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Pyrolysis of lignin and IR analysis of residues

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Abstract

The kinetics of isothermal pyrolysis of lignins occurring in hardwood found in the north of Argentina was studied using thermogravimetric techniques (TG/TGA). From the thermograms, which showed a similar behaviour in all the studied species, were determined the kinetic parameters for the isothermalpyrolysis in the temperature range between 226 and 435°C using the Avrami–Erofeev equation for solid state reactions and the Arrhenius equation. The solid residues obtained at each temperature were analysed by infrared spectrophotometry in search for the modifications taking place in the different functional groups as a result of the temperature effect. © 1997 Elsevier Science B.V.

1. Introduction

One of the main components of wood, lignin, is present in 15–20% depending on the species of wood.

The lignins are largely obtained as byproduct in the paper industry used as energy source because of combustability, but there is a worldwide tendency looking for its other uses.

The lignin has a very complex molecular structure which varies according to the wood type and the species. Its composition has not been accurately determined yet, but it is known that it is a polymer made up of a macromolecule formed by different structural units of different size which are not bonded to each other in the same way. The lignin can neither be isolated completely from the other wood components, nor can be split into its monomeric parts without affecting its structure as has been reported by Glenie et al. [1], D. Fengel et al. [2], C. Chen [3], H. Nimz [4], T.E. Timell [5] and V. Kyosti et al. [6]. These authors have suggested different probable structures of lignins because of the limited accurate data available.

Other authors D. Fengel et al. [2], Pilo et al. [7] and H. Hatakeyama [8] have studied the chemical properties and characterized the lignins and their derivatives using different chemical and instrument methods.

D. Fengel et al. [2] have employed chemical methods and UV and IR spectroscopy measured in KBr-pellets for determination of the chemical composition and characterization of acid lignins coming from softwood and hardwood. The study of the chemical structure and biogenesis of lignins as well as the main structure obtained from different types of wood were reported by Pilo et al. [7]. The quantification of groups in lignin by chemical and physical methods, and the results obtained with different types of wood were discussed. The variation of infrared spectra with temperature of different isolated lignins (Björkam lignin, dioxane lignin, calcium lignosulfate and thiolignin) in

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the range of 20 to 250°C was studied by H. Hatakeyama et al. [8].

Several works have been published concerning the degradation kinetics of lignin. Beall et al. [9] have studied the degradation process of *Picea* lignins (Picea sp.) in a nonisothermal process.

Guzman et al. [10], studied the pyrolysis in an inert atmosphere of lignin obtained through acid precipitation from *Pinus radiata* black liquor, where the kinetic parameters were determined for the application in three different models. The results showed that although the three models may be applied for describing the chemical process of lignin thermal degradation, both isothermal models fitted better than the non isothermal one. The activation energy values obtained for the isothermal processes is 27.44 kJ mol^{-1}.

On the other hand, G. Vazquez et al. [11] studied the influence of temperature, time and catalyst concentration on the rate and selectivity of HCl – delignification of *Eucalyptus globulus* wood by acetic acid. They modelled the observed kinetics with equations including terms for solubilization and, when necessary, condensation processes, and used the kinetic data to calculate activation energies.

In a previous paper Herrera et al. [12] used TG, DTG and DTA techniques to study the thermal decomposition of six species of hardwood and the kinetics of isothermal pyrolysis in dry nitrogen between 220 and 340°C. On the other hand, Honof et al. [13] studied the isothermal pyrolysis of the series of wood pulps and lignin at different temperatures from 325 to 360°C, under nitrogen atmosphere and obtained activation energy values of 42 kJ mol^{-1}.

The present work is concerned with the study of pyrolytic thermal degradation, in an inert atmosphere, of lignins from hardwoods, focused towards the study of the kinetics of the reaction. The variations of the IR spectra with temperature was determined in order to relate the modifications occurring in the functional groups of lignins with temperature effect.

2. Experimental

Lignins from Quebracho Colorado (*Schinopsis Quebracho Colorado*) (Q.C.), Quebracho Blanco (*Aspidosperma Quebracho Blanco*) (Q.B.) and Algarrobo Negro (*Prosopis Nigra*) (A.N.) were obtained as residue from wood without extractives which after acid hydrolysis (H_2SO_4) for removal of the polysaccharides gives the Klason lignins [14,15] with quantum yields. The samples were granulometric 40/60 according to ASTM. The isothermal runs were performed in a thermal scale Stanton Redcroft TG-750 with samples of 2.50 mg in a nitrogen atmosphere at a flux of 50 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. The IR analyses were performed using a Model DS-402 G grating spectrophotometer with potassium chloride pellets.

