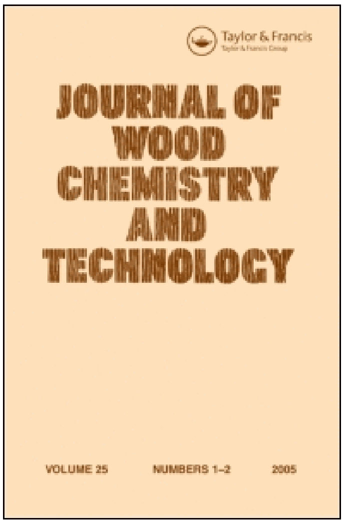

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SOLID-STATE ^{13}C NMR QUANTITATIVE STUDY OF *EUCALYPTUS* TAR PITCHES

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ABSTRACT

Solid-state ^{13}C NMR has been important to overcome analysis difficulties arising from the low solubility of carbonaceous materials. Its use provides accurate information about these materials. In this work, resonance techniques involving magic angle spinning with cross-polarisation (CP/MAS) or single pulse (SP/MAS) are used in conjunction with other analysis tools to quantitatively characterise *Eucalyptus* tar pitches and to follow their polymerisation reactions. The results showed that SP/MAS technique is more suitable for quantitative analyses, and that the pitches have a high content of aliphatic and oxygenated carbons. Moreover, they underwent thermal polymerisation, and the presence of $AlCl_3$ or formaldehyde permitted the use of lower treatment temperatures.

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The polymerisation reactions were followed by aromaticity enhancements, giving rise to higher coke yields.

INTRODUCTION

Studies from all over the world have pointed to fossil pitches as having one of the greatest potentialities as precursors of advanced carbonaceous materials (ACM). ACM will play an important role in the XXI century as an abundant and cheap raw material from which it is possible to obtain materials with particular properties and a wide number of applications.[1–3]

Thereby, there is a clear need to obtain more accurate information about the chemical composition of carbonaceous materials and their precursors (coals, pitches, cokes, etc) to better understand their behaviour under thermal treatments. However, the low solubility of these materials has always been a limitation to NMR analyses and, even the soluble fractions give rise to spectra with low signal-to-noise ratio. The development of solid-state ^{13}C NMR in the last 25 years has contributed to overcome this difficulty.[4–16]

Techniques like cross-polarisation and magic-angle spinning (CP/MAS) are frequently used to obtain high-resolution solid-state ^{13}C NMR spectra.[4–8] Magic-angle spinning is used to solve the problems resulting from chemical shift anisotropy. The indirect excitation of ^{13}C nuclei through the dipolar interaction with protons enhances signal response by a theoretical factor of about 4 when compared to the direct excitation. Moreover, in CP experiments, one deals with the spin-lattice relaxation time of protons, generally smaller than those of carbon nuclei, which allows the use of shorter delay times.[17] Therefore, in CP/MAS we can obtain a good signal-to-noise (S/N) ratio in a short period of time.

However, the efficiency of CP depends on the magnitude of the C–H dipolar interaction. Differences in the efficiency of magnetisation transfer from protons to chemically distinct ^{13}C nuclei result in quantitatively unreliable CP/MAS spectra. Furthermore, the presence of *para* and/or ferromagnetic centres can make some carbons undetectable due to their proximity to these centres, which leads to a strong reduction of the rotating-frame proton longitudinal relaxation time ($T_{1\rho}$) and makes the transference of magnetisation improbable.[10] Therefore, the concentration of non-protonated aromatic carbons (far from protons) are usually underestimated, mainly for highly aromatic compounds.[10–14] Maroto-Valer et al. found that aromaticities estimated by CP are about 5–10% smaller than those estimated in experiments with direct polarisation (also called single pulse experiments).[11,12] Then, despite being more time consuming because of the high spin-lattice relaxation time (T_1) values of carbons in this type of material and having smaller S/N ratio, the technique using single pulse and magic-angle spinning (SP/MAS) is more efficient to obtain ^{13}C NMR quantitative analyses of carbonaceous materials.

In this work, solid-state ^{13}C NMR is used in conjunction with infrared absorption spectroscopy and elemental analysis to characterise *Eucalyptus* tar pitches and to follow their polymerisation reactions. Polymerisation takes place in the pitch pre-treatment, which is the first step of the process to obtain carbonaceous materials.

