



## Original Article

## Graphitization of lignin-modified phenolic resins: role of lignin pretreatments

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**ABSTRACT**

Aiming at the generation of graphitic carbon from low-cost phenolic resins, this study investigated the role of lignin pretreatments on the amount of crystalline carbon generated from lignin-phenol-formaldehyde resins containing boron oxide, boric acid and ferrocene as graphitizing additives. Kraft lignin used to synthesize the resins was initially subjected to thermal and thermomechanical treatments to improve processability and promote greater mobility for ease of graphitization during carbonization. The results showed that the characteristics of lignin used to prepare the thermosetting resins affect the quantity of graphitic carbon that was generated during pyrolysis. The lignin-modified resin prepared using Kraft lignin, which has the lowest molecular weight and polydispersity values produced the highest amount of graphitic carbon. This formulation containing 10 wt.% boric acid presents a graphitization level value of 73%. In addition, limited amounts of crystalline carbon were generated when boron oxide and ferrocene were used as graphitizing additives.

**1. Introduction**

An alternative way to address environmental issues associated with bio-based processes involved the use of such eco-friendly materials. Their by-products can be obtained in abundance, at low cost and are from renewable biomass. Furthermore, due to concerns related to fluctuation in oil price and phenol exposure, researchers have investigated the use of bio-materials as a substitute to phenol for phenolic resins production [1, 2]. Based on challenges from contact with phenol, the Occupational Safety and Health Administration (OSHA) has set the daily permissible exposure limit (8 hours/day and 40 hours/week) to phenol as 19 mg/m<sup>3</sup>. Lignin, the by-product of paper, bioethanol and pulp industries can be a replacement for phenol in the synthesis of low cost, bio-based and environmental-friendly phenolic resins [3]. It is a sustainable material with an annual production estimated in the range of 5–36 x 10<sup>8</sup> tons [4]. As an amorphous biopolymer, it has a complex chemical structure comprising a repeating unit of 1-(p-hydroxyphenyl)

propane-3-ol that have methoxyl group in the ortho position of the phenolic ring. Lignin consists of three primary building blocks or units, which are guaiacyl (G), syringyl (S) and p-hydroxypropane (p-H) as described. As a polyphenolic macromolecule, lignin exhibits various structures, which depends on the plant species from which it is derived. Lignin reactivity is affected by the type of functional groups such as methoxyl, phenolic, aliphatic hydroxyl and aldehyde groups in its structure [5]. These functional groups occupy the interunit linkages, thereby limiting its ability to react during synthesis. To be suitable for producing phenolic resins, lignin should have a high quantity of hydroxyl groups in its aromatic ring, low molecular weight values and less methoxyl group. Lignin-modified phenolic resins have been found to exhibit good polymerization time, thermal stability, fluidity and softening point [6].

Similar to the phenolic resins, lignin-phenol-formaldehyde (LPF) resins are non-graphitizable and will yield non-

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graphitic carbon, which may limit their usefulness in applications such as binder for carbon-containing refractories where graphitic carbon generation is of the essence. In a previous study [5], an attempt was made to induce production of crystalline carbon during carbonization of lignin-modified resins in the presence of some graphitizing additives. However, for the first time, this investigation was channelled towards understanding the influence of lignin type on the graphitization of such resins.

## 2. Experimental Techniques

### 2.1 Materials

The general information about the materials used in this study is presented in Table 1.

Table 1. General information about the used materials and samples designation.

