Original Article

Characterization of the major reactions during conversion of lignin to carbon fiber

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ABSTRACT

Lightweight design is an essential part of the overall Volkswagen strategy for reducing the CO2 emissions. The use of carbon fiber offers an enormous lightweight potential. In comparison to steel enabling a mass reduction of up to 70% in automotive parts without a degradation of the functionalities is possible. Today, the use of carbon fiber is limited in mass series applications of the automotive industry by the cost of the conventional C-fiber precursor polyacrylonitrile (PAN). 50% of the cost of a conventional carbon fiber already belongs to the cost of the PAN precursor. Lignin as a precursor for carbon fiber production can realize enormous savings in cost. For qualifying lignin-based carbon fiber for automotive mass production a detailed characterization of this new material is necessary. Therefore, nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy are used. Using the results of these experiments, the major reactions during conversion of lignin to carbon fiber are proposed.

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1. Introduction

As of January 1st 2014, all new vehicles are required to meet Euro 6 emission standard. This standard requires all new light passengers and light commercial automotive manufactures to reach an average vehicle carbon dioxide (CO2) emission of 130 g/km. The average vehicle emission of a light passenger vehicle produced by the brand Volkswagen in 2012 was 130 g/km [1–3].

The emission standards for 2020 have already been determined by the European Union (EU) and by the United States of America Environment Protection Agency (EPA). The next set of regulations been set for both Euro 7 and Tier 3 with an average lightweight vehicle emission of CO2 of 95 g/km and 114 g/km, respectively [1–3].

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These new emission standards provide a vast amount of challenges for the automotive manufactures. A significant reduction in their vehicle’s emissions is necessary to prevent potential fines by the government [1–3].

To meet these onerous regulations, manufactures must focus their resources. For several years the focus was on more efficient powertrains and drivetrains but it is now clear that these emission standards will not be achieved by improvements solely on this. Manufacturers must expand their research into fields such as aerodynamics in hopes to reduce overall vehicle drag, and the usage of advanced lightweight materials to reduce the overall vehicle’s weight.

For automotive manufactures to reach the 95 g CO₂/kg requirement by 2020, the implementation of lightweight constructions cannot solely be based on steel (compare Volkswagen Golf) and aluminum (compare Audi A8) advancements. To accomplish this, a reduction of component weight must exceed 50%. Steel and aluminum can only attribute up to 40% weight reduction [4].

Carbon fiber reinforced plastics (CFRP) can provide this 50% minimum reduction in weight. A weight saving potential of up to 70% on a component without compromising its functionality is possible [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. For example, the effects of a lightweight construction that reduces the weight of a car by 100 kg, means for the standard engine, a reduction of fuel consumption of 0.3 L/100 km. For an electric drivetrain this would result in a range increase of 100 km [5–7].

However, the weight benefits are currently limited by the high production cost of the carbon fiber. The cost factors are not to be disregarded and one possibility to reduce the cost of carbon fiber is to change the precursor used to produce carbon fiber.

Today the most common precursor used to produce carbon fiber is polyacrylonitrile (PAN). When investigating the cost of producing carbon fiber, it becomes clear that more than 50% of the cost is related to the production of the precursor. The remaining cost is distributed as such: 15% to the oxidation process, 23% to the carbonization process, and the remaining to sizing and spooling [8].

The key to reducing the production cost of carbon fiber is the use of an alternative precursor. 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 50% [9]. That’s the reason for the investigation of lignin-based carbon fiber in this paper. Lignin is a natural waste byproduct of the paper industry and biorefineries, which is readily available in enormous amounts and due to this very inexpensive. Lignin is also a sustainable, renewable resource. The use of lignin offers significant cost saving potential in the production of carbon fiber. Lignin makes it possible to produce a carbon fiber based on renewable resources.

This paper will show the major reactions, which take place during carbon fiber production from lignin.

2. Experimental

2.1. Carbon fiber production from lignin

The following section will show the possibility to make a lignin-based carbon fiber in laboratory scale as performed by the Oak Ridge National Laboratory (ORNL) [4,10]. Five main steps illustrate the use of lignin as a precursor to carbon fiber:

- Washing of lignin powder and drying (HW)
- Pelletizing of the lignin powder to pellets (P)
- Melt spinning of the lignin fiber (LF)
- Oxidation of the fiber (stabilization) (OLF)
- Carbonization of the fiber (CLF)

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 the lignin powder is obtained.

The twin screw compounding extrusion technology readily reduced moisture and volatiles in the extruded lignin to low and near target levels. Furthermore, using 27 mm extrusion machine, a lignin 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 lignin for subsequent melt spinning into precursor fiber.

Using a lab scale machine, “melt blown” spinning was evaluated for producing a lignin fiber web with a filament diameter in the range of 10–20 micron. The fibers were spun into a web approximately 60 cm wide with areal density of 230 g/m² at rates approaching 15 kg/h.

