

Maria Helena Pereira¹, Luiz de Castro¹ and Ricardo Michel²

INVESTIGATING MOLECULAR MASSES FORMED DURING THE HEAT TREATMENT OF PETROLEUM PITCHES BY MASS SPECTROMETRY

¹ Centro Tecnológico do Exército (CTEX) – Avenida das Americas 28.705 Guaratiba, 23020-470 Rio de Janeiro, Brasil; helena.carbono@gmail.com.br

² Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bloco J 21945-70, Rio de Janeiro, Brasil

Received: December 12, 2012 / Revised: January 23, 2013 / Accepted: February 15, 2013

© Pereira M.-H., de Castro L., Michel R., 2013

Abstract. Mass spectrometry was used to characterize isotropic and anisotropic pitches as well as the parent heavy petroleum oil in order to investigate the molecular mass distributions (MMD) and changes during the heat treatment process. Sample preparation and matrix choice have a strong influence on MMD and results confirmed the oligomeric nature and the increasing molecular sizes as heat treatment proceeds.

Keywords: petroleum pitch, heavy oil, mass spectrometry, MALDI-TOF-MS, polyaromatic hydrocarbon.

1. Introduction

Pitches produced from aromatic heavy oils (decanted oils from fluid catalytic cracking, FCC, a unit of Brazilian refineries) are currently used as raw materials for the manufacture of high-technology products. The production of pitches suitable for such applications involves a thermal treatment with the formation of an intermediate phase (mesophase) [1-3], resulting in an anisotropic material, that is normally described as having an oligomeric nature. The starting heavy oils are already very complex materials. The hundreds of individual compounds vary in molecular structure, size, polarity, functionality, chemical and thermal reactivity. Generally, these compounds belong to distinct classes of hydrocarbons: polyaromatic (PAHs), alkylated compounds, naphthenics and heterocyclics containing oxygen, nitrogen or sulfur [4]. Accordingly, all these starting compounds undergo a great number of reactions and side reactions towards anisotropic pitch. However, the formation of such anisotropy is mainly a consequence of molecular-size-growing reactions during pyrolysis [5].

The high-mass compounds produced self-organize to form the tridimensional structures described in the literature [6].

The characterization of anisotropic pitches in terms of these high-molecular-mass compounds has been extensively studied because of difficulties in the solubilization (even in stronger solvents [7]) required by the main available analytical techniques. These techniques are unable to analyze the insoluble fractions of some anisotropic pitches. Moreover, the solubility is a function not only of molecular size, but also of molecular structure and polar moieties that may be present as the result of the complexity of the petroleum-derived starting materials [8]. Because of this complexity and the variety of possible compounds resulting from the “polymerization” of hundreds of different “monomers”, it is indeed risky to propose average structures, and thus some authors focus on studies of reliable molecular mass values [9].

The determination of such molecular-size values in pitches is important when it comes to further investigation of all the other properties related to it, such as the softening point, anisotropy and rheological properties, all indispensable to the melt spinning and subsequent processing stages in the production of advanced carbon materials, although it has been a difficult task because of the limitations of the analytical instruments. The traditional technique for molecular-size-distribution measurements, gel permeation chromatography (GPC), in addition to the solubility problem, has some other main drawbacks related to the high aromaticity and heterogeneity of the samples such as the secondary retention mechanisms between PAHs and GPC stationary phases and the need for calibration of the GPC system. Some of the first studies of the polymerization reactions were made by R. Greinke, who proposed kinetic

mechanisms based on GPC results [5]. In another paper, the group showed that centrifuged phases of mesophase pitches contain similar molecules with sizes varying from 400 to 2000 Da measured by GPC [10]. Greinke also stated that the polymerization reactions responsible for the molecular growth play a major role in the formation of mesophase, not dealkylation reactions [11]. This molecular growth process would involve primarily molecules in the mass interval 400–800 Da, while molecules with MM above 1100 Da were considered stable [5]. Diefendorf and co-workers stated that volatilization during the heat treatment was more decisive than the polymerization reactions themselves once both isotropic and anisotropic phases contained mesogenic (species capable of forming a liquid-crystal mesophase) and non-mesogenic molecules [12].

A great variety of solvents have been tested over the years, and NMP has been shown to be the most suitable for pitches and related materials [13]. Several investigations have also been conducted with model polyaromatic compounds in GPC, and it has been concluded that, depending on the solvent and system utilized, the elution was not governed by a molecular size and that highly condensed cores were abnormally retained in the columns [14]. Another study showed that polar compounds were shifted to shorter retention times which could equivocally lead to the detection of apparent high-mass materials that were actually aggregates of polar structures [15]. The Herod group studied the effect of the salts addition to the GPC solvent to mitigate the formation of aggregates [16]. Although the amount of work in this area is extensive, solubility issues still remain.