Raw materials		Supplier	
Reagent for lignin-modified phenolic resin synthesis	Phenol, C <sub>6</sub> H <sub>5</sub> OH, solid,	Aqueous, molecular weight = 94.11 g/mol	Synth Chemical Co., SP-Brazil
	Formaldehyde (37 wt.%), CH <sub>2</sub> O	Liquid, molecular weight = 30.03 g/mol	
	Kraft Lignin	Solid, pH = 4.5 at 28 °C	Fibria, Brazil
Catalyst	NH <sub>4</sub> OH	aqueous, molecular weight = 35.04 g/mol	Synth Chemical Co., SP-Brazil
Additives	Ferrocene	Solid, (150 < d < 70 μm, 98% purity)	Aldrich, USA
	Boric acid (H <sub>3</sub> BO <sub>3</sub> )	Solid, molecular weight = 61.83 g/mol, (d <sub>90</sub> < 45 μm, 99% purity)	Synth Chemical Co., SP-Brazil
	Boron oxide (B <sub>2</sub> O <sub>3</sub> )	Solid, (d <sub>50</sub> < 10 μm, 99% purity)	RHI-Magnesita refractories, Brazil

Samples Designation	Description
L	As-received Kraft lignin
L1	Thermally treated Kraft lignin
L2	Thermomechanically processed Kraft lignin prepared with 10 wt.% water content
L3	Thermomechanically processed Kraft lignin prepared with 20 wt.% water content
L4	Thermomechanically processed Kraft lignin prepared with 30 wt.% water content
LPF	Lignin-phenol-formaldehyde resin synthesized with 20 wt.% thermally treated Kraft lignin as a substitute for phenol
LPFx	Lignin-phenol-formaldehyde resin synthesized with 20 wt.% of L2
LPFy	Lignin-phenol-formaldehyde resin synthesized with 20 wt.% of L3
LPFz	Lignin-phenol-formaldehyde resin synthesized with 20 wt.% of L4
5Fc	5 wt.% Ferrocene
10H	10 wt.% Boric acid (H <sub>3</sub> BO <sub>3</sub> )
6B	6 wt.% Boron oxide (B <sub>2</sub> O <sub>3</sub> )

### 2.2. Preparation and characterization of the thermally and thermomechanically treated Kraft lignin

Different types of Kraft lignin were prepared based on thermal and thermomechanical treatments before their use for the preparation of phenolic resins. On one hand, Kraft lignin was heat-treated under a non-oxidizing atmosphere at 200 °C using a 3 °C/min heating rate for one hour in a muffle furnace. The obtained material was ground with a glass mortar and pestle into powdery form. On the other, the as-received Kraft lignin was dried at 110 °C for 72 hours in an oven and separated into three distinct samples. Thereafter, 10, 20 and 30% by mass of water were added to each with the aid of a mechanical mixer device and subjected to thermomechanical treatment in a twin-screw extruder (B & P Process Equipment and Systems, model MP-2019). The procedure was carried out at 180 °C and 160 rpm. The solid material from this process was subsequently grounded with the aid of a mortar and a pestle. These treatments were carried out in an attempt to increase Kraft lignin reactivity and investigate the effect of such processing on graphitic carbon generation during carbonization of the resin formulations containing different graphitizing additives.

The as-received and processed lignin samples were analyzed in an Agilent Technologies Cary 630 FT-IR

spectrophotometer to determine their chemical compositions. Each spectrum was obtained at 64 accumulations with a resolution of  $4\text{ cm}^{-1}$  across a wavenumber of  $650\text{--}4000\text{ cm}^{-1}$ . There was no previous treatment and data were obtained using Microlab® software. The glass transition temperatures of these samples were also determined using DSCQ200, TA Instruments. About 6-7g of each sample was placed in an aluminium capsule and the analysis was performed under a nitrogen atmosphere, with a flow rate of 10 ml/min, at a  $10\text{ }^{\circ}\text{C}/\text{min}$  heating rate. For this analysis, samples were heated from room temperature to  $105\text{ }^{\circ}\text{C}$  and kept at this temperature for 5 minutes to extract the free water previously absorbed by them before being cooled to  $-60\text{ }^{\circ}\text{C}$ , maintained for 2 minutes at that temperature and then heated to  $200\text{ }^{\circ}\text{C}$  at  $10\text{ }^{\circ}\text{C}/\text{min}$ . The glass transition temperature ( $T_g$ ) was determined from the inflection midpoint on the DSC curve according to ASTM E 1356-08.