The pitches studied are distillation residues (about 50% m/m) of the *Eucalyptus* tar, a by-product of charcoal production in Brazil. This charcoal is largely used (about 6.8 million ton/year[18]) by the steel making industries. The development of bio-pitch applications is important to stimulate the use of biomass, a renewable energy source, which in turn can contribute to reduce the green house effect, thereby answering the appeals for environment preservation.[19]

EXPERIMENTAL

Samples Preparation

The precursor pitch was obtained by vacuum distillation of *Eucalyptus* tar recovered from industrial masonry ovens with a maximum pyrolysis temperature of about 400–500°C. The cut temperature for tar distillation was 180°C at a pressure of 30–38 mmHg.

Heat Treatments

The *Eucalyptus* tar pitch was treated in a Kettle vessel using a mechanical stirrer under different conditions:

- Process 1: thermal treatment at 250°C for 2, 4 and 8 h.
- Process 2: thermal treatment at 150°C for 4 h in the presence of $AlCl_3$ (pitch : $AlCl_3$ proportion was 30 : 1 w/w).
- Process 3: thermal treatment at 100°C in the presence of an alkaline solution of paraformaldehyde [$(CH_2O)_n$] so that CH_2O is released in the medium during heating. The pitch : $(CH_2O)_n$: NaOH proportion was 75 : 1 : 12 w/w.

In Process 1, the kettle vessel was connected to a vigreux column, while in Processes 2 and 3, a reflux condenser was used. For Process 3, water was eliminated by switching off the reflux system during the last 30 min.

Solid-State ^{13}C NMR

Solid-state ^{13}C NMR analyses were carried out in a Varian INOVA-300 spectrometer at 75.4 MHz using a RT CP/MAS probe. The rotor (7 mm-zirconia) was spun at 5.9 kHz at the magic-angle (54°74′). The spectra were acquired using a spectral width of 50 kHz, acquisition time of 0.05 s, pulse of 90° (4.3 μs) and high power proton decoupling. Chemical shifts were referenced to the methyl groups of hexamethyl benzene (17.3 ppm relative to liquid TMS). Further experimental conditions were:

a) CP/MAS experiments: contact time ranging from 20 to 4000 μs, delay time of 4 s and 500 scans per spectrum.

b) CP/MAS-NQS experiments: in this case it was used a pulse sequence called "Non-Quartenary Suppression (NQS)" (also called dipolar dephasing),[15,16] with decoupler window of 60 μs, contact time of 4000 μs, delay time of 4 s, and acquisition of 3000 scans per spectrum.

c) SP/MAS experiments: delay time of 100 s and 400−2300 scans per spectrum.

Fourier Transform Infrared Spectroscopy (FTIR)

Infrared analysis was carried out in a Perkin Elmer FTIR SPECTRUM 1000 spectrometer. Samples were prepared as KBr pellets with a pitch concentration of 1%.

To follow the polymerisation by infrared spectroscopy, a baseline method[20] was used, where the relative intensities of the absorptions are calculated in relation to an absorption assumed constant. In this work, the latter was taken as the absorption at 1500 cm^{-1} (aromatic C–C stretch).

Gel Permeation Chromatography (GPC)

GPC analysis was used to determine the molar mass distribution and the weight-average molar masses ($\overline{M}w$) of the soluble fraction of pitch in THF. Analyses were carried out in a Shimadzu LC-10AD Liquid Cromatographer coupled with a Shimadzu UV-VIS SPD-10AV Detector at 254 nm and a Shimadzu C-R7A Chromatopac Integrator with software for GPC calculations. The experiments were based on techniques developed for lignin analyses.[21] 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 GPC-803). Injections of 20 μL were made with the samples dissolved in the eluant (2 mg/mL). The calibration curve was determined using polystyrene standards.

Elemental Analyses

The samples were analysed in a Perkin Elmer 2400 elemental analyser to determine carbon, hydrogen, and nitrogen content. The oxygen content was determined by difference and taking the ash content into account (around 1%).

Coke Yield

The coke yield at 650°C was determined by means of thermogravimetric analyses in a Shimadzu TGA-50 thermogravimetric analyser. 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 nitrogen dynamic atmosphere (150 mL/min).

