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Thermal Treatment under High-Vacuum of Tars Relevant in Combustion and Material Science

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The composition of tars, typically derived from coal and heavy fuel processing or formed in fuel-rich combustion, determines their transformation into carbons relevant in combustion and environmental fields as well as for material production. The speciation of the huge number of aromatic components of tars, usually found in form of viscous black liquid or solid, is not straightforward because of the tar complexity and high molecular weight, spanning from few hundreds up to thousands of Da. To this regard, the pre-separation of tar in lighter and heavier fractions simplifies the further characterization of its composition.

The present work reports a fractionation method of a typical sample of combustion-formed tar based on moderate heating in high-vacuum conditions (10^{-6} mbar). It was preliminarily tested on a single polycyclic aromatic hydrocarbon, coronene, and on synthetic mixtures of polycyclic aromatic hydrocarbons, presumed to be the basic aromatic moieties of tar components. Lighter components obtained by condensation/deposition as thin films and/or crystals, as well as the heavier residue, were analysed by optical microscopy and spectroscopy. The separation procedure allowed to get more information on the components distribution also inferring the self-organization in cluster assembly and/or crystal forms.

1. Introduction

The determination of the structure of complex carbon mixtures represented by tars derived from coal and heavy fuel processing or formed in fuel-rich combustion, is an analytical problem shared by scientific communities involved in different research fields (combustion, environment, material science, etc.)

An array of many analytical and spectroscopic tools is necessary to attempt the characterisation of such complex products, because of the tar complexity and high molecular weight (MW), spanning from few hundreds up to thousands of Da. Gas chromatography-mass spectrometry (GC-MS), conventionally used for the qualitative and quantitative analysis of polycyclic aromatic hydrocarbons (PAH), allows detecting and identifying at most 50-60wt.% of tars typically formed in combustion systems and often accompanying soot formation and emission (Apicella et al. 2002). It has not yet been established whether this is due to the presence of high molecular weight aromatic species, not analysable with the conventional chromatographic and mass spectrometric techniques. These species could be constituted of large aromatic ring systems possibly clustered together or interconnected by aliphatic bridge structures, as proposed on the basis of spectroscopic analysis, mainly fluorescence emission and UV-Visible and FT-IR absorption (Ciajolo et al. 2000, 2001).

Beside to be itself less amenable to be analysed, the heavier fraction of tars is especially difficult to be analysed when in admixture with light components. Hence, the pre-separation of tars in lighter and heavier fractions is required for their detailed analysis.

The choice of the pre-separation method should take into account for the scarce solubility and high thermal degradability of heavier components. Actually, many attempts as solvent extraction, thin layer or size exclusion chromatography did not succeed a complete separation of PAH from the matrix, presumed to be constituted of an aliphatic-aromatic network (Apicella et al. 2003, 2006, Gargiulo et al. 2015, 2016, Karaka et al. 2009, Morgan et al. 2009, George et al. 2010).

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The present work reports the results of a fractionation method applied for the first time to a typical sample of tar extracted from the particulate matter sampled in a premixed ethylene flame. The fractionation exploits the different components volatility and is based on the moderate heating of the sample in high-vacuum conditions (10^{-6} mbar). The method was preliminarily tested on a single PAH, as coronene, and synthetic mixtures of PAH, typically featuring flame-formed tars, in order to check the effectiveness of the separation, in the selected operative conditions.

2. Experimental

2.1 Samples

Three samples have been considered:
1- coronene ($C_{24}H_{12}$) from Sigma-Aldrich.
2- PAH mixture (MixPAH) constituted of: pyrene ($C_{16}H_{10}$), indeno[1,2,3 cd]pyrene ($C_{22}H_{12}$), benzo[b]crisene ($C_{22}H_{14}$), pentacene ($C_{22}H_{14}$), coronene ($C_{24}H_{12}$). The individual single PAH mixture components were from Sigma- Aldrich.
3- Soot extract sampled in a premixed laminar ethylene/oxygen flame stabilized at atmospheric pressure on a McKenna burner. The C/O ratio employed was 0.80, corresponding to equivalence ratios $\varphi=2.42$. The velocity of cold gases was 4 cm/s.

The sampling of carbon particulate matter was accomplished in isokinetic conditions to reduce perturbation effects on the reaction environment, by means of a water-cooled stainless-steel probe connected to a suction pump. Carbon particulate matter was collected for several hours by condensation in an ice-trap and on teflon filters. The flame-formed tar (soot extract) was extracted with DCM from the total carbon particulate matter. More details on the flame and sampling systems are reported in a previous work (Apicella et al. 2002, D'Anna et al. 2009).