The as-received and processed Kraft lignin samples' molecular weights and polydispersivity (PD) values were determined. For this analysis, 100 mg of each sample was weighed and dissolved in 2 ml of pyridine solution and acetic anhydride (1: 1 v/v) at  $105\text{ }^{\circ}\text{C}$  for 2 hours. The acetylated sample was precipitated in 30 ml of distilled water and centrifuged at 7500 rpm for 15 minutes. The samples were then dissolved in tetrahydrofuran (THF) in a 1:100 mass ratio and analyzed by Agilent Technologies 1260 Infinity II GPC equipment. The chromatographic run was done at a permeation time of 12 minutes, 1 ml/min solvent flow,  $30\text{ }^{\circ}\text{C}$  column temperature,  $40\text{ }^{\circ}\text{C}$  sensor temperature and 5-20 bar pressure.

### 2.3. Synthesis of the lignin-modified phenolic resins and characterization

Phenolic resins were synthesized in the laboratory using phenol, formaldehyde, and the as-received and treated lignin. The reaction was based on formaldehyde to phenol molar ratio of 1.5 in the presence of  $\text{NH}_4\text{OH}$  as a catalyst. 20 wt.% of the lignin materials were used as phenol replacement to synthesize the LPF resins. To produce LPF resins, the required quantity of phenol, water and ammonia hydroxide was initially mixed and heated to  $60\pm 5\text{ }^{\circ}\text{C}$ , under stirring and reflux with the help of a magnetic stirrer hot plate inside a glass vessel via an oil bath. At this stage, only 70% of the catalyst was added. After approximately 30 minutes, the time it takes for the phenol to dissolve in the water, the necessary amount of lignin was added, causing the mixture to change colour from translucent to

dark brown. After approximately half an hour, the formaldehyde (37 wt.%) was slowly added to the mixture, along with the rest of the catalyst and the reaction was allowed to proceed to completion at  $75\pm 5\text{ }^{\circ}\text{C}$ . The resin samples were designated as shown in Table 1.

### 2.4. Carbonization and graphitization of the lignin-modified phenolic resins

The lignin-modified resins and the graphitizing additives (5 wt.% ferrocene, 6 wt.% boron oxide and 10 wt.% boric acid) were mixed with the aid of a mechanical mixer (Etica Scientific Equipment, Model: 105, No.: 0209) at 300 rpm for 5 minutes. The quantity of each additive was selected based on results from a previous experiment, which showed that those amounts should be sufficient to induce graphitization of such resins [5]. Thereafter, each formulation was put in closed alumina containers and buried inside a refractory box filled with coke to create a reducing atmosphere during the pyrolysis process. The samples were pyrolyzed in a muffle furnace using a sequential heating procedure from  $30\text{ }^{\circ}\text{C}$  to  $100\text{ }^{\circ}\text{C}$  and kept at that temperature for 4 hours, followed by increasing the temperature to  $500\text{ }^{\circ}\text{C}$  and kept there for 1 hour and finally heating them to  $1500\text{ }^{\circ}\text{C}$  for 5 hours at  $3\text{ }^{\circ}\text{C}/\text{min}$  heating rate. 10 wt.% of boric acid was used to ensure proper comparison between the boron source compounds. The amount used is equivalent to 6 wt.% boron oxide.

### 2.5 Characterization of the derived carbon samples

The samples were pulverized after firing and analyzed using a Siemens D5005 AXS X-ray Diffractometer ( $\lambda=1.5418\text{ \AA}$  and CuK radiation nickel filter, using 40mA, 40mV and  $0.02^{\circ}$  step) for phase identification. The results were analyzed with OriginPro® software to provide quantitative parameters used to calculate graphitization level (GL) and obtain structural information such as interlayer spacing ( $d_{002}$ ) and crystallite height ( $L_c$ ). The graphitization level was calculated using Equation 1 according to the procedure outlined by Talabi *et al.*, 2018 [7]. The GL calculation was based on the total area of graphitic carbon peaks divided by the sum of those associated with graphitic and non-graphitic carbons. Non-carbon phases were not used for the calculation and the profiles were fitted using Gaussian function. Equations 2 and 3 were used to determine  $d_{002}$  and  $L_c$  values. To determine these parameters, peaks deconvolution of the XRD profiles was done in the  $2\theta$  range of  $15$  to  $30^{\circ}$  and hump and peak region were fitted using Gaussian function.