3. Results and discussion

3.1. Kinetic study

The isothermal runs were carried out in the temperature range between 226°C and 435°C in which the pyrolysis process takes place [12,9] and a similar behaviour for all the studied species was observed. From these data the conversion value α was determined as,

$$\alpha = m_\mathrm{i} - m_t/m_\mathrm{i} - m_\mathrm{f} \qquad (1)$$

where m_t is the mass in time t and m_i is the initial mass and m_f is the mass at infinite time. The mass loss $m_\mathrm{i} - m_t$ as function of the time for each temperature studied for lignins from Q.C. is plotted in Fig. 1. The kinetic parameters of the isothermal pyrolysis were calculated from the Avrami–Erofeev equation for a reaction in the solid state,

$$[-\ln(1-\alpha)^{1/n}] = k.t \qquad (2)$$

where n is the reaction order, k the rate constant and t the time.

By applying the logarithm and plotting $\ln[-\ln(1-\alpha)]$ as function of $\ln t$ (Fig. 2) the values n, $\ln k$ and r (correlation coefficient) are obtained using linear regression. Table 1 lists the values obtained for each working temperature for Q.C. The results obtained for the other species are quite similar (not shown). The Arrhenius equation in its logarithmic form,

$$\ln k = \ln A - Ea/RT \qquad (3)$$

where A = pre-exponential factor, Ea = activation energy, R = gas constant and T = temperature in Kelvin grades, yields the values of Ea, A and r

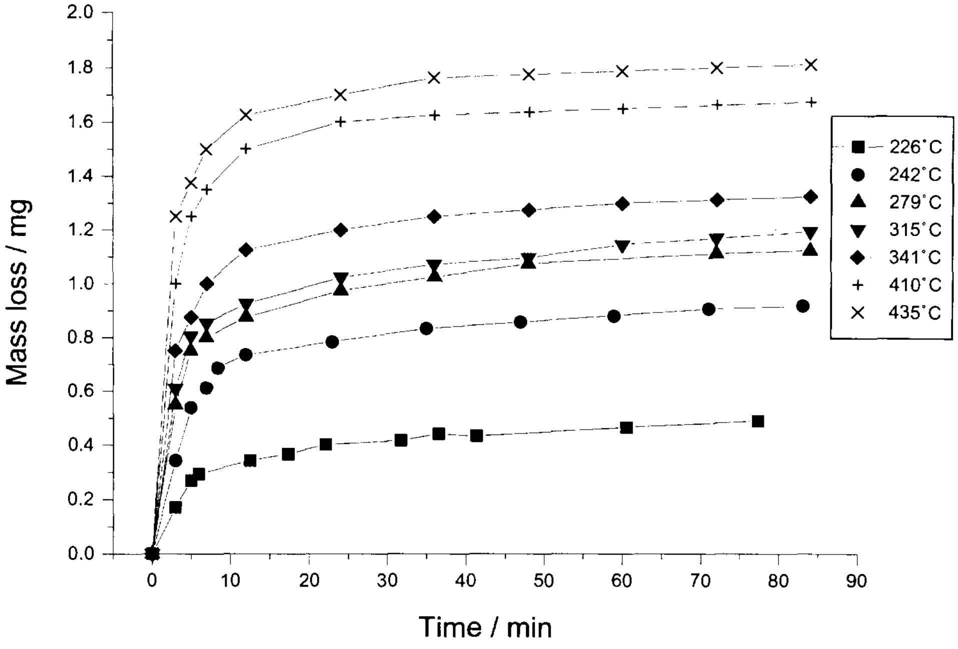


Fig. 1. Mass loss vs time for lignin of Q.C.