RESULTS AND DISCUSSIONS

Pitch Characterisation

In ^{13}C NMR spectra using CP/MAS-NQS (Figure 1), only methyl and quaternary carbon resonances are shown.[15,16] This technique was useful especially to assign some signals such as aliphatic methyls, oxy-methyls, and non-protonated aromatic carbons.

The signals in ^{13}C NMR spectra for *Eucalyptus* tar pitches were divided in 9 groups (Figure 2 and Table 1) based in a method developed by Trewhella et al.[8] to study quantitatively Green River oil shale kerogen. The results showed that, in contrast to fossil pitches, *Eucalyptus* tar pitches have a high content of oxygenated and aliphatic carbons, which is in accordance with the high O/C and H/C ratios verified by elemental analysis (Table 2). Carbons pertaining to aliphatic ethers and/or alcohols, aromatic ethers and/or phenols, esters, ketones, and aromatic and

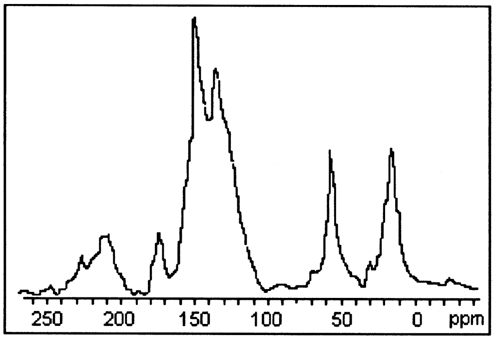


Figure 1. Typical solid-state ^{13}C NMR spectrum using CP/MAS-NQS technique for crude *Eucalyptus* tar pitches.

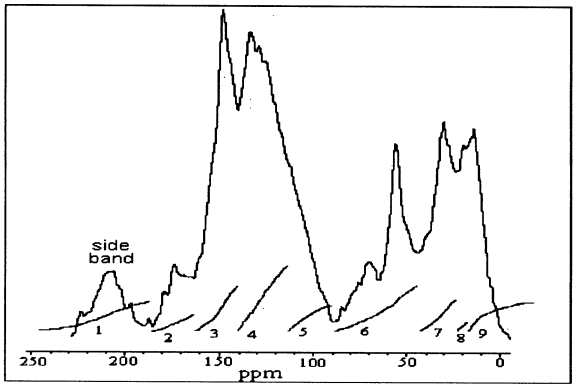
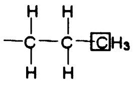
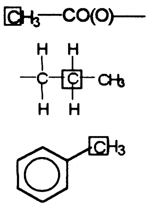
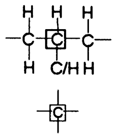
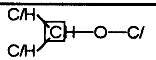
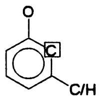
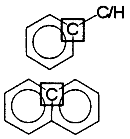
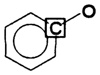
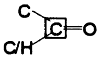


Figure 2. Typical solid-state ^{13}C NMR spectrum using SP/MAS for *Eucalyptus* tar pitches.

aliphatic hydrocarbons were assigned. The aromaticity observed for crude pitch was low (0.61) if compared to those usually observed for fossil pitches.[22,23]

The pitches gave rise to very complex FTIR spectra (Figure 3), in which some absorptions were difficult to precisely assign. Their aspects are similar to those of lignin,[24] being the functional groups basically the same. There are characteristic absorptions of aliphatic and aromatic hydrocarbons, phenols, ethers, esters and ketones. The presence of these groups is in accordance with the high H/C ratios and ^{13}C NMR assignments.

Table 1. List of Carbon Functionalities and Chemical Shifts for *Eucalyptus* Tar Pitches

Region	Group	Functionality	Chemical Shift (ppm)	Signals Intensities (%)	
3	9		15	10.4	33.6
	8		20-23	4.4	
	7		29-50	16.8	
	6		50-70	2.0	
2	5		110-115	6.6	61.2
	4		115-140	34.1	
	3		140-160	20.5	
1	2	$-\boxed{C}OOC/H$	160-185	5.2	5.2
	1		190-230	-	

These results lead to the conclusion that *Eucalyptus* tar pitches have a macromolecular structure constituted of highly substituted and oxygenated interlinked phenolic rings similar to a kind of thermoplastic lignin. Moreover, Figure 4 shows that they have a large molar mass distribution.

