

# *Eucalyptus* Tar Pitch Pretreatment for Carbon Material Processing

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**ABSTRACT:** *Eucalyptus* tar pitches are generated on a large scale in Brazil as byproducts of the charcoal manufacturing industry. They have a macromolecular structure consisting mainly of phenolic, guaiacylic, and siringylic units substituted and interlinked by aliphatic side chains rich in oxygenated polar groups (such as alcohol, ether, carbonyl, and carboxyl), similar to lignin. Under treatment around 250°C, the pitches undergo polymerization. C—O links are broken up, and, while side chains are released, the heavier fragments rich in aromatic rings react to form larger molecules. The presence of AlCl<sub>3</sub> and CH<sub>2</sub>O makes polymerization at lower temperatures (150°C and 100°C, respectively)

possible. AlCl<sub>3</sub> acts as a Lewis acid, complexing to oxygen atoms and weakening C—O bonds. In turn, CH<sub>2</sub>O acts as a polymerizing agent, as in the preparation of resol phenolic resins. These pretreatments have made it possible to adjust the softening point in order to yield spinnable pitches susceptible to post spinning thermal stabilization, besides yielding pitches with improved thermal stability. These possibilities are important because they make *Eucalyptus* tar pitches potential carbon fiber precursors. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1604–1611, 2004

**Key words:** biopolymers; renewable resources; NMR

## INTRODUCTION

Fossil pitches have been largely studied all over the world as precursors of advanced carbonaceous materials (ACM), which have very interesting properties and a large number of applications. Examples include carbon fibers,<sup>1–4</sup> carbon–carbon composites,<sup>2–6</sup> lithium–ion battery anodes,<sup>7,8</sup> and activated carbons.<sup>9–11</sup>

In Brazil, another kind of pitch, *Eucalyptus* tar pitch, is generated on a large scale as a by-residue of *Eucalyptus* wood pyrolysis in charcoal production. In a previous article,<sup>12</sup> we reported only on the production and characterization of *Eucalyptus* tar pitches. They have a macromolecular structure that consists mainly of phenolic, guaiacylic, and siringylic units substituted and interlinked by aliphatic side chains rich in oxygenated polar groups (alcohol, ether, carbonyl, and carboxyl), similar to lignin. Furthermore, they have a large molar mass distribution.

In our previous work,<sup>12</sup> investigations of *Eucalyptus* tar pitch pretreatment demonstrated that thermal polymerization takes place around 250°C and leads to

increases in the pitch softening point and thermal stability. While in that work we focused mainly on the changes in pitch physicochemical properties, in the present article we present a more detailed study on the chemical aspects of thermal polymerization, which provides valuable understanding of the chemistry of the tar pitches. Furthermore, alternative methods of biopitch pretreatment are reported, namely the use of an external agent, such as a catalyst (AlCl<sub>3</sub>) or a polymerization agent (CH<sub>2</sub>O). Chemical changes were assessed by solid-state <sup>13</sup>C-NMR, Fourier transform infrared spectroscopy (FTIR), and elemental analysis.

## EXPERIMENTAL

### Pitch Samples

A precursor pitch was obtained by vacuum distillation of the tar generated in the slow pyrolysis of *Eucalyptus* wood (Minas Gerais, Brazil) during charcoal production in industrial masonry ovens. A more detailed description of the methods of obtaining pitch (wood pyrolysis and tar distillation) is reported elsewhere.<sup>12</sup>

### Heat Treatments

The crude pitch (about 400 g) was heat treated in a 1,000 mL Kettle vessel using an electric mantle. The

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pitch was homogenized using a mechanical stirrer, and the bulk temperature was measured. Three processes were employed: (process 1) thermal treatment at 250°C for 2, 4 and 8 hours; (process 2) thermal treatment in the presence of AlCl<sub>3</sub> (pitch : AlCl<sub>3</sub> = 30:1 w/w) at 150°C for 4 h, with AlCl<sub>3</sub> slowly added to the pitch after softening; and (process 3) thermal treatment at water reflux temperature (typical of pre-polymer preparation in resol phenolic resin synthesis<sup>13,14</sup>) in the presence of paraformaldehyde [(CH<sub>2</sub>O)<sub>n</sub>] partially solubilized in an alkaline solution of NaOH. In process 3, although water does not solubilize (CH<sub>2</sub>O)<sub>n</sub> completely, it greatly improves the reagent diffusibility into the pitch. Under heating, paraformaldehyde gradually releases CH<sub>2</sub>O into the medium. The pitch : (CH<sub>2</sub>O)<sub>n</sub> : NaOH ratio was 75:12:1 w/w.