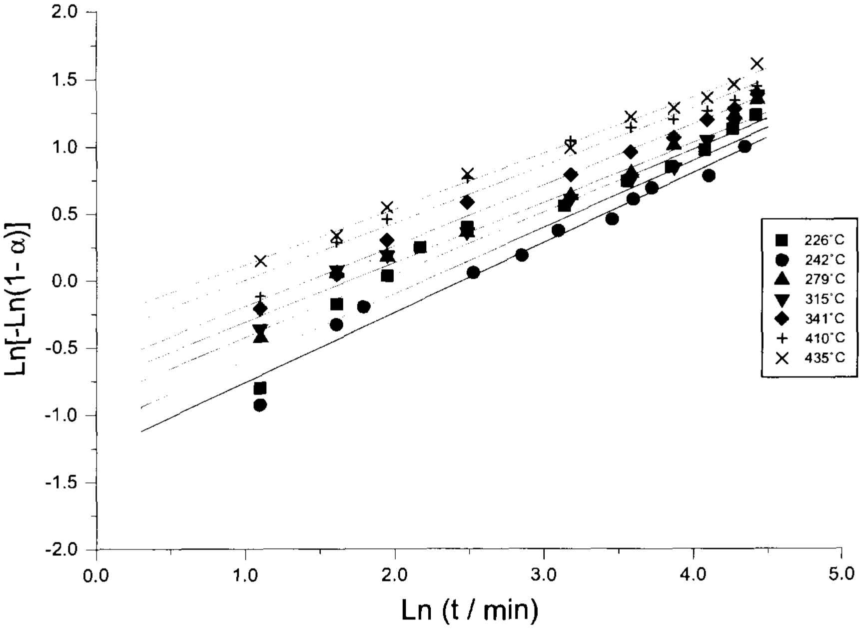


Fig. 2. Ln(−Ln (1−α)) vs ln t for Q.C.

Table 1
Values of n, ln k and r for lignin of Q.C. at different working temperatures

Temperature (°C)	n	ln k	r
226	0.52	−1.28134	0.98451
242	0.52	−1.06027	0.97491
279	0.48	−0.83848	0.99118
315	0.45	−0.75733	0.98408
341	0.46	−0.64572	0.99553
410	0.43	−0.42203	0.98571
435	0.42	−0.29832	0.99652

Table 2
Activation evergy values and r for lignins of the species studied

Lignin	Ea (kJ mol^{-1})	r
Quebracho Colorado	12.49	0.98891
Quebracho Blanco	39.40	0.98769
Algarrobo Negro	42.60	0.98329

(regression coefficient) from linear regression when ln k is plotted vs $1/T$ (Fig. 3). The values obtained with Ea and r for all the studied species are given in Table 2.

Comparison of the these results with those obtained with hardwood where lignin was extracted [12] shows that the isothermal pyrolysis process in wood is produced in two distinct steps in the temperatures between 220 to 300°C and 300 to 350°C whereas in lignins it is produced in only one step.

The activation energy values obtained for woods are in the range between 39.5 and 78.5 kJ mol^{-1} for the first step, and 92.17 to 257.9 kJ mol^{-1} for the second step whereas in lignins the values obtained are lower (12.49–42.6 kJ mol^{-1}).

There is however a distinct coincidence with the behaviour of the wood and it is that the process holds for the Avrami–Erofeev equation $[-\ln(1-\alpha)^{1/n}] = k.t$, with n=0.5.

3.2. I.R. analysis of the solid residues

Different authors [1–6] have suggested structural schemes for lignins of different wood types. Nevertheless, despite the present technological development and different techniques and methodologies applied to obtain lignins, its structure still remains to be accurately established. It varies not only depending on the time but also on the method to obtain it and the morphological regions where it was obtained [1,4,7]. Fig. 4 shows a schematic structure proposed for the lignin *Fagus silvatica* (hardwood) [4].

The lignins occurring in hardwood are made up of a polymer which seems to include structural units of 'Guaiacyl' nuclei (taken from the phenol name occurring in nature, 'guayacol') and of 'syringyl' (from phenolaldehyde, 'syringylaldehyde'), which are found