Because of the issues with GPC, mass spectrometric methods (MS) have been investigated within a variety of carbon materials [17, 18]. The most popular mass spectrometric methods for macromolecules are Laser Desorption/Ionization Time of Flight (LDI-TOF) and Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF), the latter referring to the use of a compound (matrix) to absorb laser energy and avoid fragmentation of the analytes, which is particularly interesting when the macromolecule is unstable subjected to laser desorption. The result of this soft ionization is a mass spectrum of the singly-charged molecular ions produced, which is suitable for describing molecular mass (or size) distributions for polymers or petroleum pitches. This mass/size relationship is straightforward for pitches since they are constituted of rigid polyaromatic molecules instead of the random-conformation polymeric chains.

Previous work with a charge-transfer matrix, 7,7,8,8-tetracyanoquinodimethane (TCNQ), showed good results in the analysis of giant insoluble polyaromatic hydrocarbons utilizing a solid sample preparation, without

the need of solubilizing the sample [19]. This matrix has also been successfully applied to pitches [20]. Solvent-free methods are necessary for petroleum derived samples due to the heterogeneity and great variety of compounds of these materials, leading to differential precipitation during the evaporation of solvents commonly used in solvent-based methods. In addition, the choice of matrix is significantly less restrictive.

In the present work LDI and MALDI are evaluated as ionization methods with the objective of investigating the suitability of the technique and the hardware used according to some polyaromatic standards, precursor heavy petroleum oils and isotropic and anisotropic pitches currently produced at the Army Technological Center.

2. Experimental

2.1. Materials

The model polyaromatic hydrocarbons used in this work – coronene, (molecular mass MM 300), decacyclene (MM 450), 4-methyl-dibenzothiophene (MDBT, MM 198), 1,2-benzo-diphenylene-sulfide (BDPhS, MM 234), 9-methyl-carbazole (MCabz, MM 181), all from Sigma-Aldrich - were first employed to investigate LDI experiments for the Bruker system utilized, more specifically Bruker patented laser, and to evaluate the effect of the matrices.

The heavy petroleum oil is supplied by PETROBRAS and consists of the bottoms of the fluid catalytic cracking process of PETROBRAS refineries. This heavy oil is used as the precursor of the petroleum pitches so produced and have been extensively analyzed by our group through the open-column pre-fractionation followed by Gas Chromatography-Mass Spectrometry analysis [4].

The pitches analyzed in this work were synthesized on-site from the heavy oil using a two-stage heat treatment procedure [21] that produces an isotropic pitch (IP) in the first stage followed by the production of anisotropic pitches (AP) from the parent IP by tuning the second-stage parameters. Pitches of variable anisotropy were produced and analyzed.

The MALDI matrices used in this work were obtained from Sigma-Aldrich. Dithranol (DIT), α -cyano-4-hydroxycinnamic acid (CCA), 5-chlorosalicylic acid (CSA), trans-3-indoleacrylic acid (IAA), 2,5-dihydroxybenzene (DHB), 2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) and TCNQ were used as supplied, without any modification. All solvents used were of HPLC grade. Tetrahydrofuran (THF) and dichloromethane were supplied by Tedia Brazil.

2.2. Instrumentation for MALDI-MS

LDI-TOF and MALDI-TOF mass spectra were recorded using a Bruker Ultraflex IIITM MALDI-TOF Mass Spectrometer (Billerica, USA) equipped with a smart beamTM laser operating at a pulse rate of 100 Hz. The ions were accelerated at an extraction voltage of 25 kV at positive mode under continuous extraction while the analyzer was operated in the reflection mode within the ion mass range of m/z 0–5000. The lower mass limit was adjusted to suppress matrix ions in the case of MALDI. The laser irradiation employed was set slightly above the threshold or carefully increased (as a percentage of the maximum power available) so that the molecular mass distributions did not change with any increment. Each spectrum represents a sum of accumulated laser shots acquired by moving the laser target on the sample spot. No additional data treatment was carried out such as smoothing or baseline correction.

MS data were analyzed using Flex Analysis software. The peak detection algorithm performs its own internal baseline correction and noise calculation. Signal/noise values are thus determined for sample peaks. The peak quality factor parameter (QF) mentioned in this work describes the reliability of a peak as a composition of peak intensity and consistency with known isotopic patterns, and it is also calculated by the software.

2.3. Sample Preparation for MALDI-MS

Because of their insolubility, the solvent-free method [19, 22] was used for the pitches. Solid analytes and solid matrix were mechanically mixed and alternatively ground using an agate mortar/pestle or milled in a ball mill without addition of any solvent for 2 min at room temperature. After the milling step in the ball mill, the small grinding jar was placed in a vortex shaker for additional 2 min. The process was performed using a

miniature ball mill (Wig-L-Bug 3110B, Crescent Dental Co) and stainless steel grinding jars and balls. Sample and matrix were mixed in 1:1 to 1:20 ratios. The solvent-free method minimizes miscibility problems and also avoids segregation of insoluble compounds that would not be analyzed otherwise. However, it is a matrix-consuming method since there is a minimum sample size requirement for effective grinding. 1–5 mg of sample and 10–40 mg of matrix were used for the 5 ml jar.