2.2 Set-up and procedures

A home-built temperature controlled system, operated under high-vacuum [$P=10^{-6}$ mbar], was used for separating the lighter from the heavier fractions of tars. The system, whose scheme is reported in Fig.1, is constituted by an annealing chamber and a pumping system (a rotary pump and a turbo pump in series, for reaching the high-vacuum).

The samples were introduced into the crucible at ambient temperature and brought at high vacuum (10^{-6} mbar), after then the sample was heated and kept at a temperature of 200°C for 1 hour.

A fused silica window was placed at the top of the annealing chamber (Fig.1), working as plug of the crucible and serving as a suitable substrate for applying optical microscopy and spectroscopy to the condensed/deposited material. After the heating treatment, the material left in the crucible (bottom fraction) and that condensed on the fused silica plug (top fraction) were recovered by solvent washing for the following characterization. In most cases, the bottom fraction was fully recovered in dichloromethane (DCM). In the case of partial solubilization, the insoluble material was recovered by dissolution in N-methyl pyrrolydinone (NMP). The solutions of the two fractions were further analysed by UV-Visible (UV-Vis) absorption spectroscopy and GC-MS.

UV-Vis spectroscopy and optical microscopy were applied also directly on the films of condensed samples deposited on the fused silica plug.

Figure 1: Experimental set-up: the high-vacuum annealing chamber for the thermal treatment (left) and the crucible with the fused silica plug (right).

2.3 Analytical methods

GC-MS

The GC-MS instrument, used for the qualitative and quantitative determination of PAH, was an Agilent HP6890/HP5975. The gas chromatograph was equipped with a DB-5ms capillary column (60 m × 0.25 mm i.d., 0.25-mm film thickness). Helium was used as carrier gas with a constant flow of 1.0 mL min^{-1}.

UV-Visible absorption spectroscopy

UV-Vis spectra of materials on the plugs, as well as of the top and bottom fractions, dissolved in DCM or suspended in NMP, were measured on HP 8453 Diode Array spectrophotometer. In the case of the 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 down to 250 and 260 nm for DCM and NMP, respectively.

Polarized light microscopy

Prior their dissolutions in solvents, the fractions condensed on the fused silica plug, were observed with a transmitted light polarizing microscope (Optika B-500POL-I).

The microscopic analyses were performed using plane polarized and cross-polarized light.

3. Results and discussion

In the case of pure coronene, heating for one hour at 200°C and $P=10^{-6}$ mbar resulted sufficient for evaporating about 60wt.% of the loaded material. GC-MS and spectroscopic analysis confirmed that both the top and the bottom fractions are constituted of unaltered coronene. The spectrum acquired directly on the fused silica plug presented the fine structure of coronene spectrum measured in solution, superimposed on a background probably due to the thin-film deposited. The background was found also for deposition of soot extract samples and deserves further work to establish its source.

In the case of heat treatment of the PAH mixture, about 30wt.% of the starting mixture evaporates. The distribution evaluated by GC-MS of both the Mix PAH evaporated and deposited on the top and in the bottom of the system included all the PAH of the starting Mix PAH, but enriched in the lighter PAH in the top fraction and in the heavier PAH in the bottom fraction.

Finally, 30wt.% of soot extract was evaporated and deposited on the top plate, whereas about 50wt.% was left in the crucible. In all the cases about 20wt.% of the material was lost inside the vacuum pump.

The observation under microscope of the deposited materials on the fused silica plug, obtained after thermal treatment of the three samples, (reported in Fig.1) revealed that the deposited film was homogeneous only in the case of coronene. The coronene deposit (left column of Fig. 1) is characterized by typical geminated crystals with acicular habit, in accordance with the normal crystallization form of coronene, (monoclinic, space group $P2_1/a$) (Piotrovskii, 1955; Fawcett and Trotter, 1966).

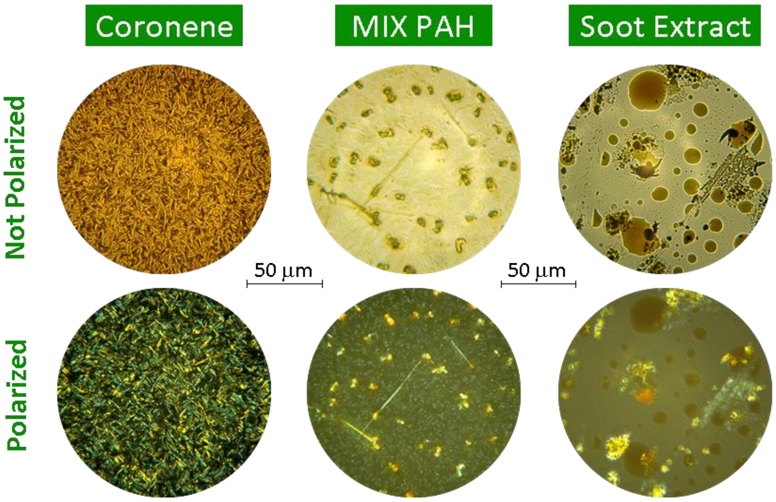

Figure 1: Microscopic images of the top fractions deposited on the fused silica plug after thermal treatment of coronene (left), PAH mixture (center) and Soot Extract (right) with not polarized and polarized light.

