

Analysis of Petroleum and Coal Tar Pitches as Large PAH

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Coal tar and petroleum pitches present quite different features, particularly in terms of structure, size and aliphatic substitution degree of the large polycyclic aromatic hydrocarbons (PAH) components. As such they are an important source of a wide range of different carbon materials mainly deriving from their thermal transformations. However, the difficulty in the controlled and modulated production of tailored carbon materials arises from the scarce compositional and structural knowledge of the parent pitches as well as that of intermediates and final products derived from their thermal treatment.

The present work reports about a detailed mapping of the characteristics of solid petroleum and coal tar pitch samples kindly provided by RÜTGERS Basic Aromatics GmbH (Castrop-Rauxel, Germany). Chemical and spectroscopic techniques have been employed in order to put in evidence similarities and differences in terms of volatility, molecular weight distribution and chemical structure. In particular, conventional and advanced tools including chromatography, elemental analysis, thermogravimetry, mass spectrometry, UV-Visible absorption and fluorescence were applied the altogether from one side to offset the limits and on the other side to exploit the advantages of each technique.

1. Introduction

Synthetic or fossil fuel-derived pitches are extremely complex mixtures consisting of a huge number of species mainly of aromatic nature. Synthetic pitches, customarily obtained by catalytic polymerization of polycyclic aromatic hydrocarbons, PAH, like naphthalene (Mochida et al., 2000), have a production cost still high. Hence, they are not considered as a real alternative to coal tar pitches whose production is rapidly decreased in the last century. On the other hand, petroleum pitches appear promising as a cheap source alternative to coal tar pitches presenting quite similar physical properties in spite of a rather different chemical composition. The present work aims to analyse and compare the chemical features of quite different petroleum and coal tar pitches having also different physico-chemical properties, namely the softening point.

Petroleum pitches derive from the thermal polymerization of aromatic decant oil, a by-product of the fluid catalytic cracking (fcc) of the heavy gas oil fraction of crude oil. It has been assessed that petroleum pitches generally consist of oligomers of alkylated polycyclic aromatic hydrocarbons (PAH), with the overall molecular weight (MW) ranging from approximately 200 to 2000 Da (Cristadoro et al. 2009). Coal tar pitches (CTP) constitute a valuable aromatic hydrocarbon resource and have been produced as a by-product of metallurgic cokes in large scale for centuries. Both poor utilization and mishandling may result in serious environmental and health issues, since CTP are rich in some PAHs that are carcinogenic and mutagenic (Friesen et al. 2010).

After proper processing, the pitches are currently used for binders and pitch cokes, whereas, they can be transformed by sophisticated processing methods into valuable precursor of advanced carbon materials, including carbon fibers and carbon-carbon composites. High yield and quality of the resultant cokes carbon, stable and sufficient source and low price are important factors driving the choice of the material and treatment method. Researchers have long recognized that both the MW and structure play a role in the suitability of a given pitch for specific applications. Regardless of the source, a better understanding of pitches composition and/or structure at the molecular level is necessary for the processing technology development. Recently, a detailed characterization of a synthetic and coal tar pitch (Gargiulo et al. 2015, 2016 and

references therein) has been carried out by crossing the information derived from the implementation of diverse chemical and spectroscopic techniques.

This analytical approach has been used herein to analyse commercially available petroleum and coal tar pitches, putting in evidence similarities and differences in terms of molecular weight distribution and chemical structure of large PAH featuring pitches.

2. Experimental

2.1 Samples

Four solid pitch samples were kindly provided by RÜTGERS Basic Aromatics GmbH (Castrop-Rauxel, Germany). The solid carbon samples listed below were produced by the selection of suitable raw materials with low heteroatom content and appropriate thermal carbonization techniques:

1- PP250: petroleum pitch (ZL 250M, CAS NO.: 68187-58-6) with softening point of 252°C.

2- PP118: petroleum pitch (ZL 118 CAS NO 68187-58-6) with softening points of 113°C.

