 60% (see Table 2). That means a theoretical conversion rate for making carbon fiber from lignin of over 60% would be possible. The experimental found conversion rates are much lower (at around 45%) as a result of loss of carbon in form of carbon dioxide and carbon monoxide during conversion.

The chemical structure of the used lignin will now be discussed with the help of nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy.

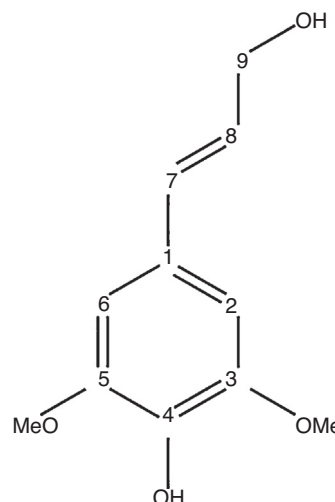


Fig. 6 – Sinapyl alcohol as an example for C₉-units.

2.2. Nuclear magnetic resonance spectroscopy

The nuclear magnetic resonance spectroscopy is a reliable technique for investigating structural features of lignin macromolecules. The NMR spectroscopy is based on the magnetic properties of the atomic nucleus. The determinations of ^1H and especially ^{13}C chemical shifts have made an important contribution for understanding the qualitative and quantitative lignin structure. Two-dimensional NMR methods like H,H-COSY (Correlated Spectroscopy), HSQC (Heteronuclear Single-Quantum Correlation) and HMBC (Heteronuclear Multiple Bond Correlation) were used to identify the primary structures of the investigated lignin derivatives [12].

The NMR spectroscopy focuses on monitoring the different magnetic properties of certain nuclei in a strong magnetic field. Atomic nuclear rotates on their own axis. That means they have a nuclear spin. The nuclear of the isotope ^1H for example is positively charged and the rotation creates a magnetic moment. In the presence of an external magnetic field two spin states exist for ^1H , the up state (lower energy) is aligned with the magnetic field and the down state (higher energy) is opposed to the magnetic field. The energy for transferring the nuclear from the lower to the higher energy state needs a specific frequency of electromagnetic radiation. This effect is called spin reversal. The corresponding energy is adsorbed and measured with the help of the nuclear magnetic resonance spectrometer [12–16].

2.2.1. Experimental

The one-dimensional (1D) and two-dimensional (2D) NMR spectra were measured on a Bruker AVANCE 600 NMR spectrometer equipped with a 5 mm TBI-1H-13C/15N/2H probe head with z-gradients. The samples were solved in DMSO- d_6 . The ^1H and ^{13}C chemical shifts were determined relative to internal DMSO- d_6 and were given in parts per million downfield to TMS.

The operating frequency was 600.13 MHz for ^1H and 150.9 MHz for ^{13}C . The temperature was constant at 295 K (± 0.1 K).

The 2D spectra were obtained by using the standard sequences. The COSY experiments were measured with a spectral width of 6 kHz in both dimensions; 256 increments of 32 scans and 1 K data points were acquired. The pulse width was 9.3 μs (^1H) and the relaxation delay was 1.5 s. The HSQC were separately measured for the aliphatic and for the aromatic part with spectral width in F2 of 1.3 kHz and 2.7 kHz, respectively. For all experiments was the spectral width in F1 8 kHz. The HSQC were detected using 2 K data points in F2 and 256 experiments of 128 scans in F1, relaxations delay was 1.5 s and pulse width for ^1H was 9.3 μs and for ^{13}C was 13.0 μs . The HMBC were also separately measured for the aliphatic and aromatic part with the same spectral conditions in F2 and sweep width in F1 is 25 kHz, 4 K data points in F2 and 512 experiments of 128 scans in F1, relaxations delay 1.5 s, delay for evolution of long-range coupling was 65 ms.

2.2.2. Results and discussion

The 2D NMR spectroscopy was used to identify the primary structures of the investigated Hardwood Lignin derivatives. The assignments of ^1H and ^{13}C chemical shifts based on the

Table 3 – Assignment of ^{13}C - ^1H correlation signals of side-chain region in the HSQC spectra of Hardwood Lignin powder.

Label	^{13}C in ppm	^1H in ppm	Assignment
R $_{\beta}$	54.0	3.05	C $_{\beta}$ in R
B $_{\beta}$	54.3	2.83	C $_{\beta}$ in B
O-CH $_3$	56.3	3.74	O-CH $_3$
A $_{\gamma}$	60.2	3.57	C $_{\gamma}$ in A
A $_{\gamma}$	61.0	4.12	C $_{\gamma}$ in A
A' $_{\gamma}$	–	–	C $_{\gamma}$ in A'
B $_{\gamma}$	64.1	3.27	C $_{\gamma}$ in B
R $_{\gamma}$	70.4	4.08/3.73	C $_{\gamma}$ in R
R $_{\gamma}$	71.4	4.16/3.75	C $_{\gamma}$ in R
A $_{\alpha}$	71.0	4.75–4.85	C $_{\alpha}$ in A linked to G
A $_{\alpha}$	72.0	4.75–4.85	C $_{\alpha}$ in A linked to S
A $_{\beta}$	81.5	4.75	C $_{\beta}$ in A linked to G
R $_{\alpha}$	85.7	4.60	C $_{\alpha}$ in R
A $_{\beta}$	85.7	4.60	C $_{\beta}$ in A linked to S
B $_{\alpha}$	87.4	4.30	C $_{\alpha}$ in B

HSQC (Heteronuclear Single-Quantum Correlation) and HMBC (Heteronuclear Multiple Bond Correlation). The spectra can be divided in three parts—the aromatic, side-chain and aliphatic region (Figs. 7 and 8).

The signals in aliphatic regions are not sensitive for structural modifications. For the structure elucidation the aromatic and side-chain regions are of particularly interest to identify the Hardwood Lignin monomers and inter-unit linkages [12–14].

Important information concerning the structure and composition of Hardwood Lignin were detected with the help of ^{13}C chemical shift in aromatic region (100–150 ppm) and side-chain region (50–90 ppm).