The resulting fine homogeneous powder (approx. 1 μm) was then pressed on the stainless steel MALDI target plate with the help of a spatula. The sample surface was then gently blown with nitrogen to remove non-attached solids.

PAHs were prepared by the standard dried-droplet method. Approximately 1 μl of each solution of PAH in dichloromethane or THF (10 mg/ml) was spotted on the sample plate and the solvent was left to air-dry. Alternatively, for MALDI analysis, PAH solutions were spotted above a pre-deposited layer of matrix or pre-mixed with matrix solutions (20 mg/ml) then spotted on the sample plate. The heavy oil is a highly viscous sample and was simply placed on the MALDI plate as a thin film or placed by the dried-droplet method after being dissolved in dichloromethane.

3. Results and Discussion

At present, the main quality control of petroleum pitches is still their physico-chemical properties. The physico-chemical analysis performed on the samples is summarized in Table 1. From the pitches synthesized, it can be noted that the increase in the anisotropy is mainly accompanied by an increase in the density and the insoluble contents. This is expected because anisotropic moieties are formed by stacked aromatic cores and are believed to contain larger molecules, which also account for the lower solubility.

Table 1

Physico-chemical analysis results obtained for oil and pitches

	SM^a	CY^b	TI^c	QI^d	$C_{ar}^e, \%$	SP^f	A^g
Oil							
A	1.084	4.8	0.03	0.00	85.25	-	-
Pitch							
IP	1.215	33.9	5.59	0.37	-	350	0.0
AP1	1.297	77.0	36.9	10.23	-	507	18.7
AP2	1.353	88.0	68.22	62.08	-	545	81.8
AP3	1.271	74.4	34.91	8.90	-	505	13.8
AP4	1.321	86.9	54.38	25.20	-	540	55.4

Note: ^a specific mass, g/cm^3 ; ^b coke yield, %; ^c toluene insolubles, %; ^d quinoline insolubles, % [23]; ^e by nuclear magnetic resonance (NMR); ^f softening point by rheology, K [24]; ^g by centrifugation, % [25]. IP is an isotropic pitch; AP_n are anisotropic pitches.

PAHs present in heavy oils and pitches are particularly suitable for laser desorption ionization because of the presence of aromatic π -electron conjugated systems which can effectively absorb the energy of the laser. For this reason, they lose an electron to form radical cations ($A^{\bullet+}$) rather than the usually observed cationized species [26, 27]. These aromatic p -electron conjugated systems are also responsible for the intermolecular interaction during the desorption process. Thus, one advantage is that because MALDI technique allows soft ionization, the PAH analyte can be detected without fragmentation as long as the laser power is adjusted only slightly above the threshold of ion production. At the same time, lower laser energies can prevent the aggregation behavior of PAHs which is a major concern in the determination of molecular mass distributions in petroleum and coal-derived materials. The higher the electronic density of condensed planar aromatic structures, the higher the tendency for aggregation in LDI-TOF-MS [27, 28]. It has also been shown that alkyl-substituted aromatics show less aggregation behavior than unsubstituted parent [28].

For this reason, it is always safer to use a matrix to disperse the analytes and prevent or reduce the intermolecular interactions (which lead to aggregation and formation of clusters), although some authors state that pitches have their own self-matrix, that is, the lower MM compounds serve as matrix for the higher MM compounds [9].

The search for a good matrix is essential and is the first step in performing a MALDI analysis for any type of sample. Some matrices can aid the desorption/ionization process, while others can simply ruin it. For example, the use of dithranol – a common matrix for polymers – with coronene in our system led to the formation of fragmentation and clustering species that appeared in the spectrum as intense peaks (Fig. 1b) below and above the molecular ion (m/z 300). However, when LDI was performed, little fragmentation and aggregation were observed at the same laser power (Fig. 1a). No peaks were observed either when IAA was used. Coronene, which is a pericondensed PAH, is suitable for LDI in our MS system. Nevertheless, even without a matrix, when the laser power was increased, severe aggregation was noted. The best matrices for this PAH were DCTB (S/N 150.6 and QF 2579) and TCNQ (S/N 1239.7 and QF 11853), which are charge-transfer matrices, the latter presenting the higher S/N ratio and quality factor compared with LDI (S/N 140.3 and QF 940). It is important to note that the resolution of the peaks is maintained high enough, around 6000.

Decacyclene, which has a less condensed aromatic core, with five-member ring moieties, showed different behavior. When laser power was increased in LDI, some well-defined clusters appeared (Fig. 2a). However, instead

of a monomer/dimer/trimer/etc behavior, as shown in the literature for some common PAHs [27, 28], decacyclene also showed some intermediate cluster ions in LDI, which can be an indication of side reactions within the desorption plume instead of just two or three analyte molecules being pushed together and ionized. With the use of DHB, for example, as the matrix, the clustering was efficiently inhibited at even higher laser powers (Fig. 2b) showing the main reason of using the matrix. This was equally true for DCTB (S/N 346.8 and QF 3983) and TCNQ (S/N 2515 and QF 3288).