$$\text{Graphitization level (GL)} = \left( \frac{\text{Total area of graphitic carbon}}{\text{Total area of graphitic carbon} + \text{Total area of non-graphitic carbon}} \right) * 100 \quad (1)$$

$$n = d_{002} 2 \sin \theta \quad (2)$$

$$k\lambda = l_c \beta \cos \theta \quad (3)$$

where  $n$  = positive integer,  $k = 0.89$ ,  $\theta$  = incident angle,  $\beta$  = full width at half maximum (FWHM)  $d_{002}$  (nm) = interlayer spacing, and  $L_c$  (nm) = crystallite height.

### 3. Results and Discussion

#### 3.1 Characterization of the as-received and treated Kraft lignin

The spectra of the as-received and processed Kraft lignin samples, which were used to synthesize the LPF resins are shown in Fig. 1. All the peaks were assigned based on information available in literature.

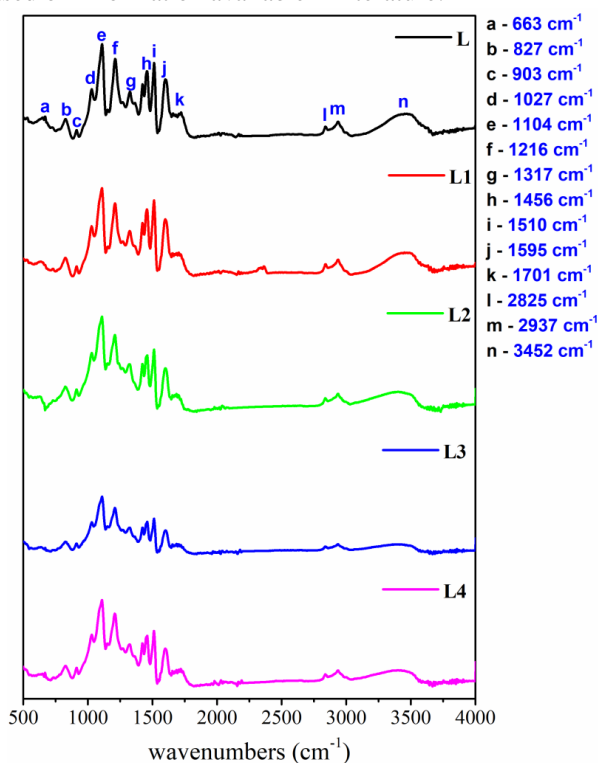


Fig 1. FTIR-ATR spectra of as-received and processed Kraft lignin.

The peaks at  $688 \text{ cm}^{-1}$ ,  $754 \text{ cm}^{-1}$  and  $824 \text{ cm}^{-1}$  were assigned to C–H vibrations [5]. Specifically, the ortho-substituted and para-substituted positions out-of-plane -CH were found at  $754 \text{ cm}^{-1}$  and  $826 \text{ cm}^{-1}$ , respectively [8]. The intensities of these peaks were determined using Spectragrphy 1.2 software at peaks finding threshold of 5.0% relative to the visible spectrum ordinate. From the obtained values, the proportion of para linkages in the samples was determined (Table 2). The thermally treated Kraft lignin has the highest proportion of para linkages. The observation might be responsible for the observed ease of processing during preparation of the LPF resins. More

so, previous studies have suggested that the presence of para linkages could favour catalytic graphitization of conventional phenolic resins [5, 9]. In this instance, the resin synthesized using thermally treated Kraft lignin presented the highest graphitization level values, irrespective of the graphitizing additives present in the formulation. The difference in the amount of graphitic carbon generated from these resins may be attributed to transformation that occurred in the lignin structure during processing.