Stabilization time was and remains a significant challenge. For the “reference” Alcell® lignin, the stabilization time requires several days. Stabilization must be accelerated to achieve acceptable process economics. A simple tuning of the thermal profile reduced the residence time from ~150 h to ~100 h. ORNL stabilized fibers using a ~100-h batch thermal treatment in a large (~5.5 m³) oven. 75 kg of lignin fibers were stabilized for further processing. This is the first reported stabilization of lignin fibers at a scale exceeding ~1 kg.

The stabilized material is carbonized in a furnace under nitrogen atmosphere. It typically operates at 500–1500 degrees Celsius for 5–10 min. Approximately 65% of the material is vaporized during carbonization, with gases exhausted through an incineration system. The remaining material is nearly 100% pure carbon – a lignin-based carbon fiber. 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.

2.2. Sample characterization

For qualifying lignin-based carbon fiber for automotive mass production a detailed characterization of this new material is necessary. Therefore nuclear magnetic resonance
spectroscopy, Fourier transform infrared spectroscopy and elementary analysis were used.

The NMR experiments were carried out with a Bruker AVANCE 600 NMR spectrometer operating at 600.13 MHz and 298 K. The spectrometer was fitted with a 5 mm TBI-1H-13C/15N/2H probe head with z-gradients. The 1H and 13C chemical shifts were determined relative to internal DMSO-d$_6$ and were given in parts per million downfield to TMS.

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 the spectral width was 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 13C was 13.0 μs.

The 31P NMR spectra were obtained by using inverse gated decoupling on a Bruker Avance 400 NMR spectrometer, operating at 161.9 MHz and using a 5 mm BOBO probe head with z-gradients. The external standard was 85% H$_3$PO$_4$. The lignin samples were dissolved in 0.75 ml of a mixture of deuterated pyridine and chloroform in ratio of 3:2 as solvent with 0.47 mol/L cyclohexanol as internal standard (145 ppm). The samples were in situ derivatized in the NMR tube with 0.1 ml 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane (TMDP). The inverse gated decoupling sequence was used with 25 s relaxation delay and 128 scans were collected.

The 13C CP/MAS spectra were obtained on a Bruker Avance 300 NMR spectrometer, operating at 75.47 MHz. The spectrometer was equipped with 4 mm CP/MAS probe head BBO/M4L. The samples were measured in 4 mm ZrO$_2$ MAS rotors. The proton 90° pulse was set to 2.55 μs and the decoupling strength during acquisition was 54 kHz. Following conditions were applied: 12 kHz spinning speed, recycle delay 3 s, contact time 1.74 ms. Chemical shifts are quoted in ppm from TMS. The samples were pulverized and mixed with equal weight of hydrated magnesium silicate to reduce the macro-current generation under radio frequency excitation.

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 amount of sample used in IR could not be kept constant. Therefore only the relative ratios of the interesting functional groups were compared.

The investigations of the contained elements in the used Hardwood Lignin for carbon fiber production are done with the Vario EL Cube 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.

To obtain the SEM measurements the high resolution SEM Zeiss Ultra 55 was used. It contains a standard Eberhart-Thornley secondary electron (SE) detector, an In-Lens SE detector, and an EsB (energy and angle selective backscattered electrons) detector. The microscope can work with an image enlargement range of 12,000–900,000 times with the SE detector, and an image enlargement range of 100,000–900,000 times with the EsB detector. The nominal resolution is about 1 nm, and even with low increase in speed, an electric tension of only 1 kV a resolution of 1.7 nm is possible. With the (In-Lens) EsB detector, material contrast can be shown. The signal from SE and BSE detector can be shown on two screens or overplayed and mixed, so that high resolution and high contrast images are available.

To perform the SEM imaging of the fibers, the fibers needed to be prepared on a sample holder for measurement. For the preparation of the fibers, concepts using a carbon pad and focusing the fibers as a bale were tested. Clamping the fibers using carbon pads offers the best way to create high resolution images. After that the sample was coated with gold using the physical vapor deposition (PVD) process. To obtain high resolution images without any influence of vibration, the fiber length was chosen as short as possible above the clamping point.

To make the high resolution images, an overview image was taken first and then representative fibers were chosen for making the high resolution images itself. Also the combination of different detectors, the optimal distance of the sample, and different increase in speed electric tension was evaluated to get the best contrast in the images. The best parameters were at a distance of 5 mm, an increase in speed electric tension of 5 kV and the use of the In-Lens SE detector. Overview images had a typical resolution of 5000 times. Detail images were captured with a resolution of 15,000–20,000 times.

## 3. Results

### 3.1. NMR

The evolution during the treatment was investigated by elementary analysis (EA), infrared spectroscopy, solution NMR and solid state NMR (CP-MAS). The complex natural structure and the associated limited solubility are important factors for the applicability of the analytical methods. Fig. 1 summarizes the chemical structures of the monolignols, the inter-unit linkages and the functional groups of Hardwood Lignin. The NMR spectroscopy is a powerful technique for the characterization of lignin structure. Capanema et al. [11,12] have used a combination of correlation 2D NMR methods and a quantitative 1D 13C NMR technique for a comprehensive approach of lignin structures. In this paper we investigated exclusively non-acetylated lignin samples to avoid the loss of components.