3- Carbores: coal tar pitch (CARBORES® P, CAS NO.: 121575-60-8) with softening point of 235°C.

4- Electrode binder: coal tar pitch (Electrode Binder BX 95KS, CAS NO.: 65996-93-2) with softening point of 110-115°C.

2.2 Analytical techniques

Elemental analysis

The elemental analysis of pitch samples were performed on a CHN 2000 LECO elemental Analyzer.

Thermogravimetric (TG) analysis

Thermogravimetric analysis was performed on a Perkin–Elmer Pyris 1 thermogravimetric analyzer. The pitch samples were heated from 50 °C up to 750 °C at a rate of 10 °C min⁻¹ in inert atmosphere (N₂, 40 mL min⁻¹).

Atmospheric Pressure Photoionization mass spectrometry (APPI-MS)

The APPI mass spectra were obtained on an Agilent 1100 Series MSD Trap (Agilent Technologies, Palo Alto, CA, USA). A PhotoMate orthogonal APPI spray source (Syagen Technology) was installed on the mass spectrometer. The APPI source was based on a radio frequency (RF) discharge of a gas mixture consisting primarily of krypton and operated on the atomic emission lines at 10.0 and 10.6 eV. The gas composition and pressure were optimized for maximum radiant output. The RF driver and coil were designed and optimized for maximum and most efficient coupling of power into the plasma.

The pitch samples, dissolved in toluene, were directly injected into the APPI source by using a syringe pump (5 µL/min). APPI measurements were performed in positive mode, using the following instrumental parameters: nebulising gas flow obtained by a pressure of 60 psi, nebuliser temperature 450°C, capillary voltage 3500 V. The nebuliser gas usually employed was N₂ obtained from a nitrogen generator (N₂ LCMS, Claind). The ion-trap mass detection limit is 4000 Da.

UV-Visible (UV-Vis) absorption spectroscopy

UV-Visible spectra of quartz plates, and of the top and bottom fractions, dissolved in dichloromethane (DCM) or suspended in N-methylpyrrolidone (NMP), were measured on HP 8453 Diode Array spectrophotometer. In the case of analysis in solvents a 1-cm path-length quartz cuvette was used. The interference of the solvents on the UV absorption limited the acquisition of the spectra to 250-260 nm (for DCM and NMP, respectively).

Fluorescence spectroscopy

Fluorescence spectra were acquired on a Perkin-Elmer LS-50 spectrofluorimeter by using a xenon discharge lamp as excitation light source. Instrumental parameters were controlled by the Fluorescence Data Manager Perkin-Elmer software. Synchronous fluorescence emission spectra were measured by applying a simultaneous scanning of the excitation and emission wavelengths, keeping constant the difference between the wavelengths ($\Delta\lambda = 10$ nm).

3. Results and discussion

The elemental composition and the hydrogen/carbon (H/C) atomic ratio of pitches are reported in Table 1. All pitch samples have a rather low content of N and O heteroatoms (below 2 wt.%). Carbores and Electrode binder present H/C ratios (0.5-0.6) typical of coal tar pitches (Gargiulo et al. 2015, 2016), whereas the PP250 and P118 pitches show higher H/C values (0.7-0.8), typical of petroleum pitches (Cristadoro et al. 2009).

Figure 1 reports the thermogravimetric profiles (left) and the corresponding derivative TG (DTG) curves (right) of all pitches measured in an inert environment where volatilization associated to vaporization and pyrolysis occurs.

Table 1: H/C ratio and elemental composition of pitches.

