Comparision of the properties of lignins as potential carbon precursors

Due to growing interest in the application of renewable resources in industry, there is a need for new carbon precursors. Lignin is a natural polymer and the main by-product of the paper industry, but its application on an industrial scale is limited. Due to its chemical composition and high aromatic carbon content, combined with a lack of toxicity, it may be a promising candidate for a carbon precursor, as well as – in carbon electrode technology – a carbon binder. The main disadvantage of lignins is the variety of their types, with differing properties. There is a need to establish the relationship between the structure of lignin and its carbon precursor potential. In this work, an attempt was made to find the dependence between the lignin structure and its properties before (chemical composition, structural studies) and after thermal treatment under an inert atmosphere (carbon residue, bonding properties and degree of carbonization and graphitization), using different techniques (FTIR, Raman spectroscopy, XPS, TG, SEM) on two softwood lignins – alkali lignin and kraft lignin. The results proved that both lignins are good candidates for carbon precursors (high mass residue after heat treatment), but only kraft lignin exhibits the bonding properties which are crucial for application as a carbon binder.

Keywords: lignin; carbonization; carbon electrode; graphitization; renewable resources

Introduction

The carbon materials industry uses a wide range of products for different applications, including carbon fibres, activated carbon, synthetic graphite, carbon and graphite electrodes, and many others. For every product, different methods of preparation and raw materials are used. Many of the common carbon precursors used in traditional carbon and graphite technology are toxic; for
example, coal tar pitch (CTP) [Cao et al. 2015]. Also, many of them come from non-renewable sources. Due to increasing awareness of the dangers of industry to the environment and higher demands from institutions responsible for environmental protection, there is a need to find new raw materials for carbon and graphite technology (e.g. biomass) [Gellerstedt 2015; Kumar et al. 2016], which may be alternatives to fossil fuels [Jasiukaitytė-Grojzdek et al. 2017] and to the CTP currently used as a binder.

In general, carbon precursors should have a high carbon content and high carbon residues after thermal treatment [Menéndez et al. 1996]. The loss of carbon is undesirable for many reasons; it may generate more porosity, which impairs the mechanical and electrical properties of the product. Also, a higher amount of carbon released in gaseous form from the precursor causes increased emission of CO$_2$. Moreover, many precursors, such as CTP, contain polycyclic aromatic hydrocarbons (PAHs), which are harmful to humans and the environment [Afanasov et al. 2009; Dhamaniya et al. 2012]. Finally, as an economic aspect, more of the precursor is needed to obtain the required amount of product, which generates additional costs.

Most of the above requirements are satisfied by lignin – a natural biopolymer present in plant biomass along with cellulose [Huang et al. 2012]. It is part of the lignin-carbohydrate complex (LCC) [Alber and Ehlting 2012; You et al. 2015] which is a protective barrier against pathogens [Verma and Dwivedi 2014; Cottyn et al. 2015]. Lignin’s structure has a high content of aromatic carbon: it is made up of three monomers, $p$-coumaryl, coniferyl and sinapyl alcohols, which form “H” ($p$-Hydroxyphenyl), “G” (Guaiacyl) and “S” (Syringyl) units [Lu and Ralph 2010]. The difference between them is the number of methoxy groups bonded to the aromatic ring. The monolignols are bonded randomly, which makes the lignin structure strongly branched and very complicated [Martínez et al. 2009]. There is no defined lignin structure as there is for other polymers, because it has no repeating sequence of atoms [Oinonen et al. 2015; Zhang et al. 2015]. Some research has cast doubt on the random mechanism of lignin synthesis and its highly branched structure, indicating it to be more linear [Davin and Lewis 2005]. Owing to this irregularity in chemical structure and problems with the repeatability of properties, it is difficult to find appropriate applications for lignin [Cabrera et al. 2017]; despite its high availability (as a by-product in the production of paper, over 50 million tonnes per year are produced), only a small amount of this material is used [Hu et al. 2017]. To date lignin has found several applications; for example, as a carbon precursor for the production of carbon fibre [Mainka et al. 2015] or activated carbon [Rodriguez et al. 2017]. However, new areas of potential application are still being sought; for example, as a binder or modifier of traditional binders in carbon-graphite technology.