The top fraction deposited from the PAH mixture (Fig. 1, middle column) exhibits two main phases: 1) small crystallites similar to those observed in the coronene deposit, and 2) large elongated crystals). The rotation in cross-polarized light shows also that both phases are anisotropic.

In the case of the flame-formed tar, the deposition showed both crystalline and amorphous phases in form of large liquid-like spherules (Fig. 1, right column).

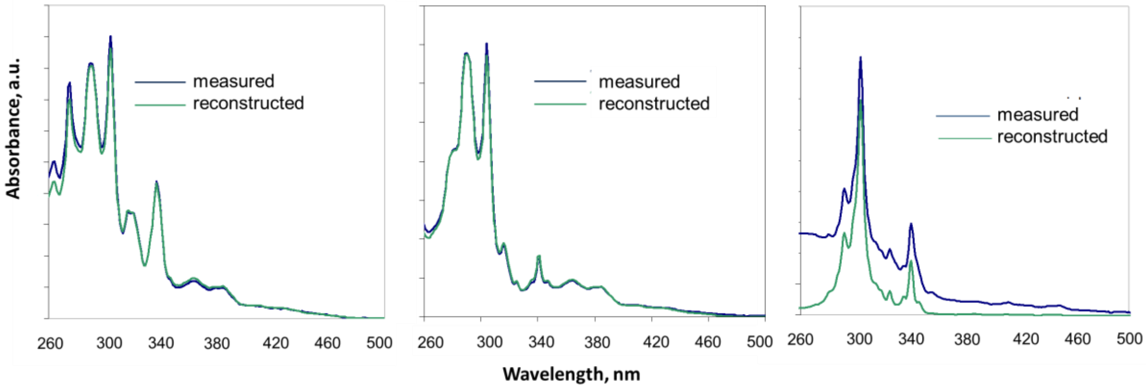

Figure 2: UV-visible spectra of the PAH mixture (left), PAH top fraction collected on the fused silica plug (center) and PAH bottom fraction (right) compared with the reconstructed spectra.

The UV-Vis spectra of the original PAH mixture and of the top and bottom fractions in DCM solution, reported in Fig.2, show sharp peaks due to individual PAH components.

The UV-Vis spectra in DCM solution of the original PAH mixture and of the top and bottom fractions have been reproduced with a suitable mathematical procedure based on the linear combination of the UV-Vis spectra of the individual PAH. The reconstruction procedure works well as shown by comparing the measured and reconstructed spectra reported in Fig. 2. The weight distribution of PAH into the top fraction used for the spectra reconstruction procedure shows the enrichment in the heavier PAH in the top fraction, as shown in Table 1, where the PAH wt.% distribution evaluated in the top fraction is compared with the original distribution into the Mix PAH. This finding is consistent with the PAH volatility and in fair agreement with the GC-MS analysis of PAH in the top fraction.

In the case of bottom fraction, the reconstruction procedure revealed the significant presence of a background whose origin will be object of future work.

The UV-Vis spectrum of soot extract and its top and bottom fraction in solution are reported in Fig. 3. It is noteworthy that the spectrum of the top fraction acquired directly on the fused silica plate (not reported here) showed the disappearance of the fine structure measured in the case of coronene and PAH mixture.

The UV-Vis spectrum of soot extract in DCM solution is reported in Fig.3 along with the reconstructed spectrum, on the basis of the PAH percentage evaluated by GC-MS. The difference between the measured and the reconstructed spectrum is an unstructured background due to heavier aromatic chromophores also present in the tar.