The HSQC and HMBC spectra for the Hardwood Lignin were presented in Figs. 11–13. The cross-peaks were assigned by comparing the literature [15–19] and are listed in Tables 3 and 4. For the labeling compare Figs. 9 and 10, which show the Hardwood lignin monomers and dimers with the side chains.

The side-chain part is ranging from 50 to 90 ppm for ^{13}C and from 2.0 to 5.0 ppm for ^1H chemical shifts (Fig. 11 and Table 3).

Besides the main signal $\delta_{\text{C}}/\delta_{\text{H}}$ 56.3/3.74 ppm for the methoxy group occur the signals for substructure A for C $_{\alpha}$ –H $_{\alpha}$ in the range of $\delta_{\text{C}}/\delta_{\text{H}}$ 71.0–72.0 and 4.75–4.85 ppm and for C $_{\beta}$ –H $_{\beta}$ at 81.5/4.75 ppm and 87.7/4.60 ppm linked to G and S, respectively (Fig. 9).

For C $_{\gamma}$ –H $_{\gamma}$ the cross peaks were observed at $\delta_{\text{C}}/\delta_{\text{H}}$ 60.2/3.57 ppm. Furthermore strong signals were observed for resinol substructure R at $\delta_{\text{C}}/\delta_{\text{H}}$ 54.0/3.05 ppm for C $_{\beta}$ –H $_{\beta}$, 71.4/4.75 and 3.37 ppm for C $_{\gamma}$ –H $_{\gamma}$ and 87.7/4.60 ppm for C $_{\alpha}$ –H $_{\alpha}$ (Figs. 9–11).

Also phenylcoumaran B is a well-known inter-unit linkage in lignin and in general it is found in the Hardwood Lignin precursor powder. The signals were detected at $\delta_{\text{C}}/\delta_{\text{H}}$ 54.3/2.83 ppm for C $_{\beta}$ –H $_{\beta}$, 64.1/3.27 ppm for C $_{\gamma}$ –H $_{\gamma}$ and 87.4/4.30 ppm for C $_{\alpha}$ –H $_{\alpha}$ (Figs. 9–11).

The aromatic region is ranging from 100 to 150 ppm for ^{13}C and from 5.5 to 7.5 ppm for ^1H chemical shifts (Fig. 12 and Table 4).

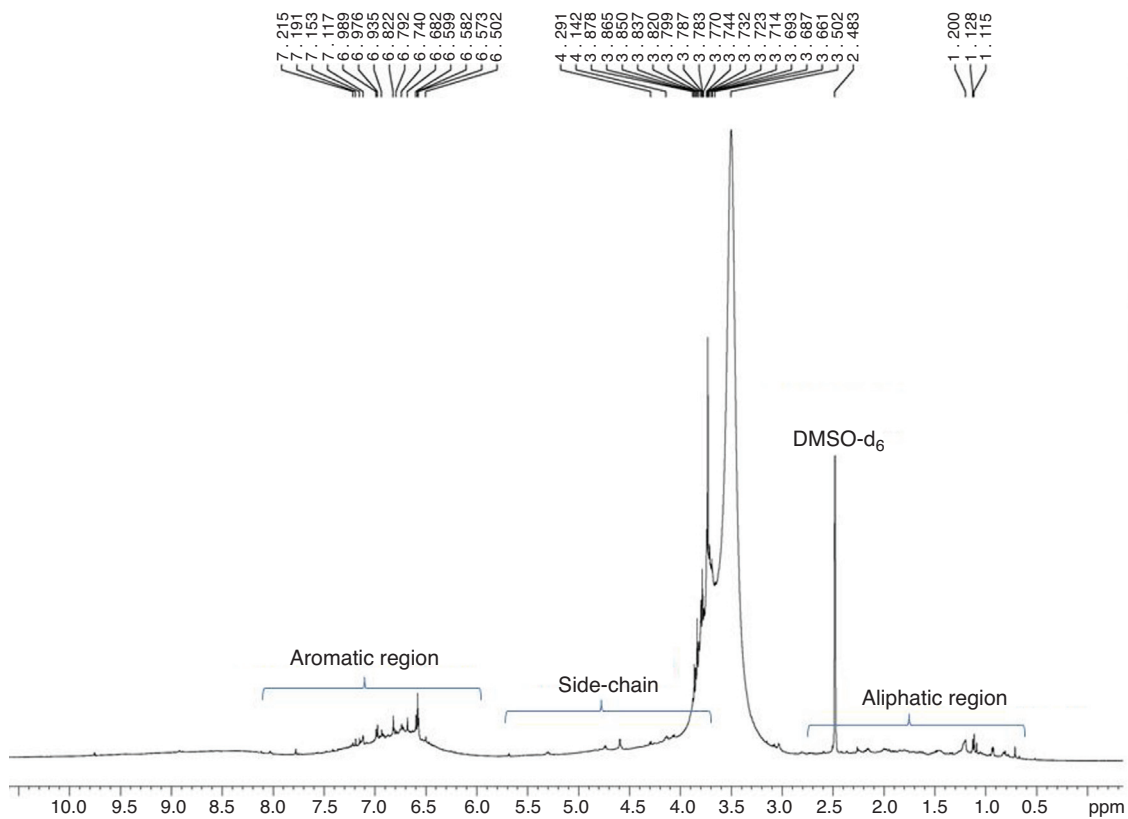


Fig. 7 - ^1H NMR spectrum of Hardwood Lignin, measured in DMSO-d₆.