The two types of lignin most mentioned in the literature are hardwood and softwood. The main difference between them is the monomer content.
Hardwood lignin has a greater amount of “S” units than “G” units, but the ratio is different in different species [Huang et al. 2017a]. Softwood lignin is built mainly of “G” units and trace amounts of “H” units in compression wood [Asmadi et al. 2011c; Huang et al. 2017b]. The structure of lignin depends on many factors, including the genus and species of plant, as well as environment, climate, lighting, daily cycle, hormones, amount of carbohydrates and many other variables that have an influence on plants [Zhao and Dixon 2011; Ghaffar and Fan 2013; Gilea et al. 2014].

The behaviour of lignin during pyrolysis depends on many factors, such as the syringyl ratio, because of the impact of its reactivity during thermal treatment [Huang et al. 2017b]. Diehl et al. [2013] investigated the pyrolysis mechanisms of hardwood and softwood lignins and proved that the mechanisms of this process are different, and the products obtained also differ. What is most important about hardwood lignin pyrolysis residue is its higher potential to form coke. Also, additional functional groups containing oxygen promote coke formation, which may be essential to obtain binding properties [Asmadi et al. 2011b, c; Lumadue et al. 2012]. Pyrolysed softwood lignin produces less coke, but more solid products in total [Asmadi et al. 2011a, 2011b, 2011c].

In industry, apart from carbon electrodes, there are also graphite electrodes produced at higher temperatures to obtain a graphite phase. A potential alternative carbon binder applied in graphite electrode production should have graphitizing ability. In the literature, there are few reports on lignin’s graphitization potential, and recent articles are particularly concerned with catalytic graphitization where transition metals are used [Demir et al. 2015; Yan et al. 2018]. One study investigates the catalytic graphitization of wood. The temperature of thermal treatment was 1600°C, which is much lower than usual during graphitization [Gutiérrez-Pardo et al. 2015]. Also, iron, copper and nickel are added as catalysts, which may be an obstacle to obtaining high-purity graphite electrodes. Popova and Serbinovskii proved in a study that hydrolysis lignin may graphitize in a two-step thermal treatment: pyrolysis at 600°C then graphitization at 2500-2800°C [Popova and Serbinovskii 2014].

The properties of lignins differ according to their origin, process of extraction, and many other factors. Their highly complex chemical structure makes it difficult to characterize them [Agarwal et al. 2017]. To obtain more information about lignins, so as to predict or explain their behaviour and the products obtained during thermal treatment, there is a need to characterize them with multiple techniques, and the results – considered simultaneously – may provide information about their elemental compositions, the functional groups present in the structure, and hardwood or softwood origin. The characteristics obtained may help to predict their behaviour during thermal treatment and determine the relation between their structure/composition and the products and by-products obtained during carbonization and graphitization, as well as their potential application as carbon binders.
In this work, two types of softwood lignin were investigated as potential precursors for carbon materials. By analysing the properties of the pure lignins as well as the products of their thermal treatment, it is possible to specify which features lignin should have in order to be used as a precursor for carbon materials.

Materials and methods

In this work two lignins were investigated: kraft lignin (KL) – Indulin AT from MeadWestvaco, and alkali low sulphonate content lignin (AL) supplied by Sigma-Aldrich (product number 471003), CAS 8068-05-1, average Mw = 10,000. Coal tar pitch (CTP) was used as a reference sample, due to its widespread application in the field of carbon precursors, especially as a binder in carbon and graphite technology.