Table 2. Results of Elemental Analysis for *Eucalyptus* Tar Pitches

	Treatment Conditions			C	H	O	H/C	O/C
Process	T (°C)	t (h)	External Agent	(%)	(%)	(%)	ratio	ratio
–	Crude pitch			68.0	6.34	24.4	1.12	0.27
1	250	2	–	70.0	5.91	22.9	1.01	0.25
	250	4	–	71.6	5.95	21.3	1.00	0.22
	250	8	–	73.8	6.15	18.8	1.00	0.19
2	150	4	$AlCl_3$	67.1	7.10	23.4	1.12	0.31
3	100	4	CH_2O	68.5	6.54	23.4	1.15	0.26

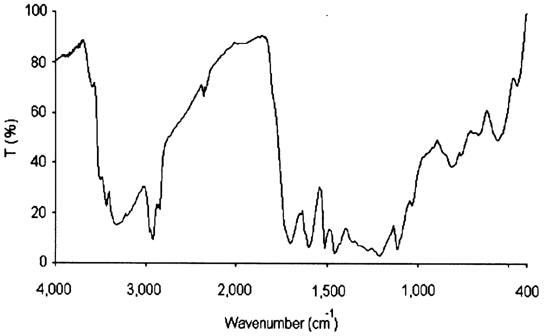


Figure 3. Typical infrared absorption spectrum for *Eucalyptus* tar pitches.

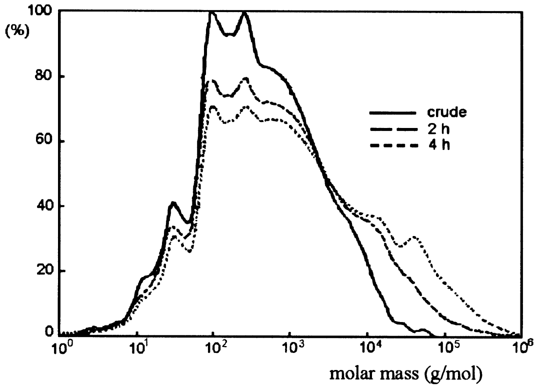


Figure 4. Molar mass distribution curves for *Eucalyptus* tar pitch crude and treated for 2 and 4 h at 250°C.

Polymerisation Assessment

The $\overline{M}w$ values (Table 3) show that all treatments bring about pitch polymerisation. Figure 4 clearly illustrates the reduction in the amount of lower molar mass molecules and the increase in amount of higher molar mass molecules that took place during polymerisation. A similar behaviour was observed for samples treated with $AlCl_3$ and CH_2O.

Thermogravimetric analysis results show that more polymerised pitches have higher thermal stability, which leads to more elevated carbon yields (Table 3).

^{13}C NMR spectra using CP/MAS and varying contact time showed a maximum of polarisation transfer around 1000 μs for all samples (crude and polymerised pitches). This indicates similarities in the stiffness of the average structures of pitches. Moreover, it indicates that 1000 μs is the analysis optimum contact time (t_{cp}), which falls in the range $T_{CH} \ll t_{cp} \ll T_{1\rho}$ (T_{CH} is the cross-relaxation time).[25] On the other hand, the spectra lead to different results depending on the contact time. There was even an inversion in aromatic/aliphatic peak ratios, as illustrated in Figure 5 for crude pitch. This indicates that there are differences in the magnetisation rate for distinct carbons, making the present technique inappropriate for the quantitative analysis of these materials. Consequently, SP/MAS experiments were used to obtain quantitative results instead.

Treatments Without External Agents

Signal intensities in ^{13}C NMR spectra using SP/MAS method are given in Table 4. The results show that pitch treated for 8 h at 250°C underwent a

Table 3. $\overline{M}w$ and Coke Yield for *Eucalyptus* Tar Pitches

Process	Treatment Conditions T (°C)	t (h)	External Agents	$\overline{M}w/10^2$ (g/mol)	Coke Yield (%) at 650°C
–	Crude pitch			2.1	33
1	250	2	–	4.2	36
	250	4	–	5.4	41
	250	8	–	6.2	50
2	150	4	$AlCl_3$	4.0	45
3	100	4	CH_2O	3.7	39