Sample	H/C	%C	%H	%N	%O (by difference)	Softening point, °C
Coal Tar pitch						
Carbores	0.52	93.1	4.1	0.7	2.1	235
Electrode binder	0.58	92.7	4.4	0.9	2.0	115
Petroleum Pitch						
Petroleum PP250	0.72	93.7	5.6	0.1	0.6	252
Petroleum PP118	0.77	92.2	5.9	0.2	1.7	118

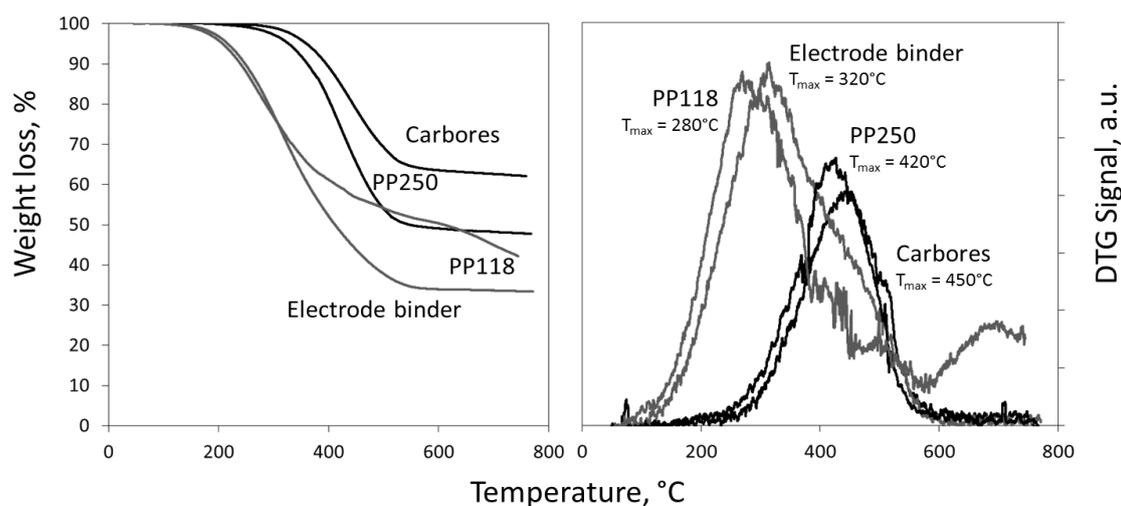
The TG analysis shows the significant difference of the volatilities of coal tar pitch samples which is consistent with their different softening point.

Particularly, the more volatile coal tar pitch is the Electrode binder featured by the much lower softening point (Table 1). Actually, it is noticeable that Electrode Binder presents a very high weight loss up to 550°C (70 wt.%), moreover the weight loss starts early, at about 110°C, and reaches the maximum around 320°C as well evidenced in the DTG curve (right part of Fig. 1). The weight loss in the case of Electrode binder is mainly attributed to the volatilization of low- to medium- molecular weight unsubstituted PAH, typically contained in coal tar pitches (Guillen et al. 1992, Gargiulo et al. 2015), which volatilize up to 300-400°C. This was demonstrated by GC-MS analysis of the Electrode Binder extract showing the significant presence of unsubstituted PAH from 4 to 7 rings. Structurally similar unsubstituted PAH, but with a much higher MW, beyond the GC-MS limit (300 Da), could be presumed to take into account for the residual low-volatile components.

On the other hand, the Carbores pitch exhibits a lower weight loss (about 40 wt.%) which begins at a temperature much higher (around 240°C). The weight loss is maximum at 450°C and ends around 500°C, as well evidenced by the DTG curve reported in the right panel of Fig.1 reporting. The GC-MS of Carbores extract was quite ineffective consistently with its much lower volatility. Like for Electrode Binder, it can be anticipated that unsubstituted PAH of large MW make up Carbores, consistently with the common origin of Electrode binder and Carbores from coal tar.

It is noteworthy that for both coal tar pitches the TG temperature at which weight loss begins is quite similar to their softening point indicating that, in the flow and heating rate conditions used, the TG method can replace rather satisfyingly the method for softening point evaluation.