Air atmosphere was used in all the three processes. In processes 1 and 2, the kettle vessel was connected to a vigreux column, but in process 3 a reflux condenser was used, and water was eliminated by switching off the reflux system for the last 30 min.

### Solid State <sup>13</sup>C-NMR

Although solid state <sup>13</sup>C-NMR involving cross polarization (CP) has been largely employed to analyze carbonaceous materials and precursors (pitches, coal, peat, cokes, etc), we used slower technique based on the direct polarization (DP) of <sup>13</sup>C nuclei, also called single pulse experiments, which have been demonstrated to be more convenient for quantitative analyses.<sup>15</sup> The spectra were obtained in a Varian INOVA-300 spectrometer at 75.4 MHz with a RT probe adequate for solid state analyses. The rotor (7 mm, zirconia) was spun at 5.9 kHz around the magic angle, 54° 44', in order to solve the problems resulting from chemical shift anisotropy (MAS method). The spectra were acquired using a spectral width of 50 kHz, an acquisition time of 0.05 s, a pulse of 90° (6 μs), a delay time of 100 s, 400–2300 scans per spectrum, and high-power proton decoupling. Chemical shifts were compared to the reference methyl carbon resonance of solid hexamethyl benzene (17.3 ppm relative to liquid TMS).

### Fourier Transform Infrared Spectroscopy (FTIR)

Infrared analyses were carried out in a Perkin-Elmer FTIR SPECTRUM 1000 spectrometer. Samples were prepared as KBr pellets with a pitch concentration of 1% (w/w).

The spectra of pitches obtained under different pretreatment conditions presented many similar aspects, although it was not possible to analyze them visually. However, the baseline method<sup>16–18</sup> provided important conclusions. For this purpose, the relative absorption intensities ( $A_i/A_{1500\text{cm}^{-1}}$ ) of more significant ab-

sorptions were calculated as the ratio between the height of the respective absorption and that of one assumed to be constant. Since biopitch polymerization basically involves reactions at aliphatic side chains, it seemed reasonable to consider the absorption of an aromatic C=C stretch at 1500 cm<sup>-1</sup> to be approximately constant. Great care was taken to follow exactly the same criteria in delineating the baseline for a given absorption in the spectra of different samples.

### Elemental Analysis

The samples were analyzed in a Perkin-Elmer 2400 elemental analyzer to determine carbon, hydrogen, and nitrogen contents. The oxygen content was calculated by difference, taking the ash content into account.

### Coke Yield

The coke yields at 650°C were determined from thermogravimetric (TG) curves obtained in a Shimadzu TGA-50 TG analyzer. Basically, the ground samples (about 5 mg) were weighed into a platinum pan, placed into the TG cell and heated at 10°C/min under a dynamic nitrogen atmosphere (150 mL/min).

### Softening Point (SP)

SP values were determined using the "ring and ball method," following the ASTM D2398-73 standard test. In accordance with the norm, the tests were carried out in duplicate. If the measurements presented a difference larger than 1°C, the analyses were repeated.

### Gel Permeation Chromatography (GPC)

GPC analyses were used to determine the weight-average molar masses ( $M_w$ ) of the soluble fraction of pitches in tetrahydrofuran (THF). Analyses were carried out in a Shimadzu LC-10AD liquid chromatographer coupled with a Shimadzu UV-VIS SPD-10AV detector at 254 nm. The elution was carried out in THF at 30°C and a flow rate of 1 mL/min, using two coupled columns of polystyrene-divinyl benzene gel (Shim-pack GPC-8025 and Shim-pack 803). Injections of 20 μL were made with the samples dissolved in the eluent (2 mg/mL). The calibration curve was built using polystyrene standards

### Acetone Insoluble Content (AI)

AI was determined according to the DIN 53.700 norm. Powdered samples (60 mesh) were wrapped in a quantitative filter paper and extracted with acetone in a soxhlet extractor until complete extraction of the soluble fraction occurred. Subsequently, acetone was

TABLE I  
Characterization of Crude and Pretreated *Eucalyptus* Tar Pitches

Pretreatment conditions								Elemental analysis				
T (°C)	t (h)	External agent	SP (°C)	AI (%)	Coke yield (%)	$M_w/10^3$ (g/mol)	Ash content (%)	C (%)	H (%)	O (%)	H/C	O/C
	Crude Pitch		76	1	33	2.1	1.3	68.0	6.3	24.4	1.1	0.27
250	2	—	97	19	36	4.1	1.2	70.0	5.9	22.9	1.0	0.25
250	4	—	112	29	41	5.4	1.1	71.6	6.0	21.3	1.0	0.22
250	8	—	<i>a</i>	41	50	6.2	1.2	73.8	6.2	18.8	1.0	0.19
150	4	AlCl <sub>3</sub>	103	16	45	4.0	2.4	69.8	6.2	21.6	1.1	0.23
100	4	CH <sub>2</sub> O	134	22	39	3.7	1.5	68.5	6.5	23.4	1.1	0.26

<sup>a</sup> Pitch pretreated for 8 h at 250°C lost flow properties.

evaporated, the residue weighed and compared to the initial mass. The tests were carried out in triplicate. If the measurements fell in a range larger than 2%, they were repeated.