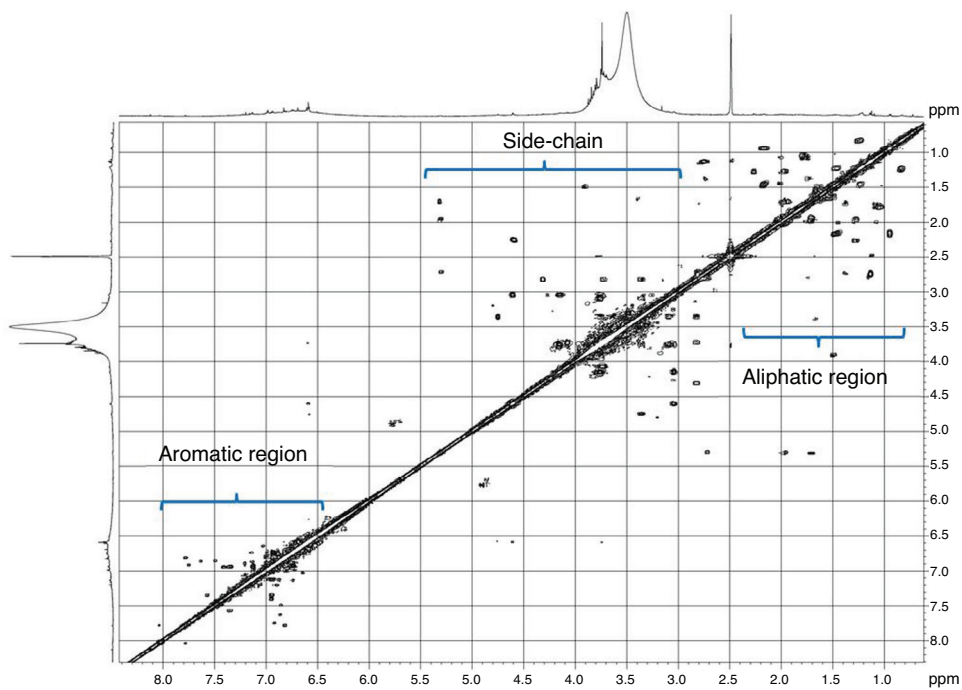


Fig. 8 - ^1H , ^1H -COSY of Hardwood Lignin, measured in DMSO-d₆.

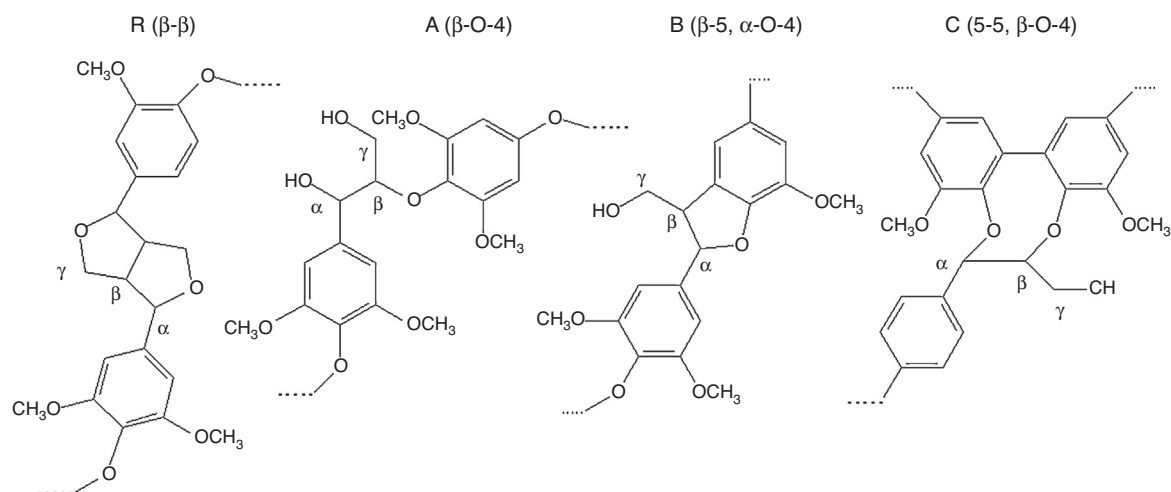


Fig. 9 – Hardwood Lignin side chains.

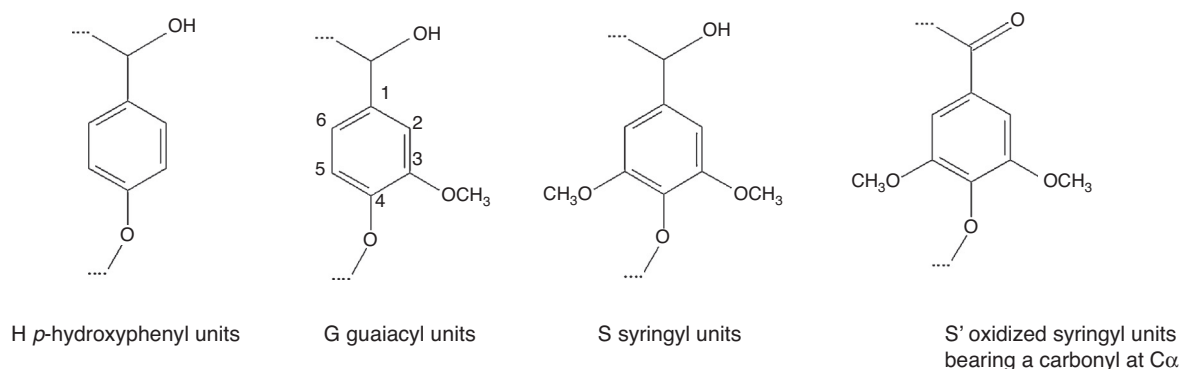


Fig. 10 – Lignin monomers.

Table 4 – Assignment of ^{13}C – ^1H correlation signals of aromatic region in the HSQC spectra of Hardwood Lignin.