#### 3.1.1. 1H and 13C NMR spectroscopy

At first 2D correlation NMR spectra were discussed to determine structural modification before quantification.

The 2D NMR spectroscopy was used to identify the primary structures of the investigated lignin derivatives. The assignments of 1H and 13C chemical shifts were based on the HSQC (Heteronuclear Single-Quantum Correlation) and HMBC (Heteronuclear Multiple Bond Correlation). The spectra were divided in three parts – the aromatic, side-chain and aliphatic. The signals in aliphatic region are not sensitive for structural modifications. For the structure elucidation the aromatic and side-chain regions are of particular interest to identify the lignin monomers and inter-unit linkages. The HSQC and HMBC spectra for the Hardwood Lignin and pelets were presented in Fig. 2. For every sample the aromatic and side-chain part were separately scanned. The cross-peaks...
**Monolignols**

S syringyl unit  

S’ oxidized syringyl units  

earing a carbonyl at Cα  

G guaiacyl unit  

H p-hydroxyphenyl

**Inter-unit linkages**

A (β-O-4)  

β-aryl ether  

B (β-5)  

phenylcoumaran  

R (β-β)  

resinol

**Functional groups**

- CHO, -COOH, -OCH₃, -OH ......

Fig. 1 – Main chemical structures in lignin.

### Table 1 – Assignment of ¹³C-¹H correlation signals of side-chain region in the HSQC spectra of HW and P

<table>
<thead>
<tr>
<th>Label</th>
<th>HW ¹³C in ppm</th>
<th>HW ¹H in ppm</th>
<th>P ¹³C in ppm</th>
<th>P ¹H in ppm</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMe</td>
<td>n.o.</td>
<td>n.o.</td>
<td>51.5</td>
<td>3.56</td>
<td>O-CH₃</td>
</tr>
<tr>
<td>R₀</td>
<td>54.0</td>
<td>3.05</td>
<td>54.1</td>
<td>3.06</td>
<td>C₅ in R</td>
</tr>
<tr>
<td>B₈</td>
<td>54.3</td>
<td>2.83</td>
<td>54.3</td>
<td>2.83</td>
<td>C₅ in B</td>
</tr>
<tr>
<td>O-CH₃</td>
<td>56.3</td>
<td>3.74</td>
<td>56.4</td>
<td>3.75</td>
<td>O-CH₃</td>
</tr>
<tr>
<td>O-CH₃</td>
<td>n.o.</td>
<td>n.o.</td>
<td>59.2</td>
<td>3.24</td>
<td>O-CH₃ in A'</td>
</tr>
<tr>
<td>A₁</td>
<td>60.2</td>
<td>3.57</td>
<td>60.2</td>
<td>3.57</td>
<td>C₅ in A</td>
</tr>
<tr>
<td>A₂</td>
<td>61.0</td>
<td>4.12</td>
<td>n.o.</td>
<td>n.o.</td>
<td>C₂ in A</td>
</tr>
<tr>
<td>A₁'</td>
<td>–</td>
<td>–</td>
<td>60.2</td>
<td>4.01</td>
<td>C₂ in A'</td>
</tr>
<tr>
<td>B₁</td>
<td>64.1</td>
<td>3.27</td>
<td>64.6</td>
<td>3.32</td>
<td>C₂ in B</td>
</tr>
<tr>
<td>R₁</td>
<td>70.4</td>
<td>4.08/3.73</td>
<td>70.8</td>
<td>4.09/3.76</td>
<td>C₂ in R</td>
</tr>
<tr>
<td>R₂</td>
<td>71.4</td>
<td>4.16/3.75</td>
<td>71.4</td>
<td>4.16/3.78</td>
<td>C₂ in R</td>
</tr>
<tr>
<td>A₀</td>
<td>71.0</td>
<td>4.75–4.85</td>
<td>72.3</td>
<td>4.88</td>
<td>C₅ in A linked to G</td>
</tr>
<tr>
<td>A₅</td>
<td>72.0</td>
<td>4.75–4.85</td>
<td>72.3</td>
<td>4.88</td>
<td>C₅ in A linked to S</td>
</tr>
<tr>
<td>A₉</td>
<td>81.5</td>
<td>4.75</td>
<td>81.9</td>
<td>4.75</td>
<td>C₅ in A linked to G</td>
</tr>
<tr>
<td>R₉</td>
<td>85.7</td>
<td>4.60</td>
<td>85.6</td>
<td>4.65</td>
<td>C₅ in R</td>
</tr>
<tr>
<td>A₈</td>
<td>85.7</td>
<td>4.60</td>
<td>85.6</td>
<td>4.65</td>
<td>C₅ in A linked to S</td>
</tr>
<tr>
<td>B₉</td>
<td>87.4</td>
<td>4.30</td>
<td>87.3</td>
<td>4.32</td>
<td>C₅ in B</td>
</tr>
</tbody>
</table>

n.o., no observed.
were assigned by comparing the literature [13–15] and listed in Tables 1 and 2.

