

COMPARATIVE ANALYTICAL CHARACTERIZATION OF TWO CARBONACEOUS BINDERS USED IN REFRACTORY MATERIALS

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ABSTRACT

The introduction of carbon compounds into refractory materials leads to significant improvements in technological properties, especially with regard to thermal shock resistance. However, regulations are becoming more stringent due to negative impact on human health and the environment. In this context, organic binders such as coal tar pitches containing high levels of polycyclic aromatic hydrocarbons are of particular scientific interest. Despite intensive research, their specific chemical composition is still not completely clarified. In this study, two commercial binder systems with different softening points used in refractory materials were investigated. For this purpose, a non-target approach was applied. Due to the complexity of the samples and the large fractions of semi- and non-volatile compounds, a combination of different analytical methods was applied. In particular, high-resolution time-of-flight mass spectrometry (HR-TOFMS) proved to be a powerful tool for gaining deeper insights into the structure of these samples, such as molecular weight distribution or aromaticity. In addition, further information on the occurrence and distribution of heteroatomic compounds such as S-, N- and O-derivates could be obtained.

INTRODUCTION

Coal tar pitches (CTP) are an important raw material for the production of carbon-containing refractory materials. The purpose of carbon is the significant improvement of the materials properties. This includes increased thermal shock resistance due to improved thermal conductivity as well as wear reduction due

to reduced slag infiltration depth¹. While the property-improving character of CTP binders is undisputed, the exact chemical composition remains unclear. This is particularly problematic in the context of the increasingly stringent regulations with regard to environmental and health protection. Polycyclic aromatic hydrocarbons (PAH), which have been shown to have carcinogenic and mutagenic properties, are mainly the focus of attention. In this context especially the 16 EPA-PAHs with their lead component benzo[a]pyrene were frequently investigated². Apart from this, CTP are often classified by their average structures through elemental analysis, by their solubility in organic solvents or their softening points³. Due to their complexity non-target analyses have been performed by a combination of different analytical methods, in particular mass spectrometry⁴⁻⁶. However, the analysis of pitches is characterized by the non-inclusion of heteroatomic compounds which is justified by the small proportion of heteroatomic elements⁶. This is unsatisfying, since the hazard potential of S-, N- and O-derivatized polycyclic aromatic hydrocarbons has been known for a long time and is in no way inferior to that of pure hydrocarbons⁷. It was not until 2020 that heteroatomic compounds in solid pitch samples were first considered and analysed by APPI-FT ICR MS and MALDI-FT ICR MS after Soxhlet extraction⁸.

The focus of this work was the separated analysis of heteroatomic compounds containing sulphur, nitrogen and oxygen. For this purpose, two CTP-binders with different softening points were investigated by the application of different analytical techniques. The

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samples were classified into specific compound classes. Thus, deeper insights into the occurrence, abundance and molecular weight distribution of the individual compound classes were obtained.

EXPERIMENTAL

Sample material

The samples analyzed in this work are two specially modified coal tar pitches that are used as binders for the manufacturing of refractory materials. Carbores[®] P (P) is present as a fine powder with a softening point of 235 °C. Carbores[®] F 112M (F) is a granule with a softening point between 109-115 °C.

Solvent extraction

Fractionation was carried out by sequential solvent extraction with n-heptane and toluene. For comparable results, granular F was grinded while P was used in its original powder form. CTP powder and n-heptane were mixed with a solute-solvent ratio of 1 g/25 ml. The extraction was performed in an ultrasonic bath for 2 h to ensure the complete dissolution. The solution was then filtered through a 0.6 µm quantitative filter to obtain heptane-soluble (HS) and heptane-insoluble (HI) fractions. After drying at 50 °C the HI fraction was extracted with toluene using the same procedure as above. Toluene-soluble (HI-TS) and toluene-insoluble (HI-TI) fractions were obtained.

Elemental analysis

The amount of carbon, hydrogen, nitrogen and sulphur was determined by inert gas fusion technique with an IR-Detector and thermal conductivity measurements (Elementar, Langenselbold, Germany). The oxygen content was calculated by difference.

Thermogravimetric analysis

Thermogravimetric analysis was performed on a STA 449C Jupiter (Netzsch, Selb, Germany). 20 mg of the samples were heated up from 25 °C to 1500 °C with a heating rate of

10 K/min in an atmosphere of argon (flux = 30 ml/min).

GC x GC – HR-TOFMS

GC x GC measurements were conducted using an Agilent 7890A gas chromatograph (Palo Alto, CA, USA) equipped with a Leco Pegasus HRT 4D (Leco, St. Joseph, MI, USA). As column combination a BPX50 (60 m x 0,25 mm; film: 0,25 µm) as the first dimension and a BPX1 (2,4 m x 0,1 mm; film: 0,1 µm) as second dimension was used. The samples were vaporized using a temperature gradient from 50 °C up to 350 °C (10 K/s) with a holding time of 10 min in the end (OPTIC 4, GL Science, Eindhoven, Netherlands). Helium was used as carrier gas. The HR-TOFMS was operated at 100 Hz within a mass range of $15 \leq m/z \leq 500$. Electron ionization took place at 70 eV at a source temperature of 300 °C.

DIP – HR-TOFMS

DIP-HR-TOFMS were performed on a Leco Pegasus HRT 4D (Leco, St. Joseph, MI, USA) which is equipped with a direct inlet probe system (SIM GmbH, Oberhausen, Germany). The solid CTP was transferred directly into the ion source. A temperature gradient from 40 °C up to 400 °C (2 K/s) with a final holding time of 2 minutes was applied. Acquisition rate and range were set as 1 Hz and $50 \leq m/z \leq 800$, respectively. Triple determination was performed.

Data processing

GC x GC-HRMS data were processed using the ChromaTOF software (Leco, St. Joseph, MI, USA) and home-built Matlab-scripts (R2020b, the Mathworks Inc., Massachusetts, USA). Briefly, all mass spectra were postcalibrated based on fragments of the internal standard PFTBA. To reduce spectral noise and processing time only peaks with a signal-to-noise ratio $s/n > 10$ and within the areas $RT1 \in [1000 \text{ s}, 8500 \text{ s}]$ & $RT2 \in [4450 \text{ s}, 6800 \text{ s}]$ or $RT1 \in [3000 \text{ s}, 7400 \text{ s}]$ & $RT2 \in [1900 \text{ s},$

2800 s] or $RT1 > 8500$ s & $RT2 > 5000$ s were considered. The base mass of each peak was then assigned to a molecular formula with the form $C_cH_hN_nO_oS_s$ based on its