Table 2. Peaks absorbance intensity of ortho and para positions.

Peaks positions ( $\text{cm}^{-1}$ )	L	L1	L2	L3	L4
754 (ortho-substituted CH-position)	0.0223	0.0155	0.0327	0.0110	0.0225
824 (para-substituted CH-position)	0.0396	0.0377	0.0566	0.0179	0.0334
para links proportion (%)	64.0	70.9	63.4	61.8	59.8

The peaks at  $1020 \text{ cm}^{-1}$  and  $1110 \text{ cm}^{-1}$  were assigned to C–O vibrations of  $\text{CH}_2\text{OH}$  group. The band that corresponds to the phenolic hydroxyl group vibration of the guaiacyl unit was detected at  $1211 \text{ cm}^{-1}$  while the one at  $1325 \text{ cm}^{-1}$  was attributed to OH in-plane bond of syringyl groups. The profiles show that the lignin materials are rich in guaiacyl unit, which makes them a suitable candidate for phenolic resins production. The observation suggests that there should be more reactive points available for the chemical reaction during resin synthesis. The intensity ratio of guaiacyl:syringyl unit of L, L1, L2, L3 and L4 samples was determined to be 1.69, 2.05, 2.06, 2.67, and 2.46, respectively.

The peaks at  $1456\text{ cm}^{-1}$  and  $1512\text{ cm}^{-1}$  correspond to C=C vibrations of the aromatic ring. The peaks at  $1595\text{ cm}^{-1}$  and  $1701\text{ cm}^{-1}$  belong to  $-\text{OCH}_3$  in acetyl groups and C=C vibrations of the aromatic ring, respectively. The peaks at  $2839\text{ cm}^{-1}$  and  $2936\text{ cm}^{-1}$  are due to  $-\text{CH}$  stretching vibration of the methoxyl group. The width of the band at  $3452\text{ cm}^{-1}$  indicated that the peak is due to OH bond vibration related to the aromatic ring. The intensity of this band decreased, especially for the thermomechanically processed samples. The thermomechanical processing could have facilitated more dissociation of the OH groups compared to the one subjected to only thermal treatment.

By superimposing the spectra, the peaks intensities of the as-received Kraft lignin was found to have decreased after the thermal or thermomechanical treatment. For example, the intensity of peaks corresponding to the methoxyl group at  $1456\text{ cm}^{-1}$  and  $2839\text{ cm}^{-1}$  reduced likely due to a slight dissociation and release of this functional group from the lignin structure during processing. This phenomenon appears to be more pronounced in L1 sample. Among the category of thermomechanically processed samples, L2, which was prepared with 20 wt.% water content has the highest level of reduction. Nevertheless, no new functional group was detected after the treatments.

As shown in Table 3, the amount of water added to the lignin before thermomechanical treatment affects its glass transition temperature ( $T_g$ ). The greater the amount of water added to the as-received lignin, the greater the  $T_g$  of the sample after extrusion. The result suggests a possible polymerization reaction during thermomechanical processing. However, thermal treatment of the as-received Kraft lignin has no significant effect on the glass transition temperature. The  $T_g$  values of the one subjected to thermal treatment at  $200\text{ }^\circ\text{C}$  were found to be  $130.2\text{ }^\circ\text{C}$ .

Table 3. Glass transition temperature of as-received, thermally and thermomechanically processed Kraft lignin.

Sample	$T_g$ ( $^\circ\text{C}$ )
L	129.4
L1	130.2
L2	129.1
L3	131.7
L4	134.1

The average molecular weights and polydispersity (PD) values of the as-received, thermally and thermomechanically treated Kraft lignin samples are presented in Table 4. After heating up to  $200\text{ }^\circ\text{C}$  and kept