To compare the chemical composition, the carbon, sulphur and hydrogen contents were measured based on SO₂ and CO₂ content on combustion of three samples of both lignins and CTP, using an ELTRA CHS 580 instrument.

Tests to determine the lignins’ chemical structure, by analysing and comparing bands and functional group content, were carried out in FTIR-ATR (attenuated total reflectance) mode using a MIRacle ATR sampling accessory (diamond/ZnSe crystal, PIKE Technologies). The spectra were recorded with a resolution of 4 cm⁻¹. Two separate measurements (each including 64 scans) at different points of the material were made for each sample. This analysis was performed with a Bruker TENSOR 27 FT-IR Spectrometer.

Raman spectroscopy was used to describe the quality of graphite obtained from AL, KL and the CTP used as a reference material, by calculating the Iₐ/Iₜ ratio. Measurements were performed using a Renishaw inVia Confocal Raman microscope. Different laser excitation wavelengths were used: 785 nm (1.58 eV), 514.5 nm (2.41 eV), 473 nm (2.62 eV), 442 nm (2.81 eV) and 266 nm (4.66 eV).

X-ray photoelectron spectroscopy (XPS) analysis (Vacuum Systems Workshop Ltd., England) was performed. The depth of analysis was about 5 nm. Mg Kα X-ray radiation with 200 W energy was used as the excitation source. The electron energy analyser was set to FAT mode with a pass energy of 22 eV. The shift of the binding energy due to a surface charging effect was calibrated by assuming the binding energy of C1s always to be 284.6 eV.

The lignin samples’ thermal behaviour was analysed by means of thermogravimetric analysis (TG) using the simultaneous thermal analyser NETZSCH STA 449 F3 Jupiter® at a heating rate of 5°C per minute under a nitrogen atmosphere (250 ml/min), to compare the mass changes of lignin samples during heat treatment and the mass of the residues with the reference material CTP. Decomposition temperature was determined with Proteus61 software.
To compare the \( d_{(002)} \) and crystallite size of carbon and graphite obtained from AL and KL, and to compare them with the reference material (CTP), X-ray diffraction (XRD) was performed using a Philips X’Pert Pro diffractometer. The X-ray tube was used with a linear focus and copper anode, and the beam was monochromatic (\( K_{\alpha 1} = 1.5406 \) Å).

To compare the microstructure of the graphitized samples a scanning electron microscope (Nova Nano SEM 200) was used.

To investigate the behaviour of lignin after high-temperature treatment, carbonization processes were conducted. Both lignin samples were put into a quartz tube furnace with a heating rate of 1°C per minute, starting at room temperature and heating to 1000°C under a nitrogen atmosphere to avoid oxidation. The flow rate of nitrogen, which provides an inert atmosphere, was 30 l per hour. After reaching the maximum temperature, the furnace was switched off, and the samples were left inside to cool to RT.

Graphitization of lignins was conducted according to Popova and Serbinovskii [Popova and Serbinovskii 2014] in two steps: firstly carbonization at 600°C in a quartz tube furnace, with a heating rate of 1°C/minute, starting at room temperature, in an inert atmosphere of nitrogen with a flow rate of 30 l per hour. The products obtained were then graphitized at 2800°C in argon with a heating rate of 1°C/minute.

**Results and discussion**

**Elemental composition**

One of the most important criteria for a carbon precursor is a high carbon content. Depending on the potential application of the carbon product, the required value of the carbon content exceeds 50 wt.%. In both lignins, carbon is the main element (Table 1), with amounts of 63.00 wt.% for KL and 47.77 wt.% for AL. The lignin carbon content was about 24% higher for KL than for AL, which may indicate that this type of lignin is a better carbon precursor. An unfavourable feature is that both lignins have a much lower carbon content than the CTP binder traditionally used in carbon and graphite technology (93.3%).