Table 1 shows the assignments of \(^{13}\text{C}\)–\(\text{H}\) correlation signals of the side chain region in the HSQC spectra of Hardwood Lignin (HW) and pellets (P), which were made from this lignin. Table 2 shows the assignments in the aromatic region.

The side-chain region is ranging from 50 to 90 ppm for \(^{13}\text{C}\) and from 2.0 to 5.0 ppm for \(^{1}\text{H}\) chemical shifts. Besides the main signal \(\delta_{\text{C}/\text{H}}\text{C} = 56.3/3.74\) ppm for the methoxy group occur the signals for substructure A for \(\text{C}_6\text{H}_3\) in the range at \(\delta_{\text{C}/\text{H}}\text{C} = 71.0–72.0/4.75–4.85\) ppm and for \(\text{C}_4\text{H}_6\) at 81.5/4.75 ppm and 87.7/4.60 ppm linked to G and S, respectively. For \(\text{C}_4\text{H}_6\), the cross peaks were observed at \(\delta_{\text{C}/\text{H}}\text{C} = 60.2/3.57\) ppm. Furthermore strong signals were observed for resinol substructure R at \(\delta_{\text{C}/\text{H}}\text{C} = 54.0/3.05\) ppm for \(\text{C}_6\text{H}_3\), 71.4/4.75 and 3.37 ppm for \(\text{C}_4\text{H}_6\), and 87.7/4.60 ppm for \(\text{C}_4\text{H}_6\). Also phenylcoumaran B is a well-known inter-unit linkage in lignin and were found in the HW and P samples. The signals were detected at \(\delta_{\text{C}/\text{H}}\text{C} = 54.3/2.83\) ppm for \(\text{C}_4\text{H}_6\), 64.1/3.27 ppm for \(\text{C}_4\text{H}_6\), and 87.4/4.30 ppm for \(\text{C}_4\text{H}_6\). The investigated samples were produced from Hardwood Lignin and typically contain guaiacyl G and syringyl S units.

The syringyl S and guaiacyl G units could be assigned in the aromatic region ranging from 100 to 140 ppm for \(^{13}\text{C}\) and 5.0 to 7.5 ppm for \(^{1}\text{H}\). The S units showed different correlations for \(\text{C}_2\text{H}_6\)–\(\text{C}_2\text{H}_6\), \(\delta_{\text{C}/\text{H}}\text{C} = 103.4–105.3/6.58–6.87\) ppm depend on the different inter-unit linkages at \(\text{C}_4\) and \(\text{C}_1\). The \(\text{C}_2\text{H}_6\)–\(\text{C}_2\text{H}_6\) correlations in \(\text{C}_6\)-oxidized S units were found at \(\delta_{\text{C}/\text{H}}\text{C} = 106.6–108.3/7.12–7.22\) ppm. The G units revealed dominant signals for the \(\text{C}_4\text{H}_6\) at \(\delta_{\text{C}/\text{H}}\text{C} = 109.6/7.12\), for \(\text{C}_4\text{H}_6\) broad signal at \(\delta_{\text{C}/\text{H}}\text{C} = 115.2–115.5/6.6–6.8\) ppm and \(\text{C}_4\text{H}_6\) at \(\delta_{\text{C}/\text{H}}\text{C} = 119.6/6.93\) ppm. Signals for H were detected at \(\delta_{\text{C}/\text{H}}\text{C} = 126.2–126.5/6.82–6.93\) ppm.

The HMBC spectra (Fig. 3) are examples for the efficiency of this technique. These spectra allowed the assignment of quaternary carbons \(\text{C}_1\), \(\text{C}_2\), \(\text{C}_4\) in S units, the carboxyl groups in oxidized syringyl groups in S’ and the \(\text{C}_1\), \(\text{C}_2\) and \(\text{C}_4\) in G units. Strong long range correlations for the aromatic protons in S and G units were observed between S/G, S/G, and the inter-unit linkages \(\text{C}_6\) in B and R, \(\text{C}_8\) in A and B.

The side-chain HSQC for HW in comparison with P are relatively identical. For the aromatic HSQC spectra we found significant differences. The signals for \(\text{C}_6\) in S’ disappeared (Iib), additional olefin resonances are observed at \(\delta_{\text{C}/\text{H}}\text{C} = 127.9/5.29\) and 129.9/5.31. It is noteworthy that the intensity and the number of the aromatic signals in the HSQC spectrum for P are lower than in the HSQC for HW. The 2D and the \(^{13}\text{C}\) spectra indicate that there are no sugar contaminants in the preparations.