### Ash Content

The pitch ash content was determined following the ISO-DIS 8006 norm, in which the residual mass after treatment at 700°C in air atmosphere for about 2 h is compared to the initial mass. The measurements were carried out in triplicate and they did not differ by more than 0.2%.

## RESULTS AND DISCUSSION

Crude and pretreated pitches are characterized in Table I. The  $M_w$  values measured by GPC show that all three processes employed gave rise to pitch polymerization. However, it is necessary to point out that these values should be considered with awareness that the ideal separation mechanism of GPC only takes place

in the case of compounds with similar structure and functionality. Because the pitch sample consists of a heterogeneous and complex mixture of compounds with different structures and functional groups, they do not fractionate in terms of only molecular size; rather, several effects such as adsorption, association, and others influence the results. Further, it is not possible to have a standard that efficiently represents such a complex structure. Therefore, the  $M_w$  measurements presented in Table I are not absolute, but only comparative values for pitches with the same origin submitted to different pre-treatments.

The pitch pretreated for 8 h at 250°C lost the flow properties.

### Treatments Without External Agents

The <sup>13</sup>C-NMR spectra of the crude pitch and that pretreated at 250°C for 8 h are presented in Figure 1. The spectra display pronounced signals around 0–47, 47–60, 108–140, and 140–163 ppm relative to alkyl, methoxyl, non-oxygenated aromatic, and oxygenated aromatic carbons, respectively, which are remnants of guaiacyl and siringyl based structures common to lignin (Fig. 2). Furthermore, there are signals around 60–88 ppm, remnants of alcoholic and/or etheric carbons (except for methoxyl ones) in lignin side chains, as well as around 163–188 ppm relative to carboxyl groups representative of partially oxidized lignin

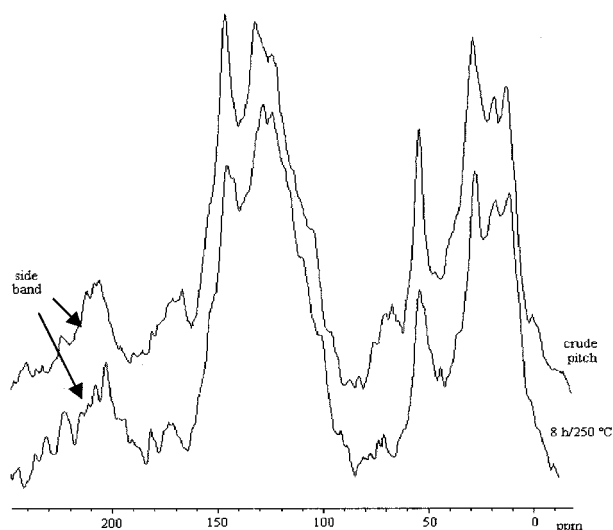


Figure 1 Solid state <sup>13</sup>C-NMR spectra for crude *Eucalyptus* tar pitch and that pretreated at 250°C for 8 h.

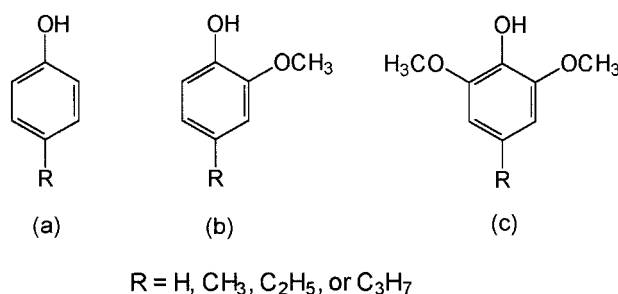


Figure 2 Derivative structures of (a) phenol, (b) guaiacyl and (c) siringyl.