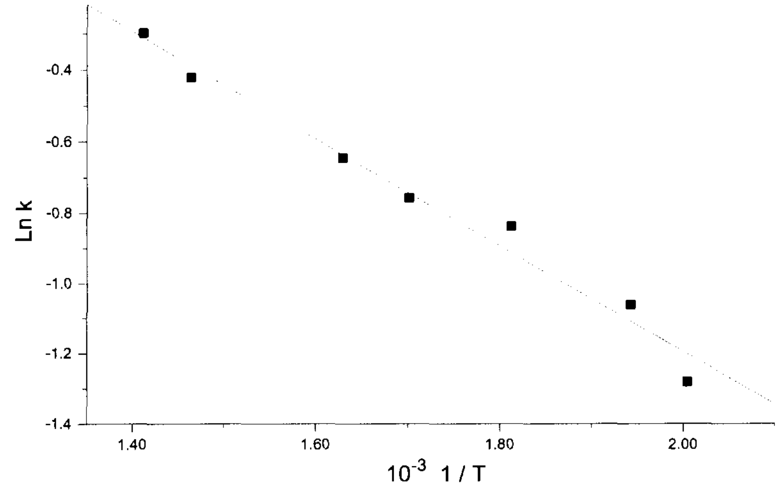
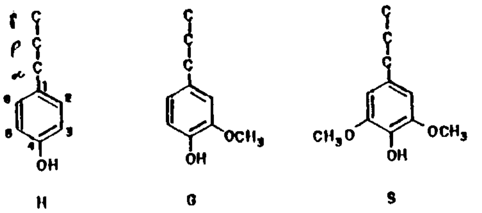


Fig. 3. Ln k vs $1/T$ for lignin of Q.C.



Basic Units C in lignins: H: p-hydroxyphenolpropane, G: Guayacilpropane, S: Syringilpropane.

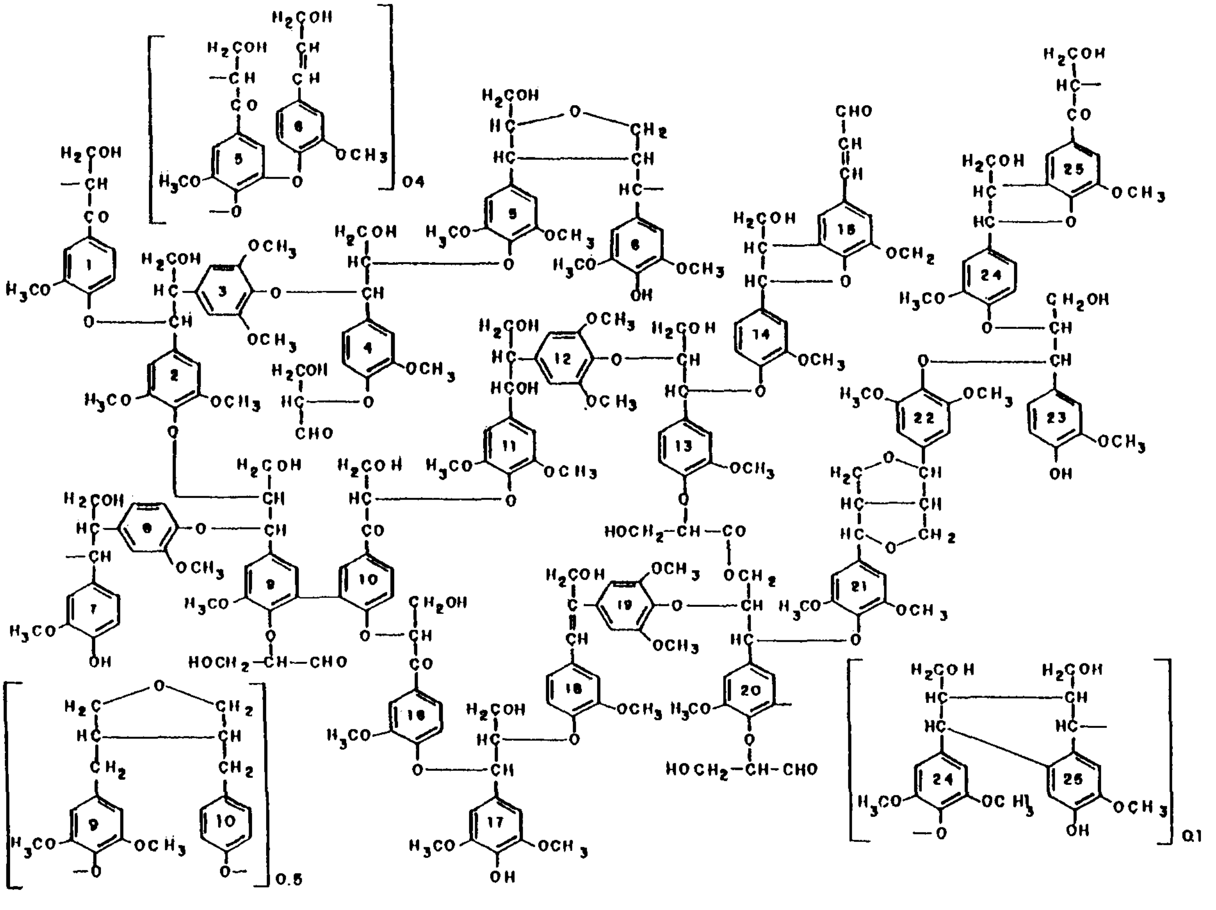


Fig. 4. Schematic structure proposed for lignin of *Fagus Silvatica* (Hardwood).

in different amounts along with a low percentage of *p*-hydroxyphenylpropane units.