3.1.2. \(^{31}\text{P}\) NMR spectroscopy

The \(^{31}\text{P}\) NMR spectroscopy is an established method to quantitatively determine the amounts and distributions of the
Table 2 – Assignment of 13C-1H correlation signals of aromatic region in the HSQC spectra of HW and P.

<table>
<thead>
<tr>
<th>Label</th>
<th>HW</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>13C in ppm</td>
<td>1H in ppm</td>
</tr>
<tr>
<td>S2/6</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>S2/6’</td>
<td>103.4</td>
<td>6.58</td>
</tr>
<tr>
<td>S2/6</td>
<td>103.7</td>
<td>6.59</td>
</tr>
<tr>
<td>S2/6</td>
<td>103.7</td>
<td>6.61</td>
</tr>
<tr>
<td>S2/6</td>
<td>103.7</td>
<td>6.83</td>
</tr>
<tr>
<td>S2/6</td>
<td>105.3</td>
<td>6.98</td>
</tr>
<tr>
<td>S2/6</td>
<td>105.3</td>
<td>7.13</td>
</tr>
<tr>
<td>S2/6’</td>
<td>105.3</td>
<td>6.69</td>
</tr>
<tr>
<td>S2/6’</td>
<td>106.6</td>
<td>7.22</td>
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<tr>
<td>well suite S2/6’</td>
<td>107.5</td>
<td>7.19</td>
</tr>
<tr>
<td>S2/6</td>
<td>108.3</td>
<td>7.16</td>
</tr>
<tr>
<td>C2</td>
<td>109.6</td>
<td>7.12</td>
</tr>
<tr>
<td>G3</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>G5</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>G6</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>H2/6</td>
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<td>n.o.</td>
</tr>
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<td>n.o.</td>
</tr>
<tr>
<td>H2/6</td>
<td>129.9</td>
<td>5.31</td>
</tr>
<tr>
<td>S1, G1</td>
<td>133.6–135.4</td>
<td>–</td>
</tr>
<tr>
<td>S1’</td>
<td>140.0–141.8</td>
<td>–</td>
</tr>
<tr>
<td>S4, S5</td>
<td>147.1–148.2</td>
<td>–</td>
</tr>
<tr>
<td>G3, G4</td>
<td>128.1/129.5</td>
<td>–</td>
</tr>
<tr>
<td>C=O</td>
<td>n.o.</td>
<td>–</td>
</tr>
<tr>
<td>C=O</td>
<td>190.8–196.3</td>
<td>–</td>
</tr>
</tbody>
</table>

3.2. 13C CP/MAS spectroscopy

Fig. 5 displays the 13C CP/MAS NMR spectra of the complete process line. The assignments of the 13C NMR signals are presented in Table 4 [20–22].

The starting material HW shows a typical 13C CP/MAS spectrum for Hardwood Lignin, carbonyl groups (200–160 ppm), aryl (155–100 ppm), aliphatic side-chain (90–60 ppm), methoxy (50–54 ppm) and the aliphatic region (10–30 ppm). The CP-MAS spectra for P and LF are very similar. In comparison with HW they show significant changes in the range of 160–225 ppm. The occurrence of ketones and/or aldehydes (190–212 ppm) and carboxylic acid group (190–203 ppm) are indicative for oxidation reactions. The autooxidation of aldehyde is summarized in Fig. 6.

The intensity for the methoxy signal is for the process steps from Hardwood powder (HW) to the lignin fiber (LF) relatively the same. Considerable changes occur during the oxidation of lignin fiber (LF). For OLF the aliphatic (10–40 ppm) and the side-chain regions (70–90 ppm) completely disappear due to progressed oxidation. The intensity of the methoxy signal around 55 ppm decreases indicating that demethoxylation is one of the reactions during the oxidation (Fig. 7).

A very broad signal was detected for Aryl C-H and Aryl C-R approximately 100–138 ppm. This is indicative for non-specific
changes in chemical environment of the aromatic carbons. This region is indicative for protonated and quaternary carbon atoms.

Beste et al. have done molecular dynamic simulations of the reactions at the side-chains of lignin during conversion to carbon fiber [20]. The formation of phenantrenes was calculated in this simulation but never experimental proven. The $^{13}$C chemical shifts measured in our experiments prove the formation of this chemical compound. The quaternary carbon atoms of phenantrenes are known in the region between 130 and 132 ppm and can be found in our experiments in this area.

Furthermore significant changes were observed in the carbonyl region. An intensive signal was detected around 164 ppm and 190–200 ppm, representing anhydride and/or
Fig. 4 – Quantitative $^{31}$P NMR spectra and assignment of Hardwood Lignin (HW), pellets (P), lignin fiber (LF) and stabilized fiber (OLF) as a result of derivatization by TMDP.