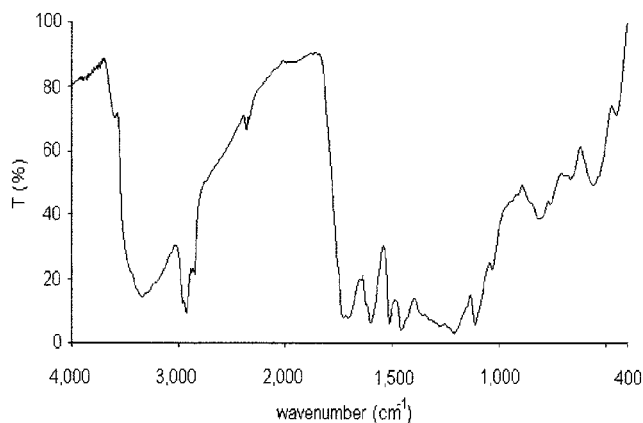


Figure 3 FTIR spectrum for crude *Eucalyptus* tar pitch.

structures. It is also important to point out the negligible presence of cellulose components in *Eucalyptus* tar pitches. The main  $^{13}\text{C}$ -NMR signal for cellulose occurs around 74 ppm,<sup>19</sup> at which point there is not any detectable resonance in the present spectra.

The rotor spinning speed in MAS  $^{13}\text{C}$ -NMR analyses was not high enough to eliminate the chemical shift anisotropy completely, and the speed was not further increased due to technical limitations. As a result, the spectra presented first order aromatic spinning side bands centered around 212 and 46 ppm. Therefore, nothing can be said in this work about the presence of carbonylic carbons, because there is a spinning side band at the corresponding chemical shift.

Although we know that the aromatic static side bands are not always symmetric around their center of mass,<sup>20</sup> the total integrated intensity of the band at 212 ppm was subtracted from the signal of the aliphatic carbons, and added twofold to the signal of aromatic carbons. However, as the signal of the supposed carbonyl carbons may overlap the spinning side band around 212 ppm, the results obtained may not be absolutely quantitatively reliable. Namely, the signal intensity of eventual carbonyl carbons would have

been inappropriately added twofold to the aromatic carbon signal. Therefore, the calculated aromaticities may have been overestimated for all samples. However, the results can be taken as approximate values, and considered perfectly useful for the sake of comparison since all samples have similar composition and were analyzed by the same method.

After polymerization, there was a strong reduction of the signals in the range 47–88 ppm (alkoxyl carbons), as well as a smaller reduction in the signals between 0 and 40 ppm (methyl and polymethylene groups). Regarding the aromatic region, we verified a reduction of the signal at about 140–163 ppm (aromatic oxygenated carbons) relative to those between 108–140 ppm (aromatic non-oxygenated carbons). Furthermore, the signal at 163–188 ppm (carboxylic groups) was significantly reduced.

The pitches studied gave rise to very complex FTIR spectra (Fig. 3). The spectra of crude and pre-treated pitches were very similar, although it was not possible to analyze them visually. However, the baseline method (Fig. 4) clearly reveals a gradual reduction in all of the relative absorptions of aliphatic functional groups with increasing treatment time. This reduction was more pronounced for absorptions at 1275–1200 and 1115–1110  $\text{cm}^{-1}$ , which involve stretches of carboxyl and/or carbonyl, phenol, alcohol, aliphatic and aromatic ether groups. Therefore, FTIR results perfectly match those of NMR.

The literature refers to the loss of alkoxyl carbons during treatment of similar materials (fossil wood,<sup>21</sup> peat<sup>22</sup>) at temperatures lower than 300°C. Rossinskaya and Domburgs<sup>23</sup> reported that at temperatures around 200°C heterolytic-hydrolytic cleavages can take place in the breaking up of  $\text{O}-\text{C}_{\text{aliph}}$  bonds in aryl-alkyl ethers, which are favored by the formation of phenoxy-like anions stabilized by negative charge delocalization along the aromatic ring, while at 250°C homolytic cleavage takes place. Antal, Jr.<sup>24</sup> reported