Also the petroleum pitches, PP118 and PP250, present a thermal behaviour quite dissimilar from each other,. Particularly, the weight loss of the PP118 and PP250 begins at about 100°C and 250°C, respectively, consistently with their softening points. Moreover, in the case of PP118 the DTG profile (Fig.1, right panel) presents two maxima, at 280°C and at about 700°C with an overall weight loss of 60 wt.%. This behaviour is indicative of the presence of two different classes of compounds that volatilize at different temperatures.

Figure 1: TG profiles (left) and derivative TG curves (right) of pitches in inert (N₂) environment.

The GC-MS analysis of PP118 indicated a small presence of unsubstituted PAH from 4 to 7 rings and a large presence of methylated PAH, whereas the analysis of PP250 reports the almost total absence of whichever kind of PAH analysable by GC-MS.

The thermal behaviour of the pitches above reported shows to be clearly correlated with their softening points, whereas it is not correlated with the elemental composition, namely the hydrogen and carbon content of pitches. More informative is the molecular structure of pitches that has been here inferred by applying APPI-MS and spectroscopic techniques for obtaining the mass distribution and the aromatic character, respectively. The APPI mass spectra of pitch samples, reported in Fig. 2, show that in all the spectra there are two peaks at m/z around 90 and some peaks around 200 m/z , which are due to the solvent (toluene). Indeed, toluene presents the base peak at m/z 91 (probably tropylium ion) and the odd-electron molecular ion (m/z 92), assigned to the radical cation of toluene C_7H_8 , is also of high abundance. The ion groups at higher masses peaked at m/z =108 and at m/z =199 were attributed to reaction products of toluene with oxygen with one and two aromatic rings, respectively (Tubaró et al., 2003, Apicella et al. 2010). After m/z 200, the peaks are really due to components of the analysed samples.

The spectra of Carbores pitch and Electrode binder are rather similar, extending mainly in the range m/z 200-750 centred around m/z 400 and 300, respectively. For the Electrode binder, beside a relatively larger abundance of lighter PAH, around m/z =200, also a much higher intensity of all mass peaks is remarkable (Fig. 2a-b). The higher abundance of relatively lighter PAH structures in the Electrode binder is quite consistent with the higher volatility above described.