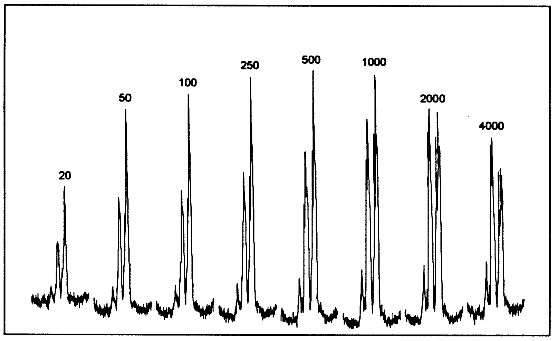


Figure 5. Typical solid-state ^{13}C NMR spectrum using CP/MAS technique (contact times varying from 20 to 4000) μs for *Eucalyptus* tar pitches.

Table 4. Signal Intensities in Solid-State ^{13}C NMR Spectra Using SP/MAS for *Eucalyptus* Tar Pitches

	Signal Intensities (%)			
Group	Crude Pitch	P_{250}	$P_{form.}$	P_{AlCl_3}
9	10.4	10.2	10.0	12.8
8	4.4	6.7	5.0	5.2
7	16.8	8.3	11.2	9.9
6	2.0	2.8	3.3	1.6
Total Region 3	33.6	28.0	29.5	29.5
5	6.6	8.7	5.4	9.3
4	34.1	39.2	36.3	34.6
3	20.5	21.6	23.5	24.0
Total Region 2	61.2	69.5	65.2	67.9
2	5.2	2.5	5.3	2.6
Total Region 1	5.2	2.5	5.3	2.6

P_{250} = sample treated at 250°C for 8 h.
P_{AlCl_3} = sample treated at 150°C for 4 h in the presence of $AlCl_3$.
$P_{form.}$ = sample treated at 100°C for 4 h in the presence of formaldehyde.

loss of aliphatic carbons with a consequent aromaticity enhancement. Temperatures as high as 250°C are sufficient to break covalent links forming free radicals. These species, in turn, react easily to form larger molecules as the aliphatic side chains are released. The ^{13}C NMR results obtained

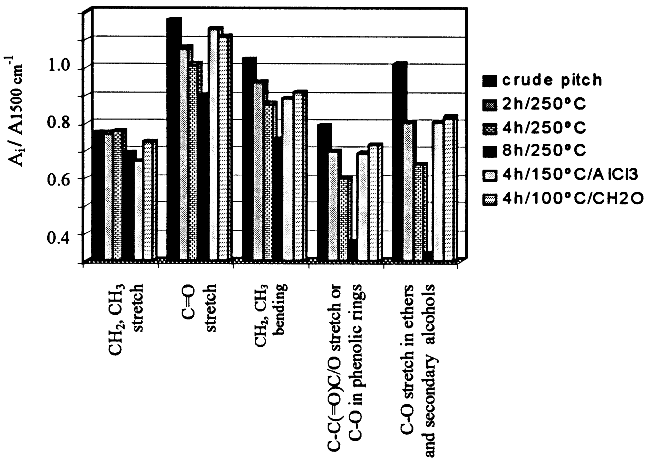


Figure 6. Relative absortivities in FTIR for *Eucalyptus* tar pitches.

separately for each carbon group are not coherent. This probably occurs due to the overlapping of signals with very close chemical shifts.

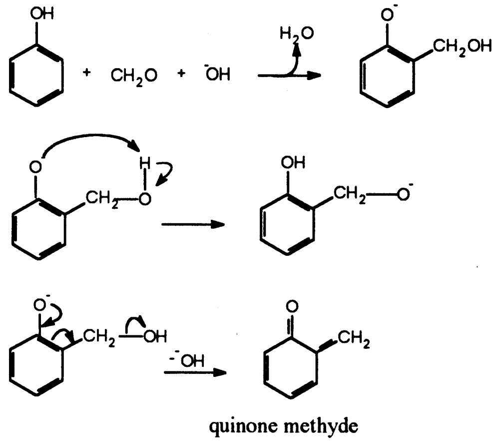
Figure 6 shows that polymerisation in process 1 was followed by a reduction in the relative absortivities of aliphatic groups in FTIR analyses. It is interesting to point out the gradual decrease in these relative absortivities with increasing treatment time, which lends confidence to the results. Further, the elemental analysis showed that there was a reduction in O/C and H/C ratios with polymerisation (Table 2). FTIR and elemental analysis results agree with the increase in aromaticity verified by NMR.