at that temperature for 1 hour, the average molecular weight by number ( $M_n$ ) and weight ( $M_w$ ) values significantly reduced from  $3064\text{ g/mol}$  and  $707\text{ g/mol}$  to  $1957\text{ g/mol}$  and  $539\text{ g/mol}$ , respectively. The decrease can be attributed to degradation reaction as a result of ether bond cracking which is one of the primary bonds in lignin [5]. Similarly, the sample with 10 wt.% water subjected to thermomechanical treatment has its  $M_n$  and  $M_w$  decreased relative to the as-received sample. However, these parameters increased for samples prepared with 20 wt.% and 30 wt.% water, likely due to polymerization and bond-linking reactions that occurred during thermomechanical processing. This observation was related to amount of graphitic carbon generated from resin formulations containing ferrocene. In this category, the highest amount of crystalline carbon was produced from the resin prepared using L1 lignin, which has the lowest  $M_w$  and  $M_n$  values.

Among the category of resins prepared using thermomechanically processed lignin, the ones synthesized using L2 (which has the lowest  $M_w$  and  $M_n$  values) yielded the highest amount of graphitic carbon. Consequently, when thermomechanical processing is employed to prepare Kraft lignin, the initial moisture content of the material should be low to reduce its molecular weight and obtain an optimum amount of graphitic carbon during pyrolysis of the resulting resin.

The samples' polydispersity was also affected by the nature of processing they were subjected to in a manner directly related to their molecular weight values.

Table 4. The average molecular weights and polydispersity index ( $M_w/M_n$ ) of the as-received and treated Kraft lignin samples.

Lignin samples	$M_w$ (g/mol)	$M_n$ (g/mol)	PD ( $M_w/M_n$ )
L	3064	707	4.33
L1	1957	539	3.63
L2	2424	629	3.85
L3	3388	708	4.78
L4	3125	738	4.23

### 3.2 XRD profiles of carbons derived from lignin-modified phenolic resins without and with graphitizing additives

The diffractogram of carbon derived from the plain LPF resin is presented in Fig. 2. The XRD profile was

characterized by low-intensity humps across  $20^\circ$  and  $30^\circ$  and across  $40^\circ$  and  $50^\circ$ . This feature represents those of non-graphitic carbon with no significant ordered atomic arrangement. Such carbon usually exhibits  $sp^3$ -hybridization that is associated with rigid  $\pi$ -bonds that limit rotation of atoms to graphene layers during pyrolysis [7].

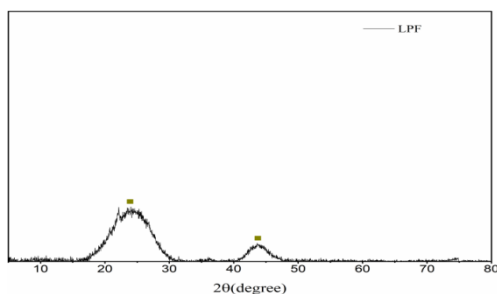


Fig 2. X-ray diffraction pattern of carbon derived from lignin-modified phenolic resin without graphitizing additives after carbonization at  $1500^\circ\text{C}$  for 5 hours.

Based on the obtained result, ferrocene, boric acid and boron oxide were investigated as graphitizing additives during pyrolysis of these resins, which were prepared based on different modifications of Kraft lignin. These compounds have shown promising results as graphitizing agents for conventional phenolic resins [7, 10]. Figure 3 shows the XRD profiles of carbon derived from the different LPF resins containing 6 wt.% boron oxide. The resin prepared using thermally treated Kraft lignin presented the highest graphitization level value (34%). The difference in the amount of graphitic carbon generated from these resins may be associated with the extent of B-O-C formation, which has been described as one of the controlling factors influencing phenolic resin graphitization [11].