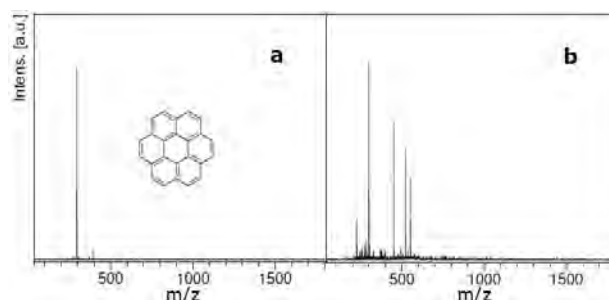


Fig. 1. LDI spectrum of coronene MM 300 (a) and MALDI spectrum of coronene in dithranol (b), both at 25 % laser energy

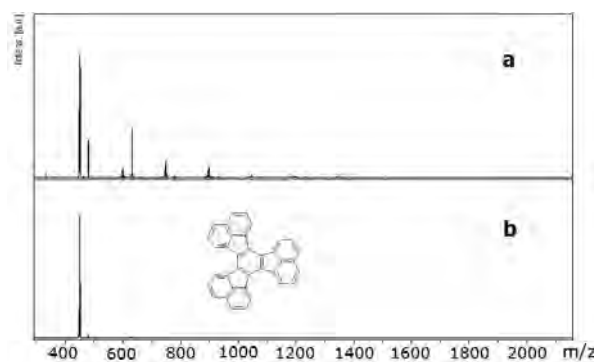


Fig. 2. LDI spectrum of decacyclene (MM 450) at 30 % laser energy (a) and MALDI spectrum of decacyclene in DHB at 40 % laser energy (b) showing that the matrix inhibits aggregation even at higher laser powers

This suggests that MALDI is indeed a complex event, especially for the highly heterogeneous, complex petroleum materials that are composed not only of neutral PAH, but also of heterocyclic PAH and compounds with naphthenic moieties that may influence the desorption/ionization mechanisms of each other. The sulfur heterocyclic PAH methyl-benzothiophene (MDBT-MM 198) is a major component of Brazilian heavy oils used as precursors to pitches [4]. In our experiments, MDBT did not ionize satisfactorily in our system either by LDI or by MALDI, with some common matrices tested – CSA, DHB, DIT, IAA and CCA. However, when TCNQ

was used, an intense, sharp peak (with its isotopic distribution) was observed in the clean spectrum (Fig. 3d). No spectra were observed with the other matrices except for IAA, which showed some other ghost peaks (Fig. 3c). With these matrices, the laser energy threshold value was found to be around 35 %, but with a noticeable number of other peaks instead of m/z 198. With TCNQ, even at lower laser power (10 %) a sharp peak was observed. This indicates that TCNQ as a charge-transfer compound not only prevents fragmentation or aggregation, but also improves ionization, as indicated by the high intensity of the peak even at low laser power. The LDI spectra of the other sulfur PAH, 1,2-benzo-diphenylene-sulfide (BDPhS) also showed no peaks. Accordingly, the use of TCNQ as the matrix also provided an intense peak of the analyte BDPhS with no additional peaks (S/N 491.0 and QF 11206). DCTB, the other charge-transfer matrix, also succeeded in ionizing BDPhS but couldn't achieve the spectral quality of TCNQ (S/N 172.7 and QF 5009) (Fig. 4) with the presence of many other peaks. The same behavior was observed with the pyrrolic nitrogen PAH, 9-methyl-carbazole (MCabz – MM 181). The use of TCNQ produced again a sharper, more intense peak with S/N 268.1 and QF 3063 (Fig. 5) than with DCTB (S/N 15.4 and QF 257) and LDI (S/N 23.1 and QF 922).

LDI enabled investigation of the first molecular growth reactions that occur during the heat treatment of precursor heavy oils to produce petroleum pitches. As observed by another research group with their pitches [20], the petroleum pitches produced from the Brazilian heavy oils that were used in our work also exhibit an oligomeric nature. This can be particularly observed in Fig. 6, where it can be seen that a new group of ions begins to appear right after the first stage of heat treatment of the precursor heavy oil. The isotropic pitch was tested with other matrices such as CCA and DHB, but no spectrum was obtained.

In our experiments, TCNQ generated much richer, higher-quality spectra than the conventional matrices. It was especially effective in mitigating the intense aggregation observed in our pitches. LDI experiments with an anisotropic petroleum pitch (AP) produced from the parent IP are shown in Fig. 7. The clear evidence that the quality of the spectra is much lower with respect to IP can be attributed to the higher cohesion of the AP molecules that can decrease the ionization efficiency. At lower laser energies, a few peaks with low intensity and high noise were observed because of the poor ionization. As the laser energy was increased, one could observe the peaks continuously growing in intensity on the spectrum. At 30 % of maximum laser energy, the oligomeric molecular mass distribution pattern was formed. However, a poor signal-to-noise ratio could still be noticed. As laser

energy continued to increase, the initial pattern began to disintegrate and the aggregation behavior could be seen above 1000 Da.