Label	^{13}C in ppm	^1H in ppm	Assignment
$S_{2/6}$	103.4	6.58	$\text{C}_{2/6}$ – $\text{H}_{2/6}$ in S linked to A
$S_{2/6}$	103.7	6.59	$\text{C}_{2/6}$ – $\text{H}_{2/6}$ in S linked to R
$S_{2/6}$	103.7	6.61	$\text{C}_{2/6}$ – $\text{H}_{2/6}$ in S linked to B
$S_{2/6}$	103.7	6.83	$\text{C}_{2/6}$ – $\text{H}_{2/6}$ in S
$S_{2/6}$	105.3	6.98	$\text{C}_{2/6}$ – $\text{H}_{2/6}$ in B
$S_{2/6}$	105.3	7.13	$\text{C}_{2/6}$ – $\text{H}_{2/6}$ in S
$S_{2/6}$	105.3	6.69	$\text{C}_{2/6}$ – $\text{H}_{2/6}$ in B
$S'_{2/6}$	106.6	7.22	$\text{C}_{2/6}$ – $\text{H}_{2/6}$ in oxidized S
$S'_{2/6}$	107.5	7.19	$\text{C}_{2/6}$ – $\text{H}_{2/6}$ in oxidized S
$S'_{2/6}$	108.3	7.16	$\text{C}_{2/6}$ – $\text{H}_{2/6}$ in oxidized S
G_2	109.6	7.12	C_2 – H_2 in G
G_5	115.6	6.6–6.6	C_5 – H_5 in G
G_5	115.2	6.6–6.8	C_5 – H_5 in G
G_6	119.6	6.93	C_6 – H_6 in G
$H_{2/6}$	126.2	6.93	$\text{C}_{2/6}$ – $\text{H}_{2/6}$ in H
$H_{2/6}$	126.4	6.82	$\text{C}_{2/6}$ – $\text{H}_{2/6}$ in H
S_1	133.6–135.4	–	C_1 in S_1
S'_1	140.0–141.8	–	C_1 in S'_1
$S_4, S_{3/5}G_3, G_4$	147.1–148.2	–	$\text{C}_4, \text{C}_{3/5}$ in etherified SC_3 , C_4 in etherified G
$\text{C}=\text{O}$	128.1/129.5	–	
$\text{C}=\text{O}$	n.o.	–	$\text{C}=\text{O}$ in acetates
$\text{C}=\text{O}$	190.8–196.3	–	α -CO/ γ -CHO

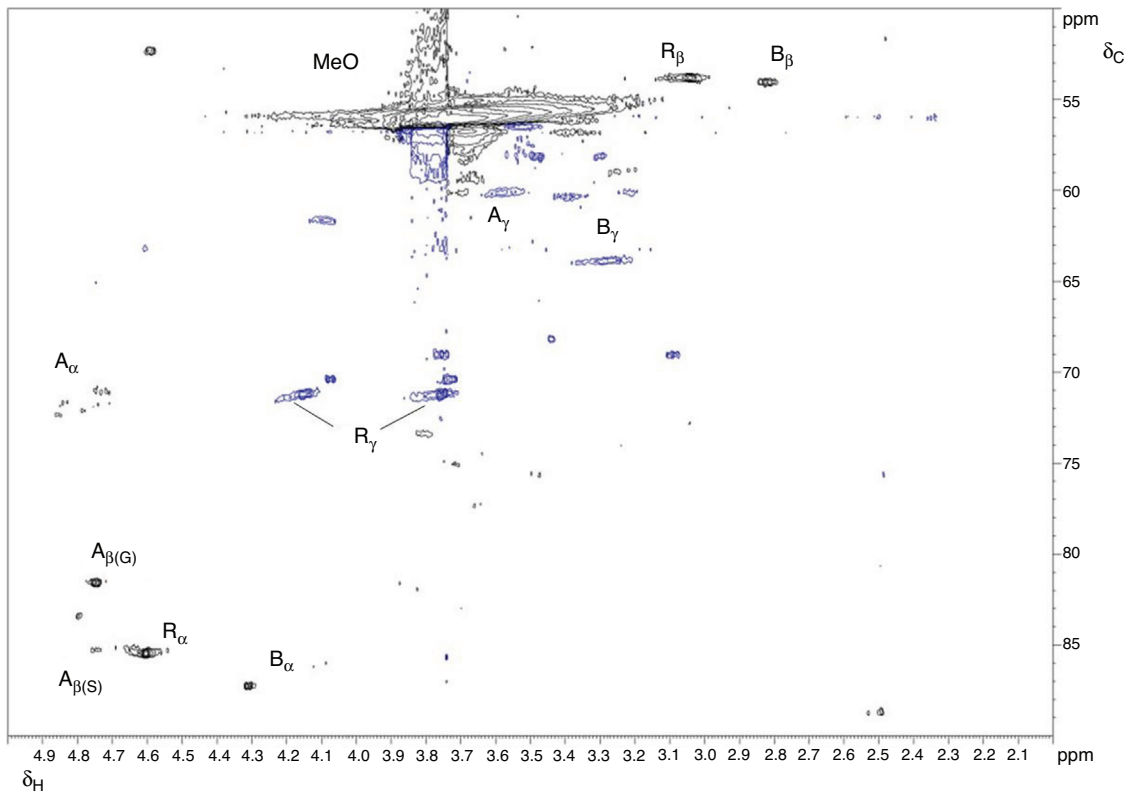


Fig. 11 – HSQC spectra for the side-chain region of Hardwood Lignin.