### Table 3 – Distribution of hydroxyl and phenolic groups obtained by $^{31}$P NMR analysis (mmol of OH/g of lignin).

<table>
<thead>
<tr>
<th>Lignin sample</th>
<th>Aliphatic OH</th>
<th>S units</th>
<th>G units</th>
<th>Carboxyl</th>
<th>H units</th>
</tr>
</thead>
<tbody>
<tr>
<td>HW</td>
<td>0.53</td>
<td>0.75</td>
<td>0.24</td>
<td>0.07</td>
<td>0.03</td>
</tr>
<tr>
<td>P</td>
<td>0.33</td>
<td>0.61</td>
<td>0.22</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>LF</td>
<td>0.35</td>
<td>0.53</td>
<td>0.15</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>OLF*</td>
<td>n.o.</td>
<td>0.06</td>
<td>0.02</td>
<td>0.01</td>
<td>n.o.</td>
</tr>
</tbody>
</table>

n.o., no observed.

* Maybe incomplete solution.

Ester and aldehydes, respectively. The relative content of oxygenated structures, exclusively for aromatic structures of treated lignin samples, could be described using the integral of carboxyl and Aryl C-OR (225–139 ppm) in relation to the integral for Aryl C-H (135–100 ppm) [23–25]. For HW the integrals have a relation of 0.5, for P the integrals relation increase to 0.8 and for LF to 0.7. A very distinct improvement was calculated for OLF with 1.1. For a good signal-to-noise ratio the measuring time for OLF was with 30,000 scans relatively long. The origin of the low signal-to-noise ratio causes in the polyanaromaticity within the sample [26]. It has been discussed that for higher temperatures and longer pyrolysis times polyanaromatic hydrocarbons like phenanthrene, naphthalene and anthracene were formed [21].

Only one signal around 165 ppm was observed for the carbonized lignin fiber CLF (number of scans 70,000),

### Table 4 – Assignment of $^{13}$C CP/MAS spectra of HW and the treated samples P, LF, OLF and CLF.

<table>
<thead>
<tr>
<th>Label</th>
<th>HW</th>
<th>P and LF</th>
<th>OLF</th>
<th>CLF</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic</td>
<td>13–36</td>
<td>13–40</td>
<td>n.o.</td>
<td>n.o.</td>
<td>CH$_3$, CH$_2$, CH</td>
</tr>
<tr>
<td>Methoxy</td>
<td>50–54</td>
<td>50–54</td>
<td>42–62</td>
<td>n.o.</td>
<td>Aryl-OCH$_3$</td>
</tr>
<tr>
<td>C$_{g,b,y}$</td>
<td>73</td>
<td>80–84</td>
<td>n.o.</td>
<td>n.o.</td>
<td>C$_{g}$</td>
</tr>
<tr>
<td>Aryl C-H</td>
<td>103</td>
<td>104</td>
<td>100–138</td>
<td>n.o.</td>
<td>S$_{2/5}$</td>
</tr>
<tr>
<td></td>
<td>109</td>
<td>n.o.</td>
<td></td>
<td></td>
<td>G$_{2}$</td>
</tr>
<tr>
<td></td>
<td>117</td>
<td>113</td>
<td></td>
<td></td>
<td>G$_{5/6}$</td>
</tr>
<tr>
<td>Aryl C-R</td>
<td>132</td>
<td>132</td>
<td>n.o.</td>
<td></td>
<td>Si, G$_1$ (no etherified)</td>
</tr>
<tr>
<td>Aryl C-OR</td>
<td>146–152</td>
<td>146–152</td>
<td>140–155</td>
<td>n.o.</td>
<td>S$_{3/5}$, S$_4$, G$_3$, G$_4$</td>
</tr>
<tr>
<td>Carboxyl</td>
<td>158–173</td>
<td>166–173</td>
<td>164</td>
<td>165</td>
<td>Aryl-COOH, anhydrides</td>
</tr>
<tr>
<td></td>
<td>182</td>
<td>n.o.</td>
<td></td>
<td>n.o.</td>
<td>$\alpha$-CO in S’</td>
</tr>
<tr>
<td></td>
<td>201</td>
<td>190–203</td>
<td>190–200</td>
<td>n.o.</td>
<td>Aryl-CHO</td>
</tr>
<tr>
<td></td>
<td>n.o.</td>
<td>212</td>
<td></td>
<td>n.o.</td>
<td>$\gamma$ (nonconjugated)</td>
</tr>
</tbody>
</table>

n.o., no observed.
Fig. 5 – $^{13}$C CP/MAS spectra with a MAS condition of 12 kHz, for OLF 30,000 scans and for CLF 70,000 scans were measured.

associated with anhydride and ester. All other signals disappeared. An explanation for this phenomenon could be the complete cross-linkage of the lignin monomers. The formed polyaromatic structures are not measurable because the presence of paramagnetic species which results in complex relaxation behavior and shielding effects for the interested nuclei in the $^{13}$C CP/MAS experiment [22].