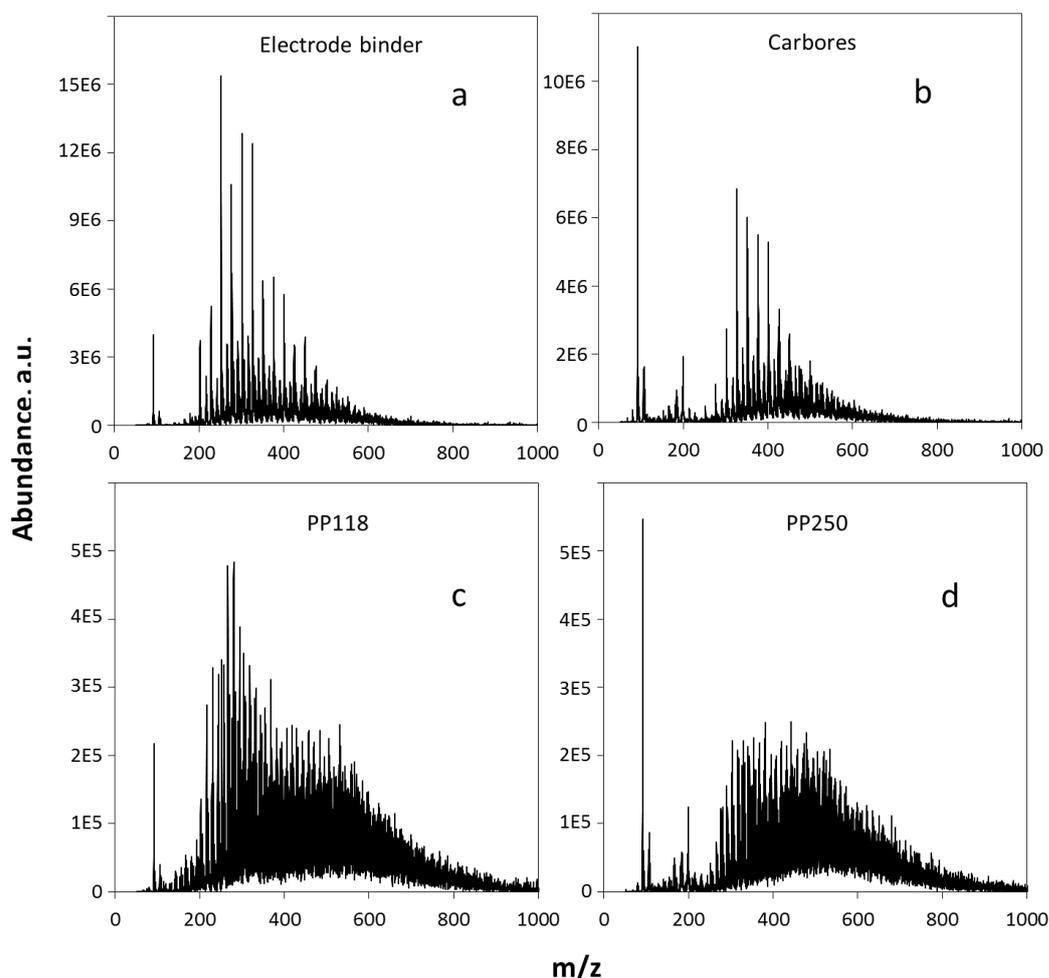


Figure 2: APPI mass spectra of toluene-extracts of Carbores (a), Electrode binder (b), PP250 (c) and PP118 (d) samples.

Both the mass spectra present a sequence of major ion peaks with a spacing of m/z 24 superimposed on a sequence of minor ion peaks which present the same spacing of m/z 24; the spacing between the major and

the minor ion peaks is 12. The gap of m/z 24 can be attributed to a neat sequential addition of C₂ as an ethylene bridge, while a gap of m/z 12 between the two sequences can be attributed to the insertion of a methylene (-CH₂-) into a bay region of angular PAH. On the basis of previous work performed on flame-formed soot extracts (Apicella et al. 2003, 2006, 2007), the higher and lower intensity sequences clearly observed up to about m/z 800, can be attributed to even- and odd-numbered PAH, respectively. In spite of the similarity in the peaks sequences detected for flame-formed PAH it has to be noticed that the spectra of coal tar pitches are more crowded of peaks and the double sequence of 12 and 24 gaps appear superimposed to other peaks with sequences not immediately identifiable. For a deep spectra analysis, the application of a mathematical method, set up in a preliminary work (Apicella et al. 2013, Passaro et al. 2015), is planned in future work.

The mass spectra of both petroleum pitches present a continuous peak distribution quite different from coal tar pitches spectra; moreover the spectra extend in a larger range, up to m/z 1000. In particular, spectra appear much more complex and crowded of peaks of comparable heights, with a gap at $m/z=1$. This spectral shape hinders an easy extrapolation of repetitive spacing at a glance and will require the support of mathematical tools for spectra resolution. Actually, the continuous sequence of peaks suggests a large presence of aliphatic functionalities, consistently with the higher H/C ratio of PP. In comparison to the PP250, it is remarkable that the PP118 presents an additional and abundant mass distribution peaked at m/z around 300, in agreement with the two different regions of volatilization observed in TG profile of PP118 (Fig. 1).

Summing up, to the similar source (petroleum or coal tar) are associated similar structural features of pitch molecules, differing only in the volatility. The more aromatic and aliphatic character, presumed on the basis of the mass spectral shapes of coal tar and petroleum pitches, respectively, can be confirmed by spectroscopic analysis shown below.