However, when TCNQ was used for the sample preparation, no aggregation was observed (no changes in the mass distribution pattern) for higher energies, and sharp, intense peaks were obtained (Fig. 8), resulting in an overall enhancement of the ion signals. Furthermore, at lower energies, the oligomeric pattern was already noticed, and the laser threshold was decreased compared to LDI which also contributes to avoid the aggregation effect. The overall signal-to-noise ratio of the experiment with TCNQ and 20 % laser energy was improved (S/N 7.3) in comparison with 30 % laser energy experiment of Fig. 7 (S/N 1.5) as well as the ion intensities, which were significantly increased with the presence of the matrix TCNQ. As laser energy was increased, the intensity of the peaks rose accordingly, with no changes in the molecular

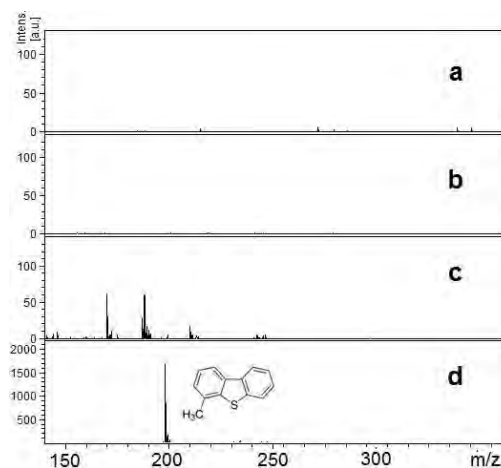


Fig. 3. MALDI spectra of MDBT (MM 198) at 30 % laser energy with different matrices: DHB (a); DIT (b); IAA (c) and TCNQ (d)

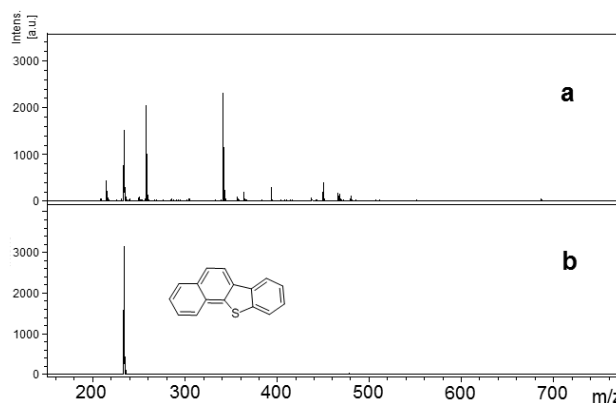


Fig. 4. MALDI spectra of BDPhS (MM 234) at 30 % laser energy with DCTB (a) and TCNQ (b)

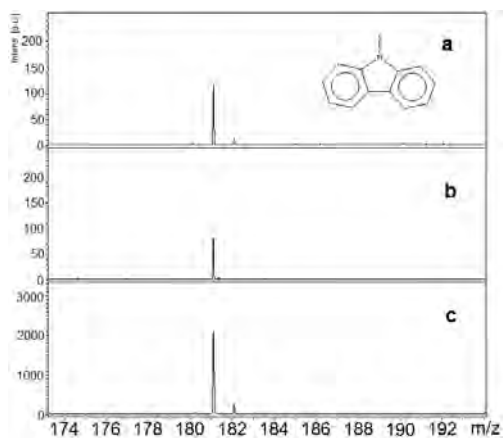


Fig. 5. MALDI spectra of MCabz (MM 181) at 30 % laser energy without matrix (a); with DCTB (b) and TCNQ (c)

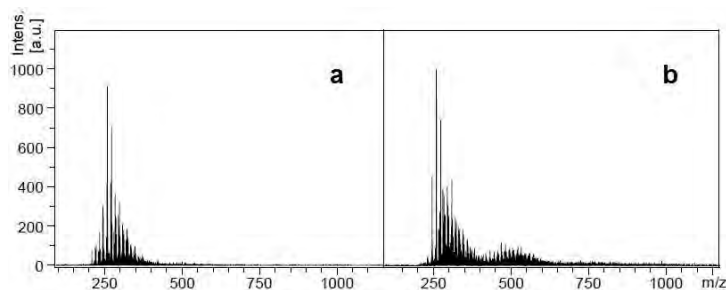


Fig. 6. LDI spectra of the precursor heavy oil (a) and the isotropic pitch IP (b)

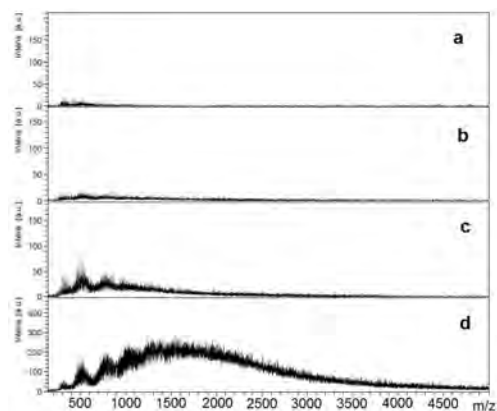


Fig. 7. MALDI spectra of the anisotropic pitch AP2 (81 % anisotropy) showing aggregation at higher laser energies: 20 % (a); 25 % (b); 30 % (c) and 35 % (d)