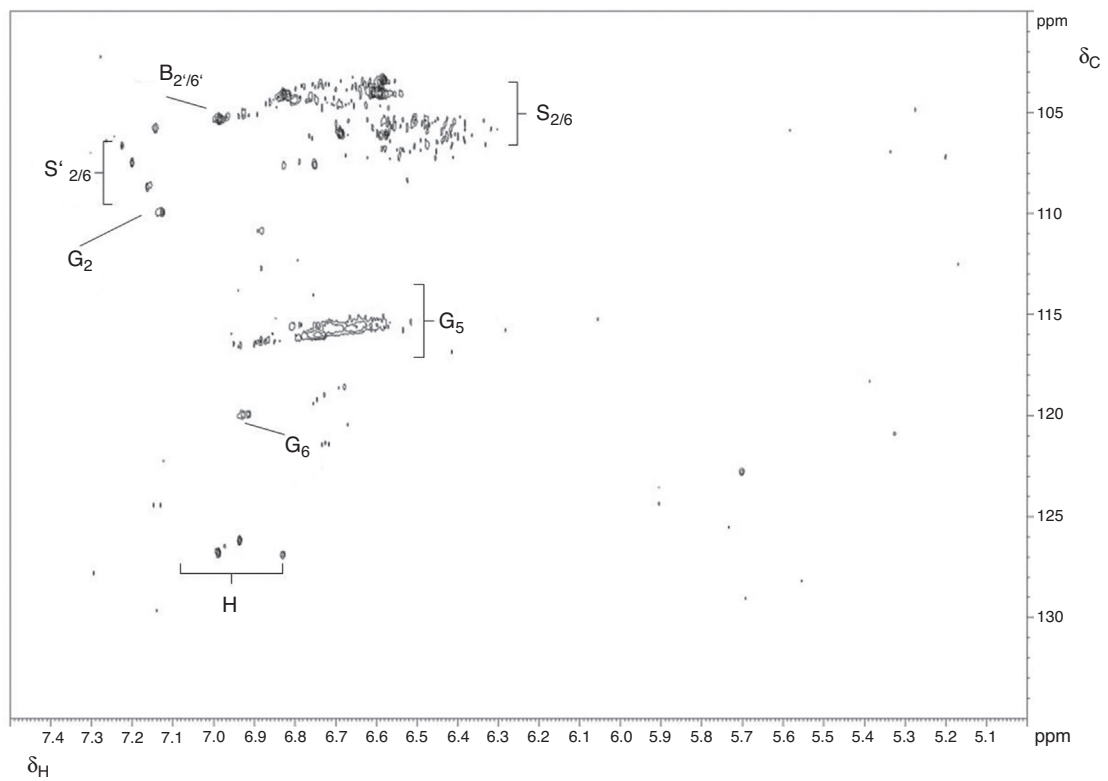


Fig. 12 – HSQC spectra for the aromatic region of Hardwood Lignin.

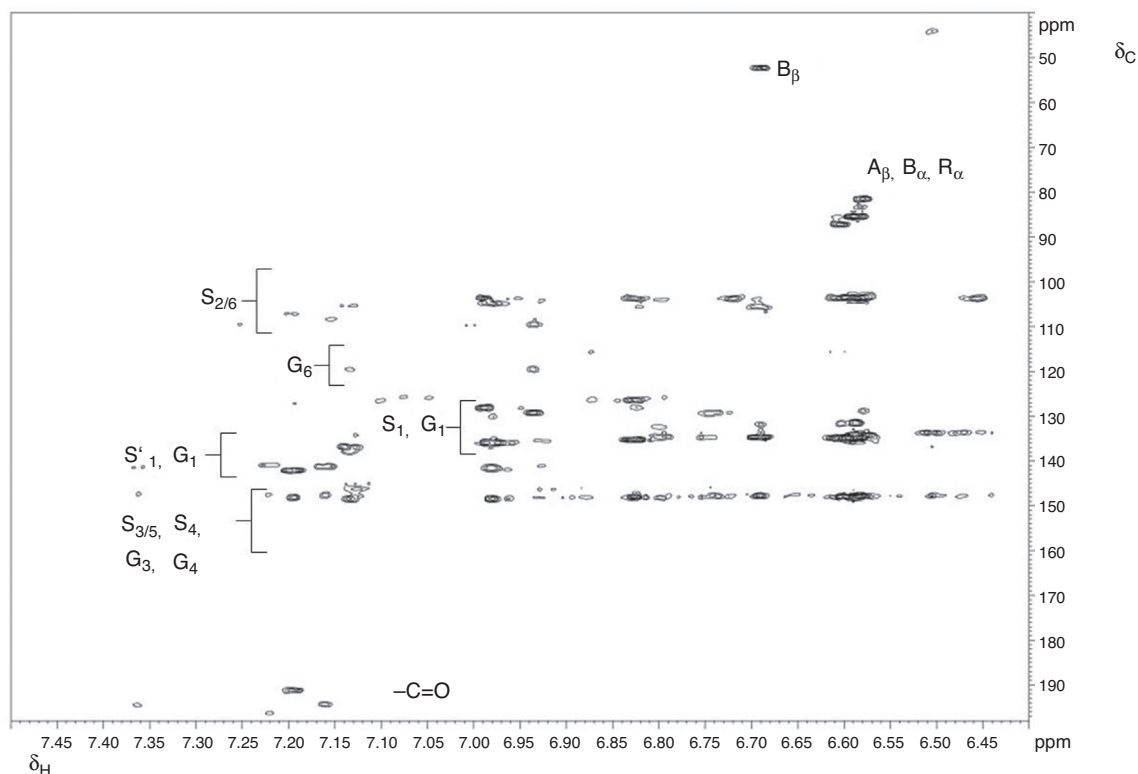


Fig. 13 – HMBC spectra for the aromatic region of Hardwood Lignin.

The investigated samples were produced from Hardwood Lignin powder which typically contains guaiacyl **G** and syringyl **S** units (Fig. 10).

The syringyl **S** and guaiacyl **G** could be assigned in the aromatic region ranging from 100 to 140 ppm for ^{13}C and 5.0 to 7.5 ppm for ^1H . The **S** units showed different correlations for $\text{C}_{2/6}\text{--H}_{2/6}$ $\delta_{\text{C}}/\delta_{\text{H}}$ 103.4–105.3/6.58–6.87 ppm depend on the different inter-unit linkages at C_4 and C_1 . The $\text{C}_{2/6}\text{--H}_{2/6}$ correlations in C_α -oxidized **S** units were found at $\delta_{\text{C}}/\delta_{\text{H}}$ 106.6–108.3/7.12–7.22 ppm. The **G** units revealed dominant signals for the $\text{C}_2\text{--H}_2$ at $\delta_{\text{C}}/\delta_{\text{H}}$ 109.6/7.12, for $\text{C}_5\text{--H}_5$ broad signal at $\delta_{\text{C}}/\delta_{\text{H}}$ 115.2–115.5/6.6–6.8 ppm and $\text{C}_6\text{--H}_6$ at $\delta_{\text{C}}/\delta_{\text{H}}$ 119.6/6.93 ppm. Signals for **H** were detected at $\delta_{\text{C}}/\delta_{\text{H}}$ 126.2–126.5/6.82–6.93 ppm.

Table 4 now illustrate the details of the signals shown in the spectra of Fig. 12.

The HMBC spectra (Fig. 13) are examples for the efficiency of NMR as an analytical technique for the characterization of lignins. This spectra allowed the assignment of quaternary carbons C_1 , $\text{C}_{3/5}$, C_4 in **S** units, the carboxyl groups in oxidized syringyl groups in **S'** and the C_1 , C_3 and C_4 in **G** units. Strong long range correlations for the aromatic protons in **S** and **G** units were observed between $\text{H}_{2/6}$, H_5 and the inter-unit linkages C_α in **B** and **R**, C_β in **A** and **B** is dominant (for chemical structure compare Figs. 9 and 10).