Another very important parameter in precursors of carbon materials is the sulphur content. In a potential graphite precursor, both sulphur and nitrogen are highly undesirable because of the phenomenon of puffing. At high temperatures sulphur is removed, and this causes swelling of the product, increases the porosity, which decreases the density, and worsens the mechanical and electrical properties [Kawano et al. 1999]. Both lignins contain a small amount of sulphur, especially KL, where the concentration of this element is 1.38%. The above results suggest that lignin may not be as good a carbon precursor as CTP, but KL exhibits greater potential due to its higher carbon content and lower sulphur content.
Table 1. Elemental compositions of KL, AL and CTP

<table>
<thead>
<tr>
<th>Element (weight %)</th>
<th>Kraft lignin</th>
<th>Alkali lignin</th>
<th>CTP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>63.00 ±0.14</td>
<td>47.77 ±0.31</td>
<td>93.30 ±0.47</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.71 ±0.21</td>
<td>5.51 ±0.41</td>
<td>4.35 ±0.19</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.38 ±0.04</td>
<td>2.83 ±0.15</td>
<td>0.45 ±0.02</td>
</tr>
</tbody>
</table>

Infrared spectroscopy (FTIR-ATR)

To evaluate the differences between the KL and AL lignins in terms of chemical groups and the functional groups in their structure, FTIR-ATR spectroscopy was used. Analysing the spectra for KL and AL, some significant differences could be observed (Fig. 1). The main differences were observed in the range 1510-1364 cm\(^{-1}\) and at 1267, 1127 and 812 cm\(^{-1}\). In the first range for KL lignin, a high intense band at 1510 cm\(^{-1}\) assigned to asymmetric aryl ring stretching is observed [Stark et al. 2016]. This band was significantly less intense for AL lignin, and additionally the relationship between this band and two other bands at 1457 cm\(^{-1}\) and 1420 cm\(^{-1}\), assigned respectively to asymmetric deformation of O–CH\(_3\) and C–H and aromatic skeletal vibration combined with C–H in-plane deformation, are different for the KL and AL lignins [Poletto and Zattera 2013; Stark et al. 2016]. Moreover, for KL lignin a characteristic, intensive band was observed at 1267 cm\(^{-1}\), derived from aryl ring breathing [Stark et al. 2016]. KL

Fig. 1. FTIR spectra of KL and AL lignins
lignin has a more intense band at 1127 cm\(^{-1}\), assigned to a mode of coniferaldehyde or sinapaldehyde [Stark et al. 2016]. Also, for KL lignin, C–H deformation out of the plane of the aromatic ring is observed at wavenumber 812 cm\(^{-1}\). This was not observed for AL lignin. The presence of bands in KL lignin which were not observed for AL lignin most probably imply the higher chemical reactivity of this material and improved bonding properties [Asmadi et al. 2011b, 2011c; Lumadue et al. 2012], which is highly desirable for applications of lignin as a binder used for the production of carbon electrodes.

**X-ray photoelectron spectroscopy (XPS)**

XPS is a useful method to analyse the surface chemistry of lignins. XPS chemical quantitative analysis was performed based on deconvolution of the bands attributed to different chemical states of carbon (C\(_{1s}\)) and oxygen (O\(_{1s}\)) atoms present in both samples. XPS analysis (Fig. 2) of both lignins shows similar quantities of these two atoms (Table 2).

![Fig. 2. XPS spectra of KL (A) and AL (B) lignins](image)

**Table 2. Carbon and oxygen content in lignins**

<table>
<thead>
<tr>
<th>Lignin</th>
<th>Atomic ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>AL</td>
<td>76.5</td>
</tr>
<tr>
<td>KL</td>
<td>76.6</td>
</tr>
</tbody>
</table>