The comparison of UV-Vis absorption spectra and fluorescence spectra of pitches reported in Fig. 3 gives information on the different sizes and structures of aromatic moieties featuring petroleum and coal tar pitches. The most intense and common feature of the absorption spectra compared in Fig. 3a is the UV absorption band typical of aromatic systems. Some fine structure, typical of a series of relatively small PAH, can be observed just in the spectrum of Electrode binder. The higher absorption coefficient shown by both coal tar pitch samples (Electrode binder and Carbores) demonstrates their higher aromatic content in respect to the petroleum pitch samples PP118 and PP250. In the case of Carbores, because of its higher MW range (Fig. 2a), the higher absorption in the visible can be also indicative of the larger size of aromatic moieties in comparison to all other ones. Beside the lower absorption, the broader feature of petroleum pitches spectra is more typical of aliphatic substituted PAH. As regards fluorescence spectroscopy, to better resolve the PAH composition of pitches, the simultaneous scanning of excitation and emission wavelengths with a fixed wavelength difference, $\Delta\lambda$, known as synchronous fluorescence, has been applied.

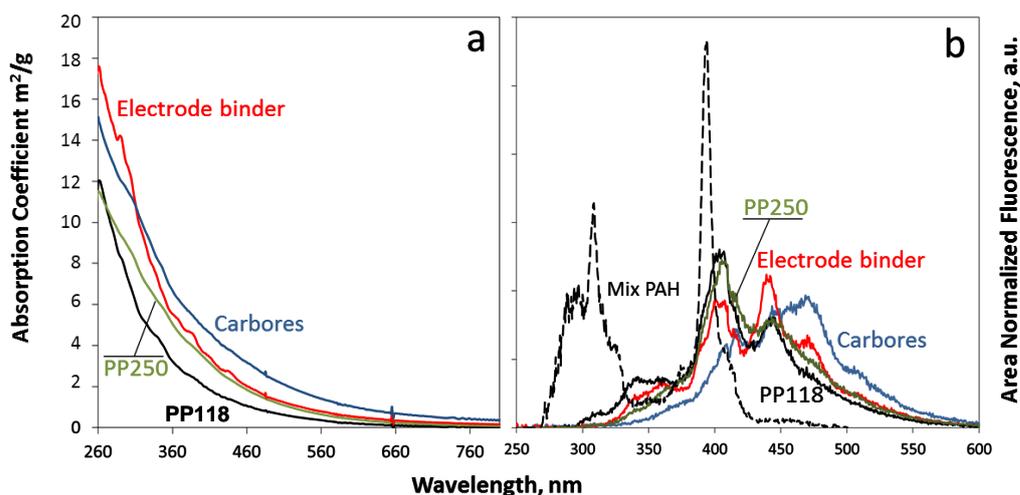


Figure 3: Profiles of the mass absorption coefficient in the UV-Vis range (a) and area normalized fluorescence spectra (b) of the pitch samples.

Indeed, synchronous fluorescence is very selective to classes of PAHs with different ring numbers, which generally appear as well-discriminated peaks providing fingerprints of specific aromatic moieties in complex

PAH mixtures. The synchronous fluorescence spectra with $\Delta\lambda = 10$ nm of the four pitch samples, along with the spectrum of a mixture of PAH, between 2 and 7 rings, are reported in Fig.3b. The comparison confirms the higher condensation degree of the aromatic moieties of the Carbores with respect to the other pitches, but the shift toward the visible of all the pitches and the absence of individual peaks suggest that they have different aromatic structure with respect to only all-benzenoid PAH mixture, whose composition is typically exhibited by flame-formed soot extracts.

4. Conclusions

The high chemical complexity of petroleum and coal tar pitches has been faced on by the use of an array of techniques for elucidating the relationship of chemical compositions with their physico-chemical properties. Actually, the bulk parameters as H/C or volatilization temperatures are not sufficient to describe the pitch properties. Mass spectrometry and spectroscopic analysis instead provide useful information on their composition that in turn is important to address their possible application.