Infrared spectroscopy in the near IR region (wave numbers: 4000–600 cm^{-1}) is a useful physical method for characterizing lignin and lignin derivatives. While the infrared spectrum is a characteristic property of compounds with exactly known structures, there are several uncertainties with the interpretation of lignin IR spectra. This is mainly caused by two factors. Firstly, there are large variations in lignin structures

Table 3
Important infrared absorption bands of lignin

Position (cm^{-1})	Band origin [a]
3450–3400	OH stretching
2940–2820	OH stretching in methyl and methylene groups
1715–1710	C=O stretching nonconjugated to the aromatic ring
1675–1660	C=O stretching in conjugated to the aromatic ring
1605–1600	Aromatic ring vibrations
1515–1505	Aromatic ring vibrations
1470–1460	C–H deformations (asymmetric)
1430–1425	Aromatic ring vibrations
1370–1365	C–H deformations (symmetric)
1330–1325	Syringyl ring breaking
1270–1275	Guaiacyl ring breaking
1085–1030	C–H C–O deformations

[a] According to Hergert 1971.

and compositions, depending on the origin of the sample and the special isolation procedure; secondly, variations are caused by different techniques of preparing of sample, in the form of films, or the most frequently applied form of potassium bromide pellets [2].

IR spectra of lignins show several major absorption bands which can be assigned empirically to structural groups, based on a great deal of result obtained both from model compounds and lignins. The IR frequency assignments were done according to [16]. The absorption bands of interest are shown in Table 3.

As the spectra obtained for lignins from different species were similar at room temperature as well as at the changes produced because of temperature effects, only IR spectra of lignin from Q.C. is shown in Fig. 5. It shows the IR spectra of lignin at room temperature and some working temperatures (226, 300, 336 and 435°C).

It is observed that the characteristic bands of lignins [2,8,16] which allow to determine their presence in unknown samples, lie about 1510 and 1600 cm^{-1} (vibration of the aromatic rings) and between 1470 and 1460 cm^{-1} (deformations C–H and vibrations of the aromatic ring). They are aromatic skeleted bands. The intensity of these bands, however is strongly influenced by structures bordering on the aromatic nuclei. The different relations between the intensities of the bands at 1510 and 1600 cm^{-1}, can be used for differentiation of softwood and hardwood lignins. In hardwood lignins, the intensities of these bands are nearly the same, while in softwood lignins the intensity of the 1510 cm^{-1} band is considerably higher [2].

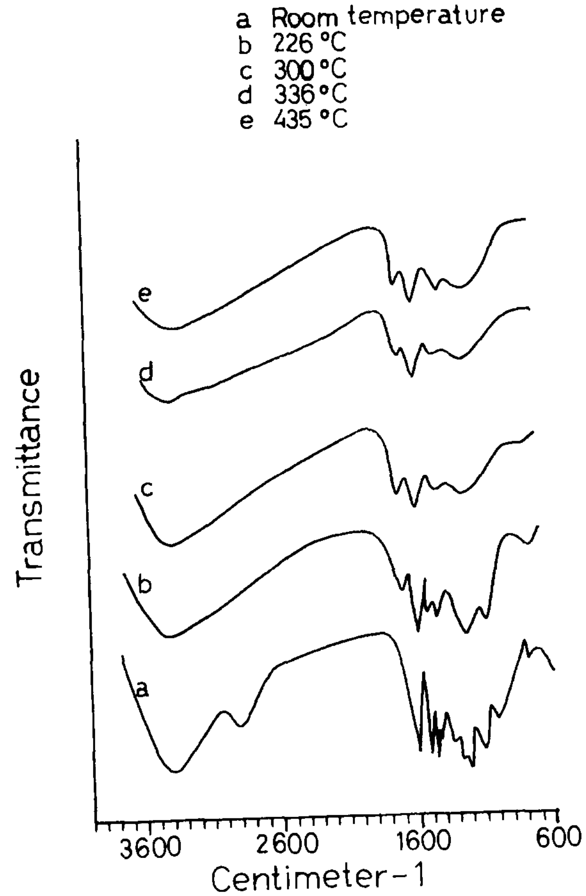


Fig. 5. IR spectra of lignin from Q.C. at room and other temperatures.