Evaluation of chemical states allows the identification of some differences in the structure of the tested lignins (Table 3). KL contains twice as much carbon in sp\(^2\) hybridization (C=C) than AL lignin. In turn, AL contains more carbon atoms in sp\(^3\) hybridization (C–C) than KL. AL has a higher content of –COO and COO than KL, but C–O, C–OH and C–O–C bondings are present to a greater degree
for KL. The existence of these bondings may also indicate the presence of (–OH) and (O–CH₃) groups, which are crucial for coke formation and the bonding properties of lignin [Asmadi et al. 2011b, 2011c; Lumadue et al. 2012]. Also, these results correspond with previously reported FTIR results that indicated a significantly higher content of (O–CH₃) groups in KL. The existence of this bonding and the higher content of carbon in sp² hybridization may suggest that KL lignin has greater potential to be used as a binder in carbon electrode application.

Table 3. Comparison of the chemical compositions of KL and AL lignins detected by XPS

<table>
<thead>
<tr>
<th>Bonding</th>
<th>Content in KL (at. %)</th>
<th>Content in AL (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C</td>
<td>26.40</td>
<td>12.84</td>
</tr>
<tr>
<td>C–C</td>
<td>46.73</td>
<td>53.92</td>
</tr>
<tr>
<td>C* –COO</td>
<td>17.90</td>
<td>21.43</td>
</tr>
<tr>
<td>C–O, C–OH or C–O–C</td>
<td>8.97</td>
<td>3.67</td>
</tr>
<tr>
<td>COO</td>
<td>–</td>
<td>5.67</td>
</tr>
<tr>
<td>CO₃ (H₂O-adsorbed CO₂)</td>
<td>–</td>
<td>2.46</td>
</tr>
</tbody>
</table>

Thermogravimetric analysis (TG)

TG analysis may be helpful to compare the residues after heat treatment of all samples (AL, KL and CTP). The decomposition of these three samples starts at different temperatures. The lowest temperature was recorded for AL: 230°C (Fig. 3). CTP starts to decompose at 252.8°C and KL at 289.1°C. The TG curves of both lignins are similar up to 350°C. At this stage, AL decomposition slows down. The KL degradation rate decreases around 400°C, but not as much as for AL. Additionally, AL exhibits changes in the degradation rate in a range of about 550-700°C, where it degrades a little more slowly. The end of decomposition for both lignins is observed at around 800°C. CTP undergoes decomposition almost evenly, slows slightly around 500°C, and slows significantly around 550°C. The mass residue at 1000°C for KL (45%) is lower than for AL (55%). A higher mass residue is desirable from the point of view of the application of lignin as a carbon binder. The heat treatment residues for both lignins are higher than for CTP (39%), which may lead to lower porosity of the final product (e.g. a carbon electrode) and improve its mechanical and electrical properties. In general, this analysis revealed that both lignins can be considered as alternative carbon precursors.
Analysis of lignin residue products after heat treatment at 1000°C

The products obtained after heat treatment (carbonization) of lignins were analysed to evaluate the elemental composition and structural properties. Moreover, a macroscopic analysis of the obtained samples was performed. The kraft lignin and alkali lignin after the carbonization process were labelled cKL and cAL respectively. Macroscopic observations show significant differences between the two types of lignin. Kraft lignin had the form of a black hard tablet in the shape of the crucible. It was made of fine grains bonded together, although during grinding the sample easily rubs off to powder. Alkali lignin directly after carbonization had the form of black cracked pieces, which easily disintegrated into powder. The powder inside the pieces had a slightly different colour, similar to the starting material, and also possessed a perceptible odour of hydrogen sulphide. These findings certainly prove the high potential of KL to give a solid, dense carbon product in the form of bonded carbon grains. The product obtained after carbonization of AL has the form of a non-bonded powder, which may not be favourable for the potential use of this material as a binder.