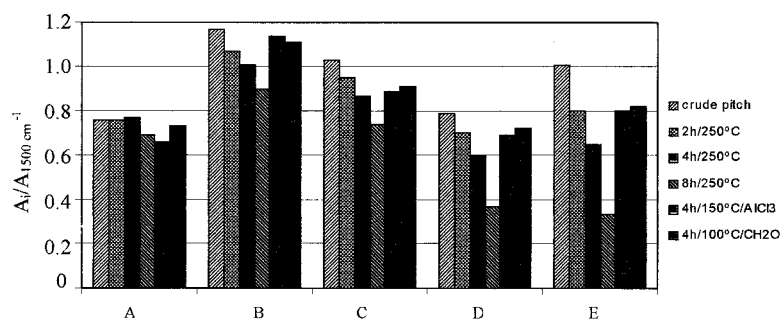
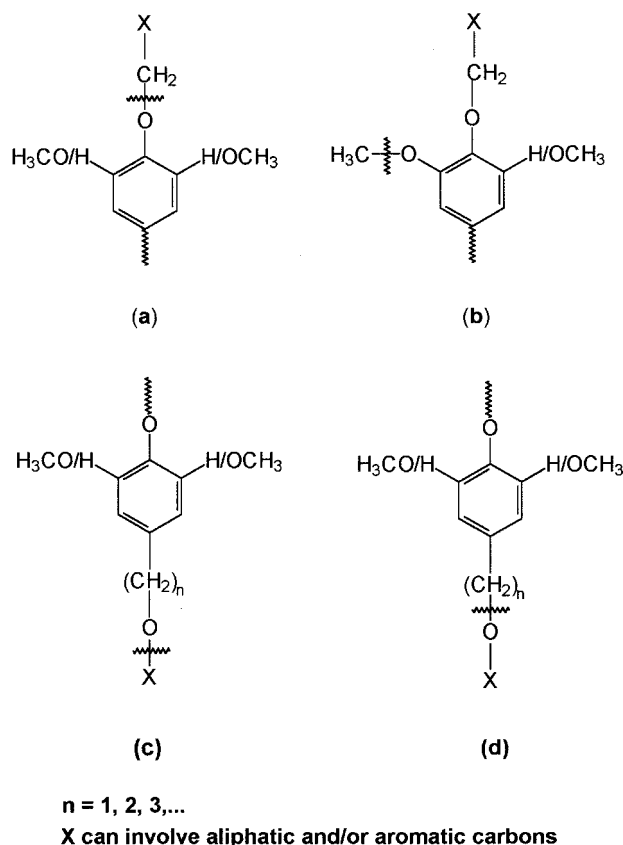


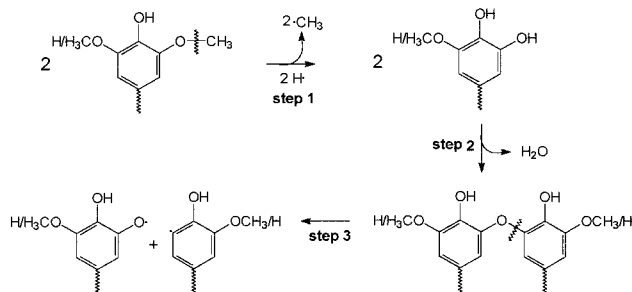
Figure 4 Relative absorptions ( $A_i/A_{1500} \text{ cm}^{-1}$ ) in FTIR analyses (baseline method): (A) 2940–2835  $\text{cm}^{-1}$ :  $\text{CH}_2$  and  $\text{CH}_3$  stretch; (B) 1740–1700  $\text{cm}^{-1}$ :  $\text{C}=\text{O}$  stretch; (C) 1460–1440  $\text{cm}^{-1}$ :  $\text{CH}_2$  and  $\text{CH}_3$  bending; (D) 1275–1200  $\text{cm}^{-1}$ :  $\text{C}-\text{C}(=\text{O})\text{O}/\text{C}$  stretch,  $\text{C}-\text{O}$  stretch in phenols, and/or asymmetric  $\text{C}-\text{O}-\text{C}$  stretch in alkyl aryl ethers; (E) 1115–1110  $\text{cm}^{-1}$ : asymmetric  $\text{C}-\text{O}-\text{C}$  stretch of aliphatic ethers, and/or  $\text{C}-\text{O}$  stretch in secondary alcohols.



**Figure 5** Cleavages during *Eucalyptus* tar pitch polymerization.

that pyrolysis of lignin-like structures at moderate temperatures involves mainly homolytic cleavages.

The abovementioned works and the results obtained in the present investigation led to the conclusion that polymerization of biopitches at 250°C involves mainly pyrolytic homolytic cleavage of C—O bonds. While side chains are released, the heavier fragments rich in aromatic rings recombine to form larger and larger molecules. Figure 5 illustrates the breaking of some probable bonds. The instances in which the X-group shown in Figures 5(a, c, and d) is



**Figure 6** Mechanism proposed to explain the reduction of the ratio of oxygenated to non-oxygenated aromatic carbons (based on ref. 21).