2.3. Fourier transform infrared spectroscopy

Infrared spectroscopy (IR) is the analysis of infrared light interacting with a molecule. IR Spectroscopy measures the

vibrations of atoms and based on this it is possible to determine the functional groups of Hardwood Lignin [20].

Infrared spectroscopy is used to determine the structures of molecules and the molecules characteristic absorption of infrared radiation. Infrared spectrum is molecular vibrational spectrum. When exposed to infrared radiation, sample molecules selectively absorb radiation of specific wavelengths, which causes the change of dipole moment of sample molecules. Consequently, the vibrational energy levels of sample molecules transfer from ground state to excited state. The frequency of the absorption peak is determined by the vibrational energy gap. The number of absorption peaks is related to the number of vibrational freedom of the molecule. The intensity of absorption peaks is related to the change of dipole moment and the possibility of the transition of energy levels. Therefore, by analyzing the infrared spectrum, it is possible to obtain abundant structure information of Hardwood Lignin [20,21].

2.3.1. Experimental

Infrared spectra were recorded on a Perkin Elmer FT/IR 2000. The samples were measured using an ATR unit. The spectral resolution was 4 cm^{-1} . The relative ratios of the interesting functional groups were analyzed.

2.3.2. Results and discussion

The Fourier transform infrared spectroscopy (FT-IR spectroscopy) is an effective method to describe the structural changes occurring during treatment of Hardwood Lignin.

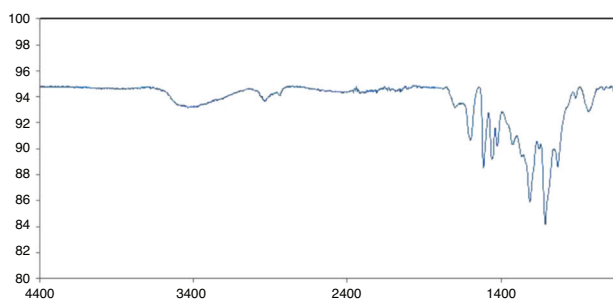


Fig. 14 – FT-IR spectrum Hardwood-Lignin.

Fig. 14 shows the FT-IR spectrum of the precursor material (Hardwood Lignin).

The typically functional groups were found and the assignment was according the literature [22,23]. Following bands were identified: O–H stretching at 3400–3460 cm^{-1} , aromatic C–H stretching at 3009 cm^{-1} , aliphatic C–H stretching at 2937 and 2846 cm^{-1} in methoxy groups and methyl as well as methylene groups arising from side chains. The band occurs around 1705 cm^{-1} coming from C=O stretching in unconjugated carbonyl/carboxyl groups is an interesting region. The Hardwood Lignin consists of a composition of syringyl and guaiacyl units. For both aromatic units the typical aromatic skeleton vibrations were found at 1600, 1514 and 1424 cm^{-1} and the aromatic ring vibration at 1462 cm^{-1} .

The region in the FT-IR Spectrum below 1400 cm^{-1} is more difficult to analyze. In this region combinations of different vibration states can influence the spectrum.

The band at 1326 cm^{-1} and 1270 cm^{-1} are the rings breathing with C=O stretching and characteristic for **S** and **G** units, respectively (compare Fig. 10: Hardwood Lignin monomers). The band at 1113 cm^{-1} dominates and is associated with the C–H in plane deformation vibrations of the **S** units. The intensive band at 1214 cm^{-1} can be combined with the C–C, C–O and C=O stretching and the band at 1031 cm^{-1} with the C–H in plane deformation of **G** guaiacyl units. The smaller band at 831 cm^{-1} is remarkable and in the range of aromatic C–H out-of-plane deformation vibrations for the **S** units (The chemical structure of lignin monomer units is shown in Fig. 10). The results of the FT-IR spectroscopy are summarized in Table 5.

All in all the results of the FT-IR spectroscopy underlines the structures, which are already found with nuclear magnetic resonance spectroscopy and Elementary analysis. FT-IR Spectroscopy will also be a useful tool for the designing of the reaction mechanism during conversion of Hardwood Lignin to carbon fiber.

3. Development of a lignin based carbon fiber

The following section will show the possibility to make a lignin-based carbon fiber in laboratory scale [4,24].

The conventional carbon fiber production process of a PAN based carbon fiber contains fiber spinning, fiber stabilization and fiber carbonization as the mayor steps. For a future scale up of the lignin based carbon fiber production it is necessary to create a process which is comparable to the conventional

PAN based carbon fiber production process. This will also help to lower the investment cost for future production facilities because conventional conversion equipment can be used for lignin carbon fiber production.

Compared to the conventional PAN based carbon fiber production process two steps were added to prepare the fiber spinning process. These steps are washing of lignin powder and drying as the first step and pelletizing of the lignin powder as the second step.

This leads to five main steps, which illustrate the use of Hardwood Lignin as a precursor for carbon fiber production:

- Washing of lignin powder and drying
- Pelletizing of the lignin powder
- Melt spinning of the lignin fiber
- Oxidation of the fiber
- Carbonization of the fiber

The following sections will describe the five steps in more detail and will show in logical order the production process of Hardwood Lignin based carbon fibers as performed at Oak Ridge National Laboratory in Tennessee, USA.

The lignin based carbon fiber project was done at Oak Ridge National Laboratory with the approval of the U.S. Department of Energy under the Cooperative Research and Development Agreement (CRADA) NFE-12-03992. For this reason the details which can be given in this context are limited.

3.1. Lignin powder

The focus on more environment friendly materials has prompted the interest in lignin as a source for new materials. There are five mayor processes for isolation of lignin from wood: the Kraft Process, the Sulfito Process, the Alcell Process, the Organocell Process and the processes in the Biorefinery.