To compare the chemical composition of both lignin samples after carbonization, an ELTRA CHS 580 analyser was used. The results are shown in Table 4.
Table 4. Comparison of elemental analysis of lignin samples after carbonization at 1000°C

<table>
<thead>
<tr>
<th>Element (weight %)</th>
<th>Kraft lignin after carbonization (cKL)</th>
<th>Alkali lignin after carbonization (cAL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>89.35 ±0.36</td>
<td>71.13 ±0.85</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.76 ±0.05</td>
<td>1.25 ±0.05</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.83 ±0.01</td>
<td>2.01 ±0.13</td>
</tr>
</tbody>
</table>

As expected, after carbonization the content of carbon in both samples increased. Carbonized kraft lignin (cKL) contains more carbon (89.35%) than carbonized alkali lignin (cAL) due to the higher carbon content in kraft lignin before carbonization (Table 1). A different trend is observed for hydrogen: cKL contains less hydrogen (0.76%) than cAL (1.25%), although the uncarbonized KL contained more hydrogen than AL (6.71% and 5.51% respectively). The difference in sulphur content between both lignins after carbonization is maintained (in comparison to the raw material), but after heat treatment, their values decreased by about 30% for KL and about 40% for AL. cAL contains more sulphur (2.01%) than cKL (0.83%), which is undesirable in graphite precursors due to puffing, which negatively affects the mechanical properties and electrical and thermal conductivity of graphite electrodes and causes their deformation. It is worth recalling that puffing of the graphitized product also strongly depends on the structure of the raw carbon precursor [Skoczkowski 1995; Kawano et al. 2000]. Typically, pitches contain up to 0.8 wt.% [Baron et al. 2009]. The concentration of sulphur in cKL is such that it may be classified as a precursor with average sulphur content.

The microstructures of the carbonized lignins are quite different: cKL has a rich, composed microstructure, a sinter made of connected grains with porosity of different shapes (Fig. 4A). The pore size varies significantly over a wide range, from a few µm to around 100 µm. The orientation of the pores and solid phase is random and does not exhibit any regularity. The sample of cAL has many free grains of different sizes, shapes and degrees of porosity. The grain size varies from tenths of micrometres to above 100 µm (Fig. 4B). Most of the grains have a round shape, but a few are irregular.

An additional tool used to evaluate the quality of the obtained carbon, by investigating the crystallite size and interplanar distance $d_{(002)}$, was XRD analysis. The parameters of the identified carbon phases in the carbonized samples are given in Table 5. Both cKL and cAL have similar $d_{(002)}$ parameters, but these are significantly higher than for the CTP sample (around 0.04 nm). The crystallite size of cKL is similar (1.8 nm) to the size of carbonized CTP (1.9 nm), whereas cAL gave a higher value (2.2 nm).
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Fig. 4. SEM microphotographs of GKL (A) and gAL (B)

Table 5. Parameters of carbonized samples obtained by XRD

<table>
<thead>
<tr>
<th>Sample</th>
<th>(D_{(002)}) (nm)</th>
<th>(L_c) (nm)</th>
<th>Reflex intensity at (002) plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonized CTP</td>
<td>0.349</td>
<td>1.9</td>
<td>389</td>
</tr>
<tr>
<td>cKL</td>
<td>0.393</td>
<td>1.8</td>
<td>911</td>
</tr>
<tr>
<td>cAL</td>
<td>0.397</td>
<td>2.2</td>
<td>177</td>
</tr>
</tbody>
</table>

Analysis of lignin residue products after the graphitization process

To verify the graphitization ability of the lignins, both kraft lignin and alkali lignin were heat-treated up to 2800°C. The same experimental scheme as in [Popova and Serbinovskii 2014] was followed in our investigation. Kraft lignin and alkali lignin after the graphitization process were labelled gKL and gAL respectively.

Similarly to the carbonized sample, graphitized kraft lignin (gKL) has the form of a fine-grained sinter in the shape of the mouldings used for graphitization. It is black, with a slightly metallic lustre under light, is porous and hard, but easily rubs off. Graphitized alkali lignin (gAL) has the form of black, fine but not bonded powder and grains.