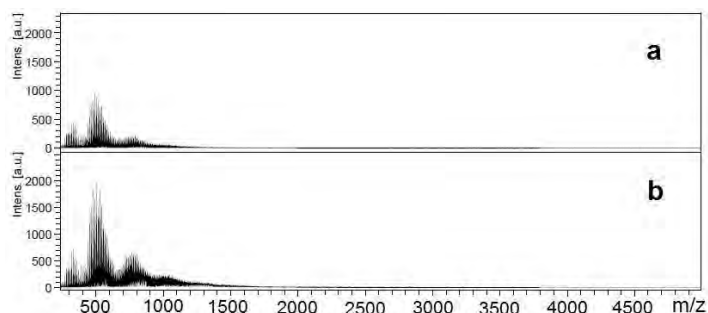


Fig. 8. MALDI spectra of the anisotropic pitch AP2 (81 % anisotropy) with different laser energies: 20 % (a) and 25 % (b)

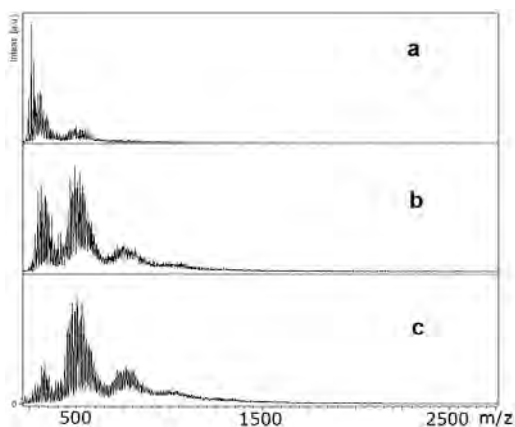


Fig. 9. MALDI spectra of the parent isotropic pitch IP1 (a) and derived anisotropic pitches AP1 (b) and AP2 (c) from different batches (properties in Table 1)

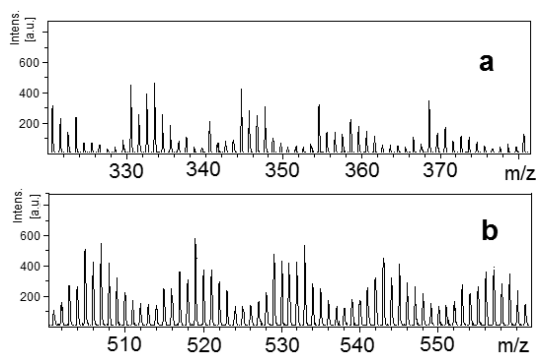


Fig. 10. 60-Da windows of MALDI spectrum of the pitch AP1 showing the differences in peak density between the first two oligomeric groups: 320–380 Da (a) and 500–560 Da (b)

mass distributions. At excessive energies, the aggregation behavior began to appear. Nevertheless, this is not a problem as one should always keep the laser energy low enough and just above the ion threshold. TCNQ, thus, proved to be a suitable matrix for the petroleum pitches produced onsite.

As heat treatment proceeds, pitches from the first stage (IP) are fed to the second preparation stage and molecular growth reactions continue, producing anisotropic pitches (Fig. 9). The mass spectrometry technique can show the basic differences in MM between the pitches and the changes they suffer during the heat treatment. It can be observed that, for the set of pitches analyzed in this work, the main difference is the increasing content of the second group, centered on 550 Da, as the heat treatment progresses. At the same time, the first group, most abundant in the heavy oil and the IP, continuously decreases in content.

If two first “oligomeric group” mass intervals are defined as 150–400 Da and 400–650 Da, the relationships between the weighted intensity (area sensitive) of the first and the second interval (R_{12}) for the pitches IP, AP1 and AP2 are, respectively: $R_{12} = 10.54$, $R_{12} = 0.51$ and $R_{12} = 0.22$. This behavior was also observed in two pitches produced in the same batch but sampled at distinct reaction times: initial pitch $R_{12} = 0.30$ and final pitch $R_{12} = 0.10$ (spectra not shown). Calculations must use the areas of the peaks instead of the relative intensities once the peak density is higher for the second group (Fig. 10). This can be explained by the combinatorial nature of the monomer molecules reactions, once it is known in the literature that the possible main mechanism of molecular

growth is through the formation of free-radicals [29]. Molecular masses no higher than 1500 Da were observed in these experiments.

The appearance of a third group in the spectra of the anisotropic pitches (650–900 Da) is also evident. The proportion of the third group in Fig. 9b and 9c with respect to the entire weighted distribution was similar for both pitches ($AP1 = 0.10$ and $AP2 = 0.11$). This fact was likewise observed in an experiment with two other anisotropic pitches also produced from the same IP under different conditions ($AP3$ and $AP4$ – properties in Table 1). For these pitches, each toluene-insoluble fraction (IT), obtained by the ASTM D4312 method, were also analyzed. The first two groups of the mass spectra of the two whole pitches exhibit the same behavior as the other experiments. The progress of the heat treatment withdraws the smaller molecules of the first group originating from the parent heavy oil. From the third group, it appears, for our set of pitches, that the proportion of the compounds with molecular masses higher than 700 Da is maintained (Figs. 11a and b).