Treatment with $AlCl_3$

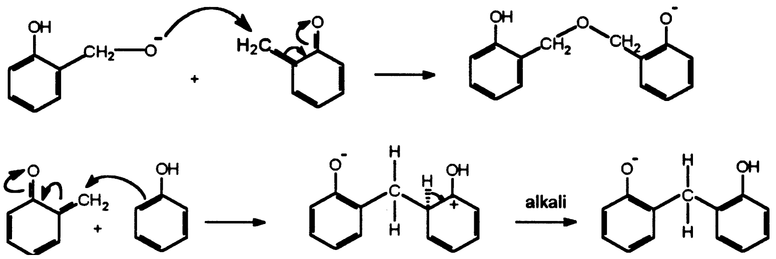
According to a parallel work under development, polymerisation at 150°C does not take place in the absence of external agents. However, considerable polymerisation occurs at this temperature if $AlCl_3$ (an acid catalyst) is used. Again, the reaction promoted aliphatic carbon loss and a consequent aromaticity increase (Table 4 and Figure 6).

Treatment with Formaldehyde

As the structure of biopitches are rich in phenolic rings, the treatment with formaldehyde in alkaline medium was carried out with the expectation that it would act as a polymerising agent as it does in the formation of resol phenolic resins.[26] A similar work was developed with lignins.[27,28] Firstly, the formaldehyde is added to activated *ortho* and *para* positions in the phenolic rings by means of electrophilic attacks, forming mono-, di- and tri-methylolphenols:[29]



After that, the following reactions take place in the reactional medium forming ether linkages or methylene bridges.[27]



The chain grows by additional attachments of formaldehyde to the rings and subsequent condensations.

$\overline{Mw}$ values showed that polymerisation took place at 100°C in the presence of formaldehyde (at this temperature no reaction took place in the absence of external agents). According to the reactions above, it would be expected that polymerisation would lead to an increase in aliphatic carbon content due to methylol insertion. However, ^{13}C NMR and FTIR analyses (Table 4 and Figure 6, respectively) show that, although in a lower extension, aromaticity increase took place again, making clear that the oxygenated side chains in pitch phenolic rings gave rise to additional reactions, which involve the release of aliphatic side chains.

Relationship Between Coke Yield and Aromaticity

According to Figure 7, coke yields are proportional to pitch aromaticities. This lends confidence to ^{13}C NMR–SP/MAS results, since the aromaticities were calculated using them.

CONCLUSIONS

Solid-state ^{13}C NMR using single pulse and magic-angle spinning has been demonstrated to be a powerful tool for quantitative analyses of wood tar pitches. The same cannot be said about the technique involving cross-polarisation instead of single pulses, because it displayed different spectra depending on the contact time, which reflects that there are differences in the magnetisation rate of distinct carbons in the material studied.

SP/MAS results associated with those of FTIR and elemental analysis showed that *Eucalyptus* tar pitches have a high content of aliphatic and

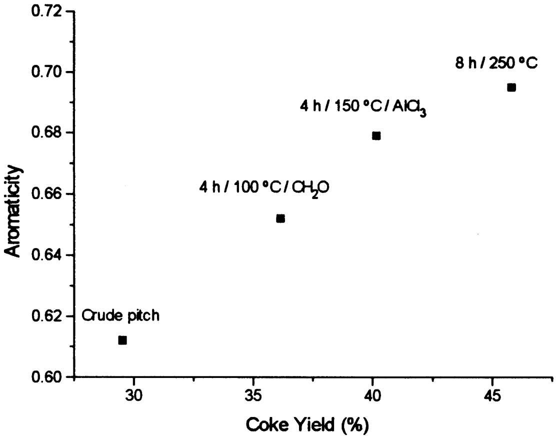


Figure 7. Coke yield vs. aromaticity for *Eucalyptus* tar pitches.

oxygenated carbons. These pitches undergo thermal polymerisation (around 250°C) by means of reactions involving free radical formation. In the presence of $AlCl_3$ or formaldehyde, alternative mechanisms take place which permit the use of lower treatment temperatures. $AlCl_3$ catalyse link cleavages while formaldehyde acts as a polymerising agent promoting condensation reactions. All polymerisations were accompanied by aromaticity enhancements, with consequent increases of material coke yields.

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