3.3. FT-IR analysis

The FT-IR spectroscopy is an effective method to describe the structural changes occurring during treatment. Fig. 8 shows the FT-IR spectrum of the starting material HW. The typically functional groups were found and the assignment

Fig. 6 – Autoxidation of aldehyde.

Fig. 7 – Demethoxylation.

Fig. 8 – FT-IR spectra from 4000 to 650 cm$^{-1}$ of the raw material the Hardwood Lignin HW.
was according the literature [27,28]. Following bands were identified: O–H stretching at 3400–3460 cm\(^{-1}\), aromatic C–H stretching 3009 cm\(^{-1}\) C–H stretching at 2937 and 2846 cm\(^{-1}\) in methoxy groups and methyl and methylene groups arising from side chains. Interesting region in the band occurs around 1705 cm\(^{-1}\) coming from C–O stretching in unconjugated carbonyl/carboxyl groups. The HW sample 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 band at 1326 cm\(^{-1}\) and 1270 cm\(^{-1}\) are the ring breathing with C=O stretching and characteristic for S and G units, respectively. 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 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.

Fig. 9 shows the FT-IR spectra of the process line. A comparison between the HW, P and the fiber LF shows that the bands are rather similar and so the chemical structures are relatively equal. Due to the experimental method ATR, the amount of samples used in IR could not be kept constant and so only the relative intensities of bands within a sample can be discussed. The O–H, C–H aromatic and aliphatic stretching bands (3400–2840 cm\(^{-1}\)) and the bands in the fingerprint region (1600–700 cm\(^{-1}\)) are identical. With growing processing level the C–O stretching band at 1705 cm\(^{-1}\) increased.

Generally, for the oxidized matt OLF a reduction in sharpness were observed for all bands. Very strong vibrations were detected for the C=O stretching band at 1705–1718 cm\(^{-1}\), aromatic skeleton vibrations 1600–1420 cm\(^{-1}\). In the region from 1400 to 1000 cm\(^{-1}\) a very broad signal without individual peaks were discernable. The out-of-plane aromatic deformations shifted to 770–750 cm\(^{-1}\). This is indicative for changes in aromatic substitutions.

![FT-IR spectra](image)

**Fig. 9 – FT-IR spectra from 1900 to 650 cm\(^{-1}\) of the raw material the Hardwood Lignin HW, the pellets P, the fiber LF and the oxidized lignin matt OLF.**

\[\begin{array}{|c|c|c|c|c|}
\hline
\text{Element} & \text{HW} & \text{P} & \text{LF} & \text{OLF} \\
\hline
\text{C} & 61.44 & 67.13 & 66.41 & 55.33 \\
\text{H} & 6.16 & 6.05 & 6.15 & 3.44 \\
\text{O} & 32.40 & 26.82 & 27.44 & 41.15 \\
\hline
\end{array}\]

**Table 5 – Results of the elemental analysis of HW, P, LF, OLF and CLF.**

3.4. Elementary analysis

The used Hardwood Lignin has a carbon content of around 60%. For the pellets the carbon content was measured a little bit higher. The oxidized carbon fiber has, as expected, the highest oxygen content, which is an indication for successful crosslinking of the linomonomeres. The highest carbon content of 97% was measured in the carbonized fiber. That means the carbonization was successfully performed. Table 5 summarizes the results of the elementary analysis.

4. Discussion

The following section will show the major reaction of lignin during conversion process. On the basis of the results of the measurements presented in Section 3, chemical reactions for the pelleting process, the fiber spinning process and the stabilization process are proposed.

4.1. Pelletizing process of lignin

The production of the pellets was done as described above. In the HSQC experiments following observations were made: On one hand the signals for the phenylcoumaran \(B_{xy}^{7,8}\) as well as for \(S_{xy}^{7,8}\) are not detectable anymore. On the other hand new signals for olefinic bonding are detected. The following reactions are postulate (Fig. 10).

Further reactions are the formation of carboxylic acids or ketone, shown in Fig. 11. The FT-IR spectrum and the \(^{13}\text{C}\)
CP/MAS experiment support this postulated reaction. In the FT-IR spectrum the band at 1706 cm\(^{-1}\) in the spectrum of the pellets is much stronger than in the spectrum of lignin. The \(^{13}\text{C}\) CP/MAS shows nuclear magnetic resonance for the reaction of the aldehyde. The elementary analysis shows also a higher carbon content of the pellets than the lignin powder.

4.2. **Spinning of the lignin fiber**

During the melt spinning process no major chemical reaction could be detected with FT-IR and \(^{13}\text{C}\) CP/MAS. The detected spectra are almost identical, which leads to the assumption, that no major chemical reaction is taking place during fiber spinning, since the fiber spinning is done only a little bit above glass transmission temperature.