This is also evident in both respective toluene-insoluble fractions (Figs. 11a_i and b_i). Although these pitches have different values of anisotropy and IT, their fractions present the same broad molecular weight distribution, as similarly noticed by Greinke and Singer [10] for isotropic and mesophase fractions of petroleum pitches of different mesophase content. In our case, the fractions in terms of solubility of both anisotropic pitches have also similar molecular masses (Fig. 11), with exclusion of the lighter compounds (non-mesogenic compounds).

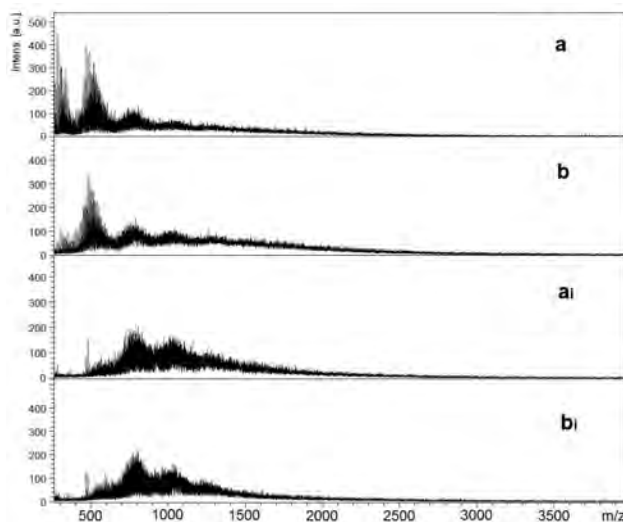


Fig. 11. MALDI spectra of two anisotropic pitches produced from IP with AP3, 13.8 % anisotropy (a) and AP4, 55.4 % anisotropy (b), along with each insoluble fraction in toluene (a_i), (b_i)

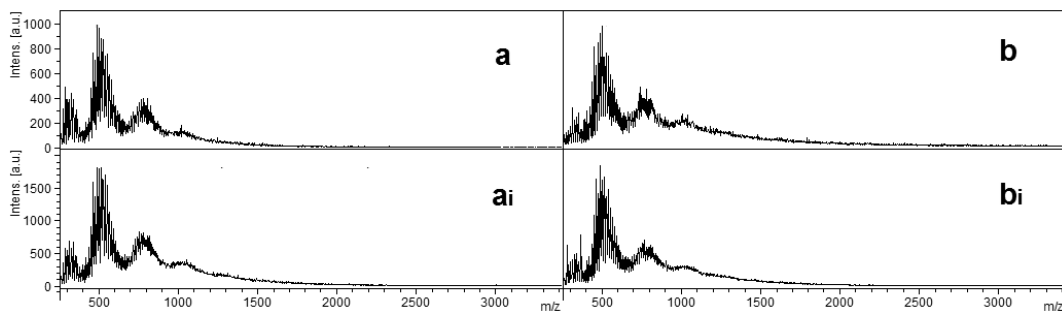


Fig. 12. MALDI spectra of pitches: AP1 anisotropic phase (a) and isotropic phase (ai) and AP2 anisotropic phase (b) and isotropic phase (bi)

Furthermore, MALDI was performed on the isotropic and anisotropic phases of pitches AP1 and AP2. The phases were separated by centrifugation as described in another paper by our group [25]. The spectra show the presence of essentially the same molecular mass distribution in both phases for both pitches (Fig. 12). Diefendorf and co-workers, who investigated mesophase formation as a selective physical separation of mesogenic and non-mesogenic species [12], already mentioned at that time of the existence of both such species either in an isotropic pitch or in a mesophase one [12]. The existence of the same molecular sizes in both centrifuged phases of our work is feasible since 100 % isotropic pitch IP already contains some amount of the second group, attributed to mesogenic compounds.

From the results it appears that during the heat treatment these medium-sized molecules belonging to the group centered on 550 Da can exist in the isotropic phase or the anisotropic phase and are transferred from one to the other; or they eventually polymerize to form the latter oligomeric groups.

4. Conclusions

We have demonstrated the use of Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) for the analysis of heavy petroleum oils and pitches produced at the Army Technological Center. Characteristic oligomeric distributions were obtained for all pitches analyzed. Mass spectrometry provides a versatile and fast method for desorption and analysis of intact ions and, thus, for the observation of molecular weight distributions in the materials presently produced by the research group. Charge-transfer matrix 7,7,8,8-tetracyanoquinodimethane (TCNQ) has been established as an excellent choice for the analysis of pitches because of its capacity to enhance ionization of polyaromatic hydrocarbons (because of its electron acceptor character) and of promoting ionization of different classes of compounds also present in pitches

such as sulfur and nitrogen compounds. It was observed that increasing the laser power results in an increase in the aggregation of the molecules in Laser Desorption/Ionization (LDI) due to the high density and cohesion of the molecules in the solid sample, particularly in anisotropic pitches. Molecular information can already be obtained at lower laser fluencies by dispersing the analyte molecules into a proper matrix. Some matrices were tested with standard polyaromatic hydrocarbons and pitches and it was shown that TCNQ was the only one capable of effectively ionizing the sulfur compounds and preventing the aggregation behavior of the samples.