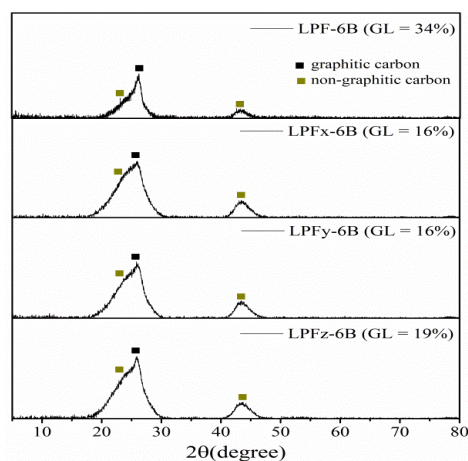


Fig 3. X-ray diffraction pattern of carbon derived from lignin-modified phenolic resins containing  $\text{B}_2\text{O}_3$  after carbonization at  $1500^\circ\text{C}$  for 5 hours.

Regarding the resin formulations containing  $\text{H}_3\text{BO}_3$  (Fig. 4), it is remarkable that the degree of graphitization increases considerably as typified by a sharp peak at  $26^\circ$  and other minor ones, around  $54^\circ$  and  $78^\circ$ , which are associated with graphitic carbon. The best graphitization level value of 76% was attained for the resin formulation prepared using thermally treated Kraft lignin. Among the category of resins prepared using thermomechanically processed lignin, LPFy yield carbon with the highest amount of crystalline carbon. The lignin used to prepare this resin was not the one with the lowest molecular weight values. Nevertheless, it yields the highest quantity of graphitic carbon. The generation of ordered carbon from phenolic resins containing boron source compounds has been greatly linked to B-O-C bond formation during carbonization [9, 11]. The attained results agree with this submission, hence the contributing effect of lignin component in the modified resins on graphitization operation may not be significant regarding these formulations. Nevertheless, resins prepared using thermally treated Kraft lignin, which has the lowest molecular weight and polydispersivity values present the best values of graphitization level.

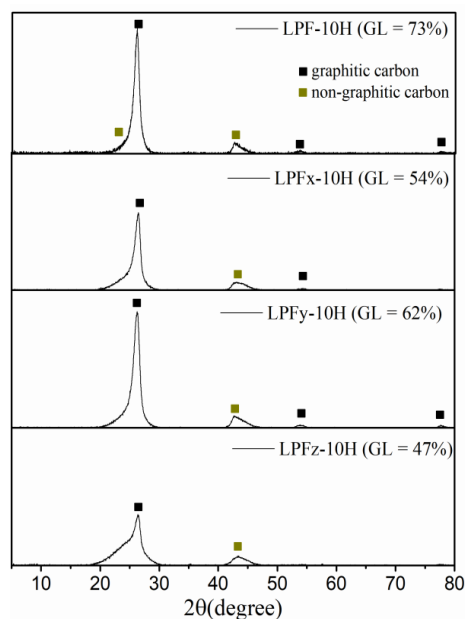


Fig 4. X-ray diffraction pattern of carbon derived from lignin-modified phenolic resins containing  $\text{H}_3\text{BO}_3$  after carbonization at  $1500^\circ\text{C}$  for 5 hours.

Consequently, between the two boron source compounds, boric acid provided a greater degree of graphitization for the investigated resins. As mentioned earlier, the graphitization of such resins by boron-compound additives depends on the formation of a B-O-C bond during pyrolysis [9, 11]. This bond, due to its lower energy, compared to C-C bonds allows rotation and

rearrangement necessary for graphitic carbon generation during pyrolysis.

Again, there was a significant reduction in the amount of graphitic carbon generated when ferrocene was introduced as the graphitizing additive. As observed in Fig. 5, the peak intensity at  $26^\circ$  corresponding to 002 plane of the carbon samples decreased, especially for resins synthesized using thermomechanically processed Kraft lignin. In this instance, the molecular weight of Kraft lignin that was used for the resin preparation appears to be the controlling factor affecting the degree of graphitization.