The pulping industry alone provides every year around 128 million tons of lignin as waste. The most important process in pulping industry is the Kraft Process with 75% of the worldwide lignin production. Second important is the Sulfito process with 8%. The other 17% are produced by special processes (the Alcell Process, the Organo-cell Process), which are used for the production of special papers and special kinds of cellulose [24].

A detailed detection of the properties and the chemical characterization of the Hardwood Lignin precursor powder were given above.

At the pulp mill, lignin is dissolved away from the cellulose into black liquor. Then the lignin is precipitated out of the black liquor. After the washing and drying process Hardwood Lignin powder is available. An example of the Hardwood Lignin powder, how it was received from the lignin producer is shown in Fig. 15 [4,25].

3.2. Compounding and pelletizing

The Hardwood Lignin powder cannot be used for fiber spinning. The main reason is the bad flow ability of the Hardwood Lignin powder. The reason for bad flow ability is high components of moisture (water content: 6.1%) and volatiles, which can be detected in the hydrophilic Hardwood Lignin powder.

Table 5 – IR-bands (b – bright, m – medium, s – strong, w – weak).

Band	Intensity	Chemical group
3400–3460 cm ⁻¹	b	O–H stretching in aromatic and aliphatic structures
2936–2840 cm ⁻¹	m	C–H stretching of methoxy groups, methyl and methylene groups in side chains
1701–1705 cm ⁻¹	m	C=O stretching of unconjugated carbonyl and carboxyl groups
1598–1600 cm ⁻¹	s	Typical aromatic skeleton vibrations
1513–1514 cm ⁻¹		
1423 to –1424 cm ⁻¹		
1459–1462 cm ⁻¹	s	Aromatic ring vibration
1365–1368 cm ⁻¹	w	O–H stretching of phenolic OH-groups
1326–1327	m	C=O stretching at the ring
1267–1270		
1212–1214	s	The C–C, C–O and C=O stretching
1151–1112	m	C–H stretching in plane deformation of the ring
1031–1130		
829–831	B	Aromatic C–H out-of-plane deformation vibrations

**Fig. 15 – Hardwood Lignin powder.**

For realizing a better flow ability and for reducing the moisture and the volatiles compounds for the melt spinning process a pelletizing of the Hardwood Lignin powder was done.

The twin screw compounding extrusion technology readily reduced moisture and volatiles in the extruded Hardwood Lignin pellets to low and near target levels by vaporizing moisture and volatiles. Also a vacuum removes additional moisture and volatiles.

For making carbon fiber mainstream it is necessary to demonstrate large scale production of the pelletizing process. This was done with two sizes of extrusion machines.

Using the 27 mm extrusion machine a Hardwood Lignin powder throughput of 45 kg/h was demonstrated. Semi-production scale lignin pelletizing was also done. A 53 mm diameter extrusion machine equipped with a hot die face cutter was used to successfully pelletize almost 1000 kg of Hardwood Lignin for subsequent melt spinning into Hardwood Lignin precursor fiber [4,25]. Fig. 16 shows the used extrusion machine with the following dimensions: Centerline Height 1090 mm; Length 5410 mm; Width 1030 mm; Height 1470 mm and Weight 5440 kg. The moisture and volatiles are removed from the lignin by heating and under vacuum (Fig. 16).

For analyzing the influence of the compounding and pelletizing process on the chemical structure of Hardwood Lignin

pellets NMR and FTIR studies were made. The results of the characterization can be found in our paper in the magazine Carbon. The changes of the chemical structure compared to the Hardwood Lignin powder is shown as well as the reactions which lead to these changes and are also shown in this paper.

The in laboratory scale pelletized Hardwood Lignin with a better flow ability, less contents of moisture and volatiles is shown in Fig. 17.

3.3. Precursor fiber production

The most important step during production of a Hardwood Lignin based carbon fiber is the spinning process of the precursor fiber since the quality of the precursor fiber defines the quality of the carbon fiber after conversion.

The thermal properties of the Hardwood Lignin can be analyzed with the help of Thermo Gravimetric Analysis and Differential Scanning Calorimetry. In single fiber spinning experiments the conditions for the melt spinning process were defined (temperature profile, kind and amount of plasticizer, spinning speed etc.). After several single fibers spinning tests a scale up with a melt blow spinning system was made.

Using a laboratory scale machine, “melt blown” spinning was evaluated for producing a Hardwood Lignin fiber web with a filament diameter in the range of 10–20 μm. The fibers were spun into a web approximately 60 cm wide with areal density of 230 g/m² at rates approaching 15 kg/h. Fig. 18 illustrates the precursor fiber production using the melt blow process [25].

This is the worldwide first presented process which makes it possible to produce Hardwood Lignin fibers in a Semi-production scale.

From the experiences in the fiber production trials an establishment of a lignin specification for melt spin able lignin was made, as follows [25]:

- >99% lignin
- <500 ppm residual carbohydrates
- <5 wt% volatiles
- <1000 ppm ash
- <500 ppm non-melting particles larger than 1 μm diameter

The definition of Hardwood Lignin specifications for carbon fiber production is also completely new (no specification like

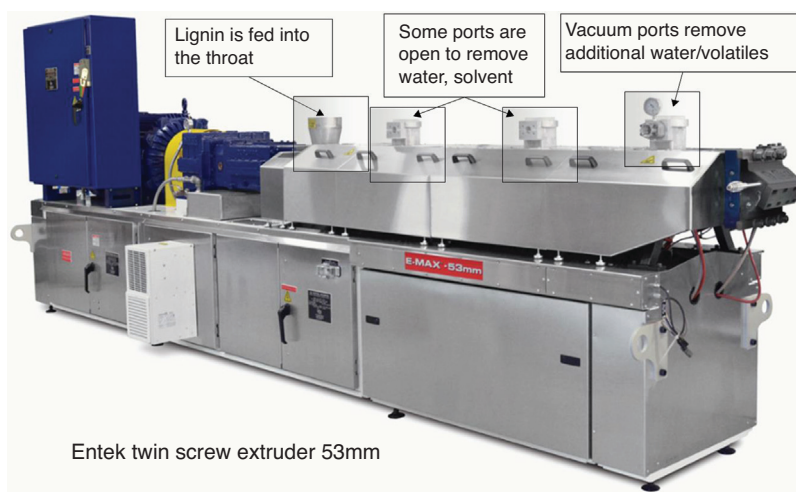


Fig. 16 – 53 mm diameter extrusion machine used for pelletizing lignin [4].

this is available in literature and publications) and will help to define a profile of properties for lignin producers, how and in which for their lignin is useful for carbon fiber production.