Acknowledgements

The authors thank Petrobras for financial support and Centro Tecnológico do Exército (CTEx) for laboratory facilities.

References

- [1] Brooks J. and Taylor G.: *Chem. and Physics of Carbon*, 1968, **4**, 243.
- [2] Oberlin A., Bonnamy S. and Rouxhet P.: *Chem. and Physics of Carbon*, 1999, **26**, 1.
- [3] Torregrosa-Rodríguez P., Martínez-Escandell M., Rodríguez-Reinoso F. *et al.*: *Carbon*, 2000, **38**, 535.
- [4] Pereira M.-H., Castro L. and Michel R.: *Proceed. of the IV Congresso Brasileiro de Carbono*, Brazil, Gramado 2007.
- [5] Greinke R.: *Carbon*, 1986, **24**, 677.
- [6] Oberlin A.: *Chem. and Physics of Carbon*, 1989, **22**, 1.
- [7] Guillen M., Blanco J., Canga J. and Blanco C.: *Energy & Fuels*, 1991, **5**, 188.
- [8] Altgelt K. and Boduszynski M.: *Composition Analysis of Heavy Petroleum Fractions*. Marcel Dekker, New York 1993.
- [9] Morgan T., George A., Alvarez P. *et al.*: *Energy & Fuels*, 2009, **23**, 6003.
- [10] Greinke R. and Singer L.: *Carbon*, 1988, **26**, 665.
- [11] Greinke R.: *Carbon*, 1990, **28**, 701.
- [12] Diefendorf R., Yen T., Needles H. *et al.*: *Polymers for Fibers and Elastomers*, ACS Symp. Ser., 1984, **260**, 209.
- [13] Johnson B., Bartle K., Herod A. and Kandiyoti R.: *J. Chromatogr. A*, 1997, **758**, 65.

- [14] Lafleur A. and Wornat M.: J. Anal. Chem., 1988, **60**, 1096.
[15] Lafleur A. and Nakagawa Y.: Fuel, 1989, **68**, 741.
[16] Karaca F., Morgan T., Behrouzi M. *et al.*: Fuel, 2005, **84**, 1805.
[17] Herod A., Bartle K. and Kandiyoti R.: Energy & Fuels, 2007, **21**, 2176.
[18] Morgan T., George A., Alvarez P. *et al.*: Energy & Fuels, 2008, **22**, 3275.
[19] Przybilla L., Brand J., Yoshimura K. *et al.*: J. Anal. Chem., 2000, **72**, 4951.
[20] Edwards W., Jin L. and Thies M.: Carbon, 2003, **41**, 2761.
[21] Castro L.: J. Brazil. Chem. Soc., 2006, **17**, 1096.
[22] Trimpin S., Rouhanipour A., Az R. *et al.*: Rapid Commun. Mass Spectr., 2001, **15**, 1364.
[23] Freitas L. and Castro L.: Fuel, 2008, **87**, 2842.
[24] Braga C., Dutra C. and Castro L.: Fuel, 2009, **88**, 853.
[25] Vieira F., Dutra C. and Castro L.: Fuel, 2011, **90**, 908.
[26] Yoshimura K., Przybilla L., Ito S. *et al.*: Macromol. Chem. & Phys., 2001, **202**, 215.
[27] Cristadoro A., Rader H. and Mullen K.: Rapid Commun. Mass Spectr., 2007, **21**, 2621.
[28] Martinez-Haya B., Hortal A., Hurtado P. *et al.*: J. Mass Spectr., 2007, **42**, 701.
[29] Lewis I.: Carbon, 1982, **20**, 519.

ДОСЛІДЖЕННЯ МАС-СПЕКТРОСКОПІЧНИМ МЕТОДОМ МОЛЕКУЛЯРНИХ МАС НАФТОВИХ ПЕКІВ ОДЕРЖАНИХ ВНАСЛІДОК ТЕРМООБРОБЛЕННЯ

Анотація. За допомогою мас-спектрометрії охарактеризовані ізотропні і анізотропні пеки, а також вихідна важка мінеральна олива з метою встановлення розподілу молекулярних мас (РММ) та змін, що відбуваються під час термооброблення. Показано, що метод приготування проб і вибір матриці мають значний вплив на РММ. Одержані результати підтверджують олігомерну природу пеків та збільшення розмірів молекул при термічному обробленні.

Ключові слова: нафтовий пек, важка олива, мас-спектрометрія, поліароматичні вуглеводні.