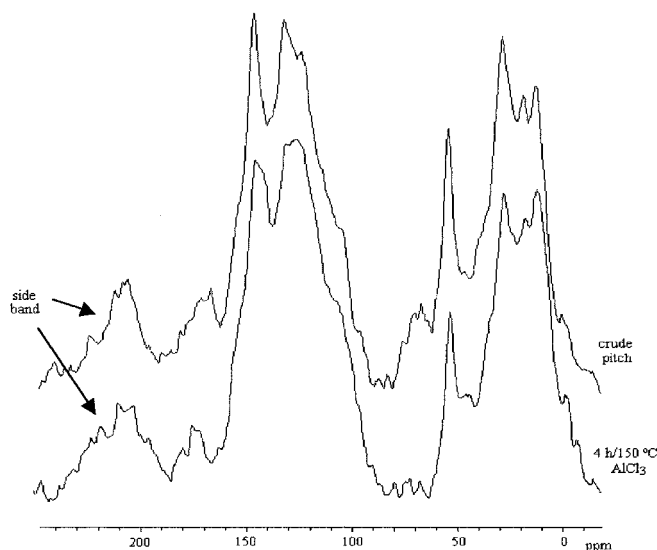
**TABLE II**  
 $^{13}\text{C}$ -NMR Signal Intensities for Crude and Pretreated *Eucalyptus* Tar Pitches

Treatment conditions			Relative intensity (%)		
$T$ (°C)	$t$ (h)	External agent	Aliphatic saturated	Aromatic	Carboxylic
Crude Pitch			34	61	5
250	8	—	28	70	2
150	4	$\text{AlCl}_3$	29	68	3
100	4	$\text{CH}_2\text{O}$	30	65	5

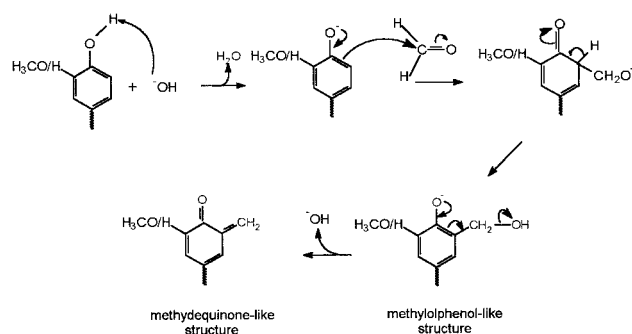
an aliphatic chain explain the reduction of the NMR signals relative to alkyl carbons at 0–40 ppm.

Decarboxylation reactions are also reported in the literature for the studied temperature range, according to the release of  $\text{CO}_2$ , as identified by gas chromatography methods.<sup>21</sup> This is in accord with the reduction verified in the present work regarding the NMR signal at 163–168 ppm.

The reduction in the ratio of oxygenated to non-oxygenated aromatic carbons verified in the  $^{13}\text{C}$ -NMR spectra can be explained based on a mechanism proposed by Behar and Hatcher<sup>21</sup> for the artificial coalification of fossil woods. The demethylation of the pitch guaiacyl and siringyl units would lead to the formation of catechol-like molecules (step 1 in Fig. 6). These molecules would undergo condensation (step 2) with the formation of an ether bridge. The resulting unstable structures<sup>25</sup> would be degraded (step 3) to yield both catechol-like and phenol-like radicals. Besides the changes in  $^{13}\text{C}$ -NMR spectra, Behar and Hatcher supported their proposal by means of the increasing content of catechol- and phenol-like mole-



**Figure 7** Solid state  $^{13}\text{C}$ -NMR spectra for crude *Eucalyptus* tar pitch and that pretreated for 4 h at 150°C with  $\text{AlCl}_3$ .



**Figure 8** Mechanism for insertion of methylol groups in *Eucalyptus* tar pitch phenolic rings and resultant structures.

cules in the coalification residue, as verified by analytical pyrolysis.

The results so far presented show that the high reactivity of biopitches is explained by their high content of oxygenated side chains. Due to their poor oxygen content, fossil pitches can be pretreated at temperatures as high as 440°C to yield mesophasic structures,<sup>5,26,27</sup> while biopitches undergo cracking at around 300°C.

The loss of aliphatic side chains during pretreatment is reflected by increases in pitch carbon content (Table I) and aromaticity (Table II). The former occurs because the side chains carry a substantial proportion of hydrogen and oxygen content.

Despite the higher aromaticity of more polymerized pitches, they present a higher hexane soluble fraction, which is composed of mainly aliphatic compounds. The crude pitch and that pretreated at 250°C for 4 and 8 h present hexane soluble fractions of 1, 4, and 8%, respectively, as determined in triplicate using a soxhlet extractor. These results show that a large fraction of aliphatic side chains removed from the aromatic rings during the pretreatment remained trapped in the system due to reflux. Only the fraction composed of the smaller and more volatile molecules would have been released from the system.