3.4. Fiber stabilization

The fiber stabilization is like in the conventional carbon fiber production process the most critical step during conversion. The oxidation process must be handled very carefully to prevent any damage of the fiber. If the oxidation conditions are too harsh, a complete oxidation of the fiber is possible, which means fire in the oxidation oven and CO_2 and ash as the result of this step. To prevent such issues the stabilization time in laboratory scale was chosen extremely long with very soft temperature ramp.

Stabilization time was and remains a significant challenge. For the Hardwood Lignin in laboratory scale, the stabilization time requires several days. It was possible to show that a successful stabilization is possible at temperatures between 200 and 300 °C by using an extremely soft temperature ramp (Fig. 19) [4].



Fig. 17 – Pellets made from Hardwood Lignin.

Stabilization must be accelerated to achieve acceptable process economics. A simple tuning of the thermal profile semi-production scale reduced the residence time from ~150 h to ~100 h. That means a reduction of more than 33% was realized.

ORNL stabilized fibers using a ~100-h batch thermal treatment in a large (>5.5 m³) oven (Fig. 20). 75 kg of lignin fibers were stabilized for further processing. This is the first worldwide reported stabilization of lignin fibers at a scale exceeding ~1 kg and shows the possibility to scale up the stabilization in industrial scale. The material darkens in color from brown to

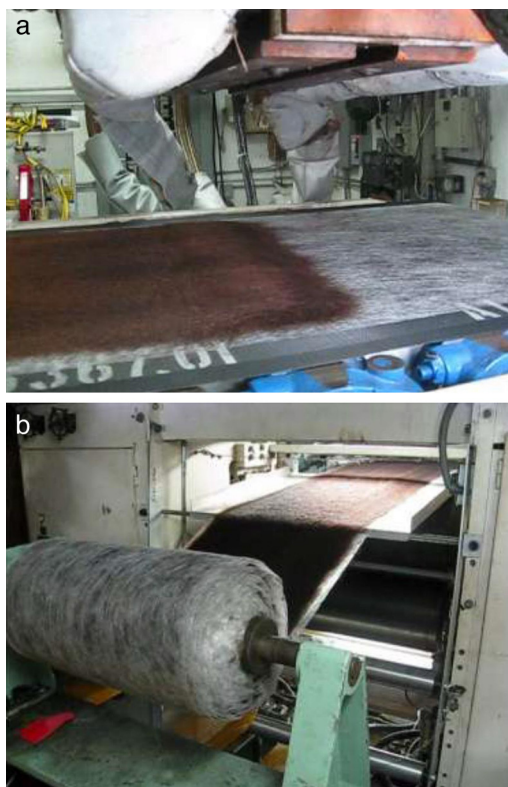


Fig. 18 – Melt blow process for producing lignin fiber.

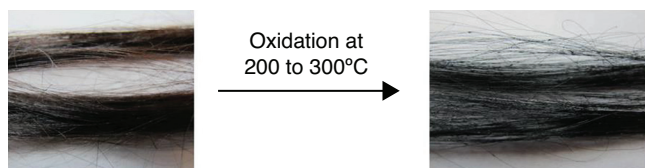


Fig. 19 – Stabilizing of lignin fiber.

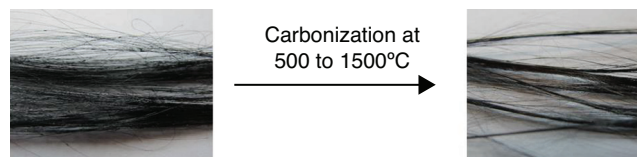


Fig. 21 – Carbonizing of stabilized lignin fiber.



Fig. 20 – Batch stabilization of Hardwood Lignin fibers.

black (Fig. 19) as it heat treated in the oxidation oven (Fig. 20) [25].

Additional reductions of the stabilization time are possible by future optimization of the temperature ramp and the concentration of oxygen in the stabilization oven. Also a transfer of the results from a batch process to a continuous process will help to improve the economically of the stabilization process. All in all a reduction of the stabilization time in an industrial process below 3 h should be possible (compare conventional process using PAN).

3.5. Fiber carbonization

The stabilized material is carbonized in a furnace under nitrogen atmosphere. It typically operates at 500–1500 °C for 5–10 min. Approximately 65% of the material is vaporized during carbonization with gasses exhausted through an incineration system. ORNL heat treated the stabilized fibers to produce ~25 kg of lignin-based carbon fibers. This is the first reported carbonization of lignin fibers at a scale exceeding ~1 kg and shows the possibility to scale up the stabilization in industrial scale. The remaining material is nearly 100% pure carbon – a lignin-based carbon fiber (Fig. 21) [4].

All in all this paper presents the establishment of the laboratory scale process for making lignin based carbon fibers and shows worldwide the first Semi-production scale for producing Hardwood Lignin based carbon fibers. It was demonstrated that more than 1000 kg of Hardwood Lignin were successfully pelletized and spun to Hardwood Lignin precursor fiber. Also stabilization and carbonization of higher amounts of Hardwood Lignin fibers is worldwide unique and shows a possible

way to scale up the production process of lignin based carbon fibers.

4. Summary and next steps

This article shows the investigation process of new low cost carbon fiber for the automotive industry. After identifying that the precursor is the biggest cost factor in conventional carbon fiber, new precursors were investigated. Lignin seems to have a high potential as a new precursor. For producing new carbon fiber from lignin, lignin itself must be characterized and analyzed for understanding the chemistry and behavior of this new precursor. With this consolidated findings a process for producing carbon fiber laboratory scale is possible. After making carbon fiber the characterization of these fibers is the next important step.

The next steps will be to optimize the lignin-based carbon fiber reaching property targets of the automotive industry and creating demonstration parts which show the potential of this new precursor.

Conflicts of interest

The authors declare no conflicts of interest.

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