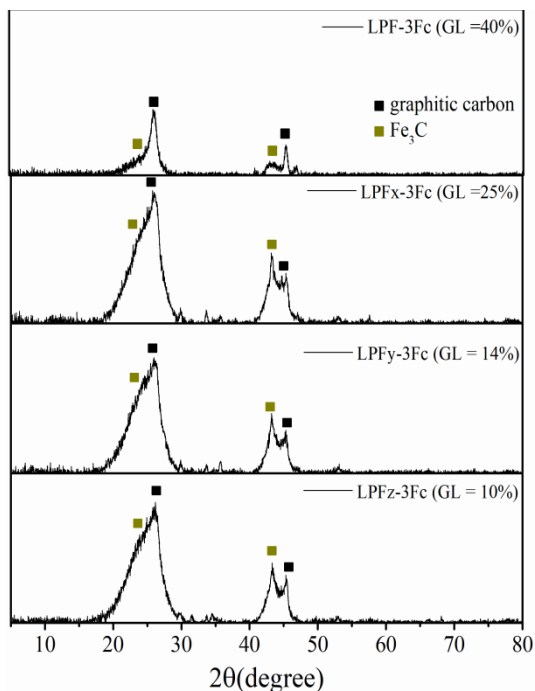


Fig 5. X-ray Diffraction pattern of carbon derived from lignin-modified phenolic resins containing ferrocene after carbonization at 1500 °C for 5 hours.

The interlayer spacing ( $d_{002}$ ) and crystallite height ( $L_c$ ) of the derived carbon samples were determined. These structural parameters were used to describe the degree of graphitization. The closeness of  $d_{002}$  value to that of graphite, which is 0.3354 nm and the increasing value of  $L_c$  indicate a greater graphitization degree [7]. The values obtained for the analyzed carbon samples are presented in Table 5. As expected, carbon derived from the resin without any graphitizing additives had the highest interlayer spacing (0.3658 nm) and lowest crystallite height (3.16 nm) values. Similarly, carbon derived from the resin formulations containing boric acid presented the lowest and highest values of  $d_{002}$  (0.3376 nm) and  $L_c$  (0.3401 nm), respectively. Also, regarding carbon samples derived from formulations containing ferrocene, their  $d_{002}$  and  $L_c$  were lower and higher, respectively than those derived from resins containing boron oxide. These results are in agreement with information derived based on

graphitization level calculation. The values obtained are similar to those recorded in similar studies involving conventional phenolic resins [7, 12] and showed that the incorporation of these additives can promote graphitic carbon generation from lignin-modified phenolic resins. Moreover, the corresponding increase in both  $d_{002}$  and  $L_c$  values supports the assertion that good planar stacking requires the growth of crystals in the c-direction [13].

Table 5. Crystal parameters of carbon samples derived from LPF resins with and without graphitizing additives after carbonization at 1500 °C for 5 h under a reducing atmosphere

Samples	$d_{002}$ (nm)	$L_c$ (nm)
LPF	0.3658	3.16
LPF-3Fc	0.3411	15.65
LPFx-3Fc	0.3409	11.18
LPFy-3Fc	0.3404	11.22
LPFz-3Fc	0.3406	10.42
LPF-6B	0.3402	14.76
LPFx-6B	0.3422	8.68
LPFy-6B	0.3412	10.40
LPFz-6B	0.3424	11.70
LPF-10H	0.3376	19.12
LPFx-10H	0.3401	16.58
LPFy-10H	0.3379	15.50
LPFz-10H	0.3396	15.11

#### 4. Conclusion

Different Kraft lignin samples were produced based on thermal and thermomechanical treatments and used to synthesise lignin-phenol-formaldehyde resins to study the effect of such processing on catalytic graphitization of the resins. Firstly, the treatments affected glass transition, molecular weight, polydispersivity and chemical composition of the as-received Kraft lignin. The Kraft lignin subjected to thermal treatment has the lowest molecular weight and polydispersivity values while



increasing water content in the lignin before thermomechanical processing increase the value of those properties. On top of that, the characteristics of lignin used to prepare the lignin-modified phenolic resins affected the quantity of graphitic carbon that was generated during pyrolysis. Resins prepared using thermally treated Kraft lignin, which has the lowest values of molecular weights and polydispersivity yielded the highest amount of graphitic carbon during carbonization operation.

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## Conflict of Interest

The author declares that he has no conflict of interest.

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