To verify the degree of graphitization of both lignins, XRD analysis was carried out. The results are shown in Figure 5 and collected in Table 6.

The XRD diffractograms (Fig. 5) obtained for the lignins after graphitization are significantly different from that obtained for the graphitized CTP. The intensities of the (002) peak are an order of magnitude lower for both lignins in comparison with the reference sample (CTP). For the lignins, the peak intensities are below 4,000, while for CTP it is around 40,000. The peaks of the graphitized
lignins are wide in comparison with CTP. Alkali lignin clearly has two sharp peaks, whereas gKL has one peak, although it is broadened, which may indicate the existence of at least two phases in this material (Figures 5A and B). In contrast to the lignins, the characteristic peak for CTP after graphitization is very regular and narrow (Fig. 5C). After fitting, three peaks are detected in each sample. The crystallites in the lignins are comparatively small – up to 18.833 nm – while the maximum value for CTP is 77.360 nm, and that crystallite has the highest intensity. The interplanar distances $d_{(002)}$ for both lignins are higher than for CTP (Table 6). The value of the most intensive peak for CTP is about 0.3379 nm, which is higher than for pure graphite ($d_{(002)} = 0.3354$ nm), but shows a tendency towards graphitization, which is not observed for the lignins. All of these results prove that pure, unmodified lignin has no graphitization potential.

Table 6. Parameters of graphitized samples obtained by XRD

<table>
<thead>
<tr>
<th>Phase</th>
<th>$D_{(002)}$ (nm)</th>
<th>$L_c$ (nm)</th>
<th>Reflex intensity at (002) plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft lignin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>0.3445</td>
<td>18.14</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>0.3495</td>
<td>5.25</td>
<td>2685</td>
</tr>
<tr>
<td>3.</td>
<td>0.3709</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>Alkali lignin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>0.3427</td>
<td>18.83</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>0.3514</td>
<td>4.55</td>
<td>3884</td>
</tr>
<tr>
<td>3.</td>
<td>0.3875</td>
<td>2.60</td>
<td></td>
</tr>
<tr>
<td>CTP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>0.3379</td>
<td>77.36</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>0.3396</td>
<td>40.87</td>
<td>38888</td>
</tr>
<tr>
<td>3.</td>
<td>0.3420</td>
<td>13.56</td>
<td></td>
</tr>
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</table>

Another method which confirms the lack of graphitization potential of both lignins is Raman spectroscopy. The results are shown in (Fig. 6).

The results obtained from Raman spectroscopy make it possible to compare the graphite crystallite quality by calculating the ratio between the intensities of
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Fig. 6. Raman spectra of graphitized KL (A), AL (B) and CTP ©

the D and G peaks ($I_d/I_g$) according to the method described in detail in our previous paper [Zambrzycki and Frączek-Szczypta 2020]. A lower value indicates a more ordered structure, which can be interpreted as a higher graphite content in the sample. The carbon obtained from both lignins is significantly different from the product after graphitization of CTP. The $I_d/I_g$ ratio of the graphitized CTP sample is 0.25, while the value for gAL is around 2.5 times higher, and that for gKL almost 4 times higher. The results obtained prove conclusively that none of the lignins used has any graphitization potential.

Conclusions

The lignins used in this work are promising carbon precursors. Both of them have high carbon content, and the residues after thermal treatment are even higher than for CTP (a key feature for the application in question), but exhibit different properties. In general, the FTIR and XPS results prove that KL has a greater variety of functional groups, which may be responsible for its higher reactivity and probably its bonding properties. XRD and Raman spectroscopy results ($d_{(002)}$, $L_c$ and $I_d/I_g$) confirmed the graphitization ability of CTP, in contrast to the lignins, which in their pure form are not graphitized. The better candidate as a carbon binder in the carbon electrode industry is KL. It forms a hard, solid product whose grains are bonded together, which makes KL suitable for consideration as an alternative carbon binder.

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