Table 1: PAH wt.% distribution into the starting mixtures and into the top fraction

	PAH Mixture, wt.%	PAH Top Fraction, wt.% (by UV-vis spectra reconstruction)
Pyrene	34.2	3.0
Indeno[1,2,3-cd]pyrene	33.5	38.2
Benzo[b]chrysene	17.6	31.9
Pentacene	3.2	4.9
Coronene	11.5	22.8

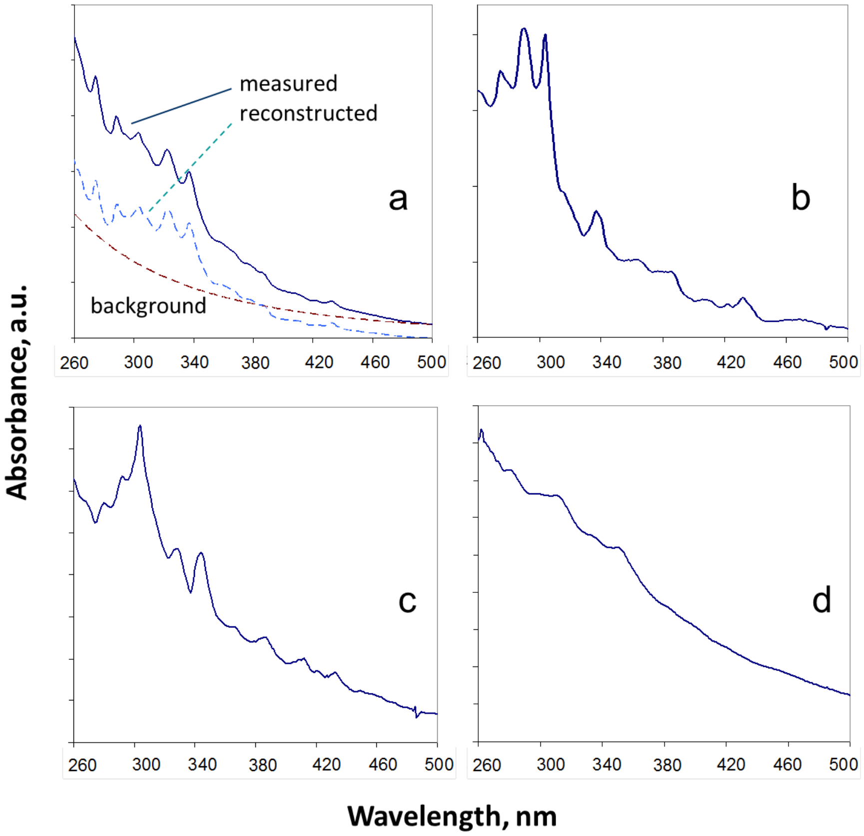

Figure 3: UV-Vis spectra of soot extract (measured and reconstructed) (a), top fraction of soot extract (b), DCM-soluble of the bottom fraction (c), DCM-Insoluble of bottom fraction (d).

Also the UV-Vis spectrum of the top material, dissolved in DCM reported in Fig.3, presents a background under the fine structure, confirming the presence of heavier MW material with respect to PAH, already observed by optical microscopy. Therefore, although 30-40% of flame-formed tar is constituted of PAH (Apicella et al. 2002), a high-vacuum treatment, able to evaporate standard PAH, is not able to separate them from the heavier fractions present in tar.

It is noteworthy that the bottom fraction did not completely dissolve in DCM requiring further spectroscopic analysis on both the DCM soluble and insoluble fractions. The fraction not soluble in DCM was instead dissolved in NMP for the spectroscopic analysis. Their spectra, reported in Fig.3, show the co-presence of PAH and high-MW aromatic species in the DCM-solubles opposed to the almost total absence of PAH in the DCM-insoluble fraction.

It is conceivable that PAH interactions with the heavy matrix featuring the tar, are so strong to cause the dragging of some of the heavier fraction of tar during their evaporation. PAH and such heavy material could be just the species responsible for the crystalline and liquid-like morphology, respectively, before observed by microscopic analysis.

4. Conclusions

In the present work a fractionation method based on moderate heating in high-vacuum conditions (10^{-6}mbar) has been set up and preliminarily tested on a single polycyclic aromatic hydrocarbon (coronene) and on a PAH synthetic mixture. The procedure was subsequently applied to a typical sample of tar extracted from flame-formed soot for inferring the structure/composition of flame-formed PAH contained in the soot extract and for inferring their self-organization in coalesced amorphous and/or crystal forms. GC-MS, optical microscopy and spectroscopy have been applied on the separated fractions (top and bottom). The PAH evaporation was effective only in the case of PAH mixture and the quality of the obtained film on the top was high only in the case of the single PAH.

The effectiveness of the separation performed with this high-vacuum heating procedure depends on the complexity of the starting materials. However, the thin films obtained with this technique allowed performing microscopy in order to obtain information on the self-organization of these condensed species. Moreover, the use of a fused silica substrate allows the direct acquisition of an UV-visible spectrum, avoiding the time-consuming solubilisation in solvent.

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