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References

- Apicella, B., Ciajolo, A., Barbella, R., Tregrossi, A., Morgan, T.J., Herod, A.A., Kandiyoti, R., 2003, Size exclusion chromatography of particulate produced in fuel-rich combustion of different fuels, 2003, *Energy&Fuels*, 17 (3), 565-570.
- Apicella, B., Millan, M., Herod, A.A., Carpentieri, A., Pucci, P., Ciajolo, A., 2006, Separation and measurement of flame-formed high molecular weight polycyclic aromatic hydrocarbons by size-exclusion chromatography and laser desorption/ionization time-of-flight mass spectrometry, *Rapid Commun. Mass Spectrom.*, 20 (7), 1104-1108.
- Apicella, B., Carpentieri, A., Alfè, M., Barbella, R., Tregrossi, A., Pucci, P., Ciajolo, A., 2007, Mass Spectrometric Analysis of Large PAH in a Fuel-rich Ethylene Flame, *Proc. Comb. Inst.* 31: 547–553.
- Apicella, B., Alfe, M., Ciajolo A., 2010, Mass Spectrometric Advances in the Analysis of Large Aromatic Fractions of Heavy Fuel Oils and Carbon Particulates, *Combustion Science and Technology*, 182: 4, 640-652, DOI: 10.1080/00102200903466335
- Apicella, B., Bruno, A., Wang, X., Spinelli, N., 2013, Fast Fourier Transform and autocorrelation function for the analysis of complex mass spectra, *Int. J. Mass Spectrom.*, 338, 30–38.
- Cristadoro, A., Kulkarni, S. U., Burgess, W. A., Cervo, E. G., Räder, H. J., Müllen, K., Bruce, D. A., Thies, M. C., Structural characterization of the oligomeric constituents of petroleum pitches 2009, *Carbon*, 47(10), 2358–2370.
- Friesen, M. C., Demers, P.A., Spinelli, J.J., Eisen, E.A., Lorenzi, M.F. and Le, N.D., 2010, Chronic and Acute Effects of Coal Tar Pitch Exposure and Cardiopulmonary Mortality Among Aluminum Smelter Workers, *Am J Epidemiol*, 172:790–799, DOI: 10.1093/aje/kwq208
- Gargiulo, V., Apicella, B., Alfè, M., Russo, C., Stanzione, F., Tregrossi, A., 2015, Structural Characterization of Large Polycyclic Aromatic Hydrocarbons. Part 1: The Case of Coal Tar Pitch and Naphthalene-Derived Pitch, *Energy & Fuels* 29 (9), 5714-5722 and ref therein.
- Gargiulo, V., Apicella B., Stanzione, F., Tregrossi, A., Millan, M., Ciajolo, A., 2016, Structural Characterization of Large Polycyclic Aromatic Hydrocarbons. Part 2: Solvent-Separated Fractions of Coal Tar Pitch and Naphthalene-Derived Pitch, *Energy & Fuels* 30 (4), 2574-2583;
- Guillen, M. D., Iglesias, M. J., Dominguez, A., Blanco, C. G., 1992, Semi-quantitative FTIR analysis of a coal tar pitch and its extracts and residues in several organic solvents, *Energy Fuels*, 6 (4), 518–525.
- Mochida, I., Korai, Y., Ku, C. H., Watanabe, F., Sakai, Y., 2000, Chemistry of synthesis, structure, preparation and application of aromatic-derived mesophase pitch, *Carbon*, 38, 305–328.
- Passaro, M., Apicella, B., D'Anna, A., Ciajolo, A., Tregrossi, A., 2015, Mass Spectrometric Tools for Structure Elucidation of Carbonaceous Materials, XXXVIII Meeting of the Italian Section of the Combustion Institute, Lecce, Italy, DOI: 10.4405/38proci2015.II4
- Tubaro, M., Marotta, E., Seraglia, R., Traldi, P., 2003, Atmospheric pressure photoionization mechanisms. 2. The case of benzene and toluene, *Rapid Comm. Mass Spec.*, 17, 2423.