4.3. **Stabilization of the lignin fiber**

Four chemical reactions are detectable during stabilization process:

- Formation of ketones  
- Formation of carbon acids/autoxidation of aldehydes  
- Formation of cross-linkages

4.3.1. **Formation of ketones**

In the \(^{13}\text{C}\) CP/MAS spectrum of the oxidized fiber no aliphatic side-chains are detectable. The aliphatic side-chains were dismantled by oxidation reactions. An example for these reactions is the formation of ketones, which can detected at 190 ppm in the \(^{13}\text{C}\) CP/MAS.

The proof of all reactions, presented in Fig. 11, can also be found in the IR spectra. The rising of the signal at 1700 cm\(^{-1}\) is characteristic for the C=O valence vibration, which is directly connected to the formation of ketones, carbon acids, aldehydes and anhydrides.

4.3.2. **Formation of carbon acids/autoxidation of aldehyde**

In the \(^{13}\text{C}\) CP/MAS measurements a strong signal in the region between 190 and 200 ppm is detectable. This signal is an indicator for the reaction of aldehydes, which creates carbon acids as described in Fig. 11.

4.3.3. **Formation of cross-linkages**

In FT-IR spectrum the region from 1400 to 1000 cm\(^{-1}\) a very broad signal without individual peaks was discernible. The explanation could be the increased cross-linked of the lignin macromolecules as described in Fig. 12.

The results of the elementary analysis show a decrease of the hydrogen content and an increase of the oxygen content in the OLF. A further increase of the carbon content is detectable in the CLF.

4.4. **Carbonization of the fiber**

The formation of the graphitic structure of the lignin-based carbon fiber can be proven by the used analytical tools.

The detected signal at 165 ppm in the \(^{13}\text{C}\) CP/MAS spectrum is a quaternary carbon atom and describes relics at the aromatic rings. This relict contains oxygen, which are left over from reactions of anhydrides or esters (compare Fig. 5).

The graphitic structure itself is not detectable with \(^{13}\text{C}\) CP/MAS, but the high carbon content of 97% measured with the elementary analysis is a strong indication for the graphitic structure.

4.5. **Scanning electron microscopy of lignin-based carbon fiber**

The scanning electron microscope (SEM) was used to show the surface and friction area of the lignin-based carbon fiber. The SEM can be used to show the porosity of the fiber and some representative defects.
4.5.1. Lignin fiber
The structure of the lignin fiber is partly irregular. The fiber cross section is round with different diameters in a range between 10 and 25 μm. The fiber surface is smooth with some pores. The fiber cross section shows round voids which are mostly located at the fiber edge (Fig. 13).

The reason for the round defect in the lignin fiber are vaporously components in the lignin, which vaporize during melt spinning and create air bubbles in the fiber (compare Section 5). This defects cause lower mechanical properties.

4.5.2. Stabilized lignin fiber
After the stabilization process, the fiber diameter is reduced. The voids created during the melt spinning process do not change in size causing the ratio between voids and cross-sectional area to decrease. A higher inhomogeneity concerning the fiber diameter is detectable (Fig. 14). It is noticed
that the fiber surface is smooth and the pores at the surface are greatly reduced.

4.5.3. Lignin-based carbon fiber
The lignin-based carbon fiber shows the same defects like the lignin fiber and the stabilized lignin fiber (Fig. 15). After the carbonization process, the fiber diameter is reduced. The voids created during the melt spinning process do not change in size causing the ratio between voids and cross-sectional area to decrease.

The heat treatment of the lignin fiber leads to a reduction of the fiber diameter, since all other elements except carbon is removed from the fiber to create a lignin-based carbon fiber. The mechanical properties improve during conversion process and the fiber becomes less elastic and more brittle.

4.5.4. Comparison of the area of fracture
Using samples from the single fiber testing, the area of fracture for both the lignin fiber as well as the lignin-based carbon fiber

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**Fig. 13** – SEM images of lignin fiber: (a) overview image, (b) fused fibers, (c) voids at the fiber edge, (d) pores at the surface.

**Fig. 14** – SEM images of stabilized lignin fiber: (a) overview image, (b) defects at the edge, (c) defects at the surface.
was analyzed with SEM. Fig. 16 shows the area of fracture of both fiber types. The lignin fiber exhibits a ductile fracture. This is an indication for a more elastic fraction behavior. The lignin-based carbon fiber shows a brittle fraction behavior since the fraction area is very even without any deformation.

5. Conclusions

The NMR spectroscopy and the FT-IR spectroscopy are useful tools for analyzing the conversion process of lignin to carbon fiber.

The major reactions could be postulated by detecting specific structural elements. During the pelletizing process the creation of double bonding carbon and carbonyl bonding could be established. The fiber spinning process is taking place without any detectable major reactions. In the stabilization process of the fiber the major reaction support cross-linking in the fiber, which leads to higher mechanical properties. Also the creation of carbon acids, ketones and anhydrides is detectable in this step of the conversion process. In the carbonized fiber the graphitic structure can be postulated.

The knowledge of the reactions during the conversion process and the SEM measurements of the fibers make it now possible to optimize the production process of lignin-based carbon fiber, which will lead to higher mechanical properties in the future.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