### Treatment with AlCl<sub>3</sub>

In a previous work,<sup>12</sup> we demonstrated that polymerization of *Eucalyptus* tar pitches is effective during

thermal treatments only if temperatures above about 220°C are used. However, Table I shows that considerable polymerization took place at 150°C in the presence of AlCl<sub>3</sub>, an acid catalyst<sup>28</sup> employed during carbonization of aromatic hydrocarbons<sup>29,30</sup> and to modify ethylene tar pitch in order to favor mesophase growth.<sup>31</sup>

The biopitch pretreatment in the presence of AlCl<sub>3</sub> gave rise to a reduction in the relative absorption of aliphatic functional groups (Fig. 4) and an increase in aromaticity (Table II), showing that aliphatic side chains had been released. The changes in the <sup>13</sup>C-NMR spectra (Fig. 7) are basically the same as those described for heat treatments at 250°C without external agents, revealing that, once more, carboxyl and alkoxy groups reacted during pretreatment. Accordingly, the pitch carbon content increased (Table I).

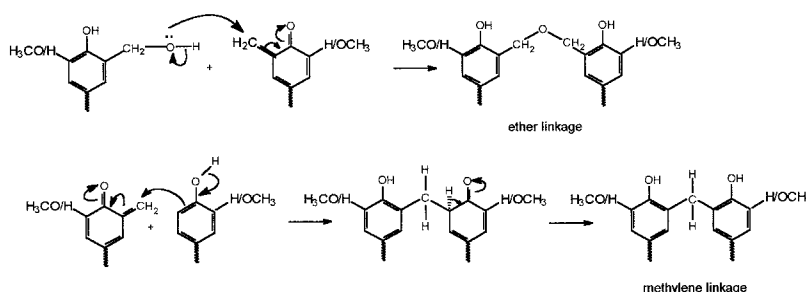
Taking into account these results, we are led to suppose that AlCl<sub>3</sub> acts as a Lewis acid, complexing to oxygen atoms through their pairs of non-bonding electrons, thus weakening O—C bonds and favoring their cleavage under heating. Although the broken bonds were the same as proposed for thermal polymerization alone, in this case the cleavages would have been preferentially heterolytic.

### Treatment with Formaldehyde

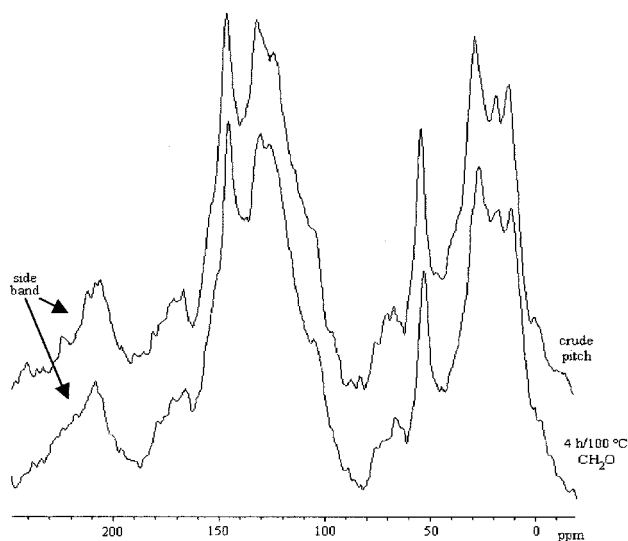
As the structure of biopitches is rich in phenolic rings, treatment with formaldehyde in an alkaline medium was carried out with the assumption that it would act as a polymerizing agent, as it does in the formation of resol phenolic resins.<sup>13,14</sup> Firstly, formaldehyde would be added to the activated *ortho* and *para* positions of phenolic rings by means of electrophilic attack,<sup>32</sup> thereby forming methylolphenol-like or methoxyquinone-like structures (Fig. 8).<sup>14</sup>

Next, the crosslinking reactions shown in Figure 9 would take place in the reaction medium, forming ether linkages or methylene bridges, as in phenolic resin synthesis.

The results (Table I) show that a temperature of 100°C was sufficient to promote pitch polymerization in the presence of formaldehyde in an alkaline medium. The resulting material presented a SP higher



**Figure 9** Crosslinking of pitch molecules after reaction with formaldehyde according to resol phenolic resin synthesis.



**Figure 10** Solid state  $^{13}\text{C}$ -NMR spectra for crude *Eucalyptus* tar pitch and that pretreated for 4 h at  $100^\circ\text{C}$  with formaldehyde in alkaline medium.

even than that obtained from thermal treatment alone at  $250^\circ\text{C}$  for the same period of time (4 h).