In our case, bands with similar intensity are observed in the lignins at room temperature which would be indicative of the predominance of 'syringyl' compounds in these hardwood lignins. As heating of the sample is produced and the pyrolysis process starts, it can be observed that although the band at 1606 cm^{-1} decreased, the band at 1511 cm^{-1} disappears at 242°C. The band at 1460 cm^{-1} decreases until it disappears at temperatures above 300°C.

The typical guaiacyl and syringyl bands (ring breaking) are located at about 1270 and 1330 cm^{-1}

Table 4
Characterization and changes of the IR spectra of lignin and solid residues after heating

Band (cm^{-1})	Characteristics	Lignin at room temperature	Lignin after heating
1606	Vibration of the aromatic ring	The intensity of three bands (1606, 1511 and 1460) are similar	Its intensity decreases
1511	Aromatic ring vibrations		It disappears at 242°C
1460	Deformations of the C–H bond		Its intensity decreases
1330	Syringyl	Syringyl less intense than guaiacyl	Disappears at 226°C
1270	Guaiacyl		Its intensity decreases
1710	C=O stretching	—	It appears at 226°C.
3400	O–H stretching	Broad	Its intensity decreases
2940	O–H stretching in methyl and methylene groups	Less intense	It disappears
1221	Of combination and overlapping of C–H	Less intense	It decreases until it disappears at 279°C.
1000–1100	Stretching bands and their deformations	Acute and intense	It decreases and disappears at 242°C

respectively, at room temperature. It is observed that the band at 1330 cm^{-1} disappears while that at 1270 cm^{-1} decreases with heating.

The band of the carbonyl group appearing in the range between 1660 and 1770 cm^{-1} is not observed at room temperature but appears at 1710 cm^{-1} once the pyrolysis has already started at 226°C and remains almost with the same intensity during heating. This would be indicating that the C=O groups are not in conjugation with the aromatic ring [2,8,16,17].

The intensity of the 3400 cm^{-1} absorption bands representing O–H stretching decreased with heating and a lower intensity band between 2800 and 3000 cm^{-1} of bond stretching O–H in methyl and methylene groups was observed only at room temperature.

The bands in the region of 1000 and 1400 cm^{-1} caused by combination and overlapping of C–O stretching bands and by deformations, that appear in the samples at room temperature, decreased up to disappearance with increasing temperature. A band between 1000 and 1100 cm^{-1} (C–H, C–O deformations) is observed but disappears at 242°C. No variations in the spectra from 330 to 450°C (highest studied temperature) were observed which is indicative of the stability of a new structure. All these data are in agreement with those reported by other authors [8] who observed higher variations at temperatures lower than 250°C.

The results obtained from the IR spectra of Q.C. lignin and the residues obtained at different temperatures (Fig. 5), are listed in Table 4.

4. Conclusions

The isothermal pyrolysis of lignins of hardwood species mentioned above obeys Avrami–Erofeev equation reasonably describing a nucleation and growth process. The value obtained for the energy activation of lignins of these hardwoods are in the range between 12.49 and 42.60 kJ mol^{-1}, for the reaction order n=0.5, with correlation coefficients between 0.9832 and 0.9889 for the different species studied. The result obtained from the application of Avrami–Erofeev equation are in concordance with those presented by other authors [6,14,15] who studied other wood species.

The data obtained with IR spectrometry of the residues allowed us to observe that from the temperature where pyrolysis starts at 226°C up to 330°C, substantial changes take place in the bands characteristic of some functional groups having a complex structure of the lignins. The bands at 1511, 1330, 1221, 1100 and 1000 cm^{-1} disappear; those at 1600 cm^{-1} remain slightly modified, those at 3400, 1460 and 1270 cm^{-1} decrease and the band at 1710 cm^{-1} appears at 226°C. Between 330°C to 450°C (highest studied temperature), no variations in the spectra were observed which is indicative of the stability of a new structure.

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