According to the reactions described in Figures 8 and 9, an aromaticity decrease (NMR analyses), and increases in the relative absorption intensities at  $2940\text{--}2835$ ,  $1460\text{--}1440$ , and  $1115\text{--}1110\text{ cm}^{-1}$  (FTIR analyses) would be expected. However, an aromaticity increase (Table II) and a reduction of all relative absorption intensities of aliphatic functional groups took place (Fig. 4), once more making clear that the oxygenated side chains in pitch phenolic rings gave rise to additional reactions. In all likelihood, the methydequinone-like structures (Fig. 8) undergo attacks from other nucleophilic species present in the system, such as carboxyl and ether groups; these reactions could involve the release of aliphatic chains.

Only the signals of non-oxygenated carbons ( $108\text{--}140\text{ ppm}$ ) underwent substantial changes according to the aromatic carbon region in NMR spectra (Fig. 10). Namely, the signal intensity of substituted carbons in the *ortho* position of phenolic rings (around  $125\text{ ppm}$ ) underwent a pronounced increase. These results are in accord with the reactions proposed in Figures 8 and 9.

### Coke Yield

Figure 11 shows that pitch aromaticity is proportional to coke yield, which reflects the disposition of aromatic rings to survive carbonization to yield carbon structures. Therefore, we can conclude that the pitch obtained in the presence of formaldehyde underwent a low coke yield increase, compared to the large enhancement of its SP (Table I), because its aromaticity did not rise pronouncedly (Table II). On the other

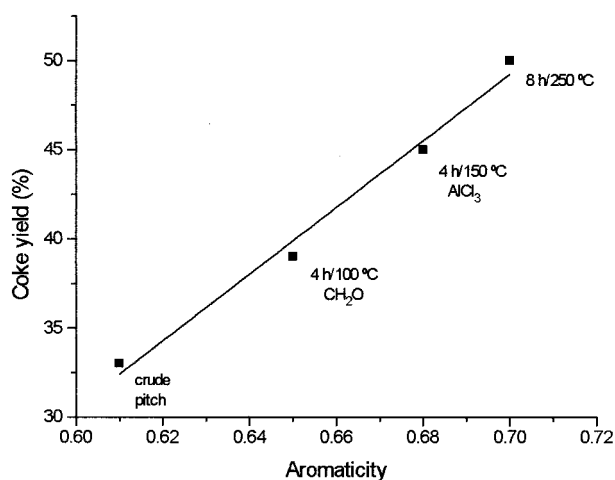
hand, the large coke yield increase experienced by the pitch pretreated with  $\text{AlCl}_3$  reflects its large aromaticity increase. The low dispersion of the plot of aromaticity against coke yield ( $R = 0.993$ ) lends credence to the  $^{13}\text{C}$ -NMR results.

### CONCLUSIONS

The results of solid state  $^{13}\text{C}$ -NMR, FTIR, and elemental analysis show that thermal polymerization of *Eucalyptus* tar pitches involves the breaking of  $\text{C}\text{--}\text{O}$  bonds. While side chains are released, fragments rich in aromatic rings react to form larger molecules. Although thermal treatments without external agents give rise to effective polymerization only at temperatures above  $220^\circ\text{C}$ , the presence of  $\text{AlCl}_3$  makes it possible at  $150^\circ\text{C}$ .  $\text{AlCl}_3$  acts as a Lewis acid, complexing to oxygen atoms, thereby weakening  $\text{O}\text{--}\text{C}$  bonds and favoring their breaking up under heating. Another successful alternative employed for the pretreatment of biopitches was the use of formaldehyde as a polymerizing agent, as in the production of resol phenolic resins. In this case,  $100^\circ\text{C}$  was sufficient to initiate polymerization. Methylol groups were added to activated *ortho* and *para* positions in pitch phenolic rings, promoting subsequent condensation reactions.

The pronounced increases in SP values that follow pitch polymerization are important because they facilitate post-spinning pitch thermal stabilization during carbon fiber production.<sup>33</sup> In addition, polymerization is followed by aromaticity increase, which is important to raise pitch coke yield and reduce excessive weight loss during stabilization and carbonization of the filaments, contributing to the prevention of crack formation in the fibers.

The use of additives such as  $\text{AlCl}_3$  and  $\text{CH}_2\text{O}$  has been shown to be appropriate for cases in which lower



**Figure 11** Coke yield vs. aromaticity for *Eucalyptus* tar pitches.

polymerization temperatures are required, although more detailed research on the subject is needed. The use of  $\text{AlCl}_3$  should be undertaken with special caution, because the difficulties of removing it after treatment can constitute a drawback for pitch processing and for the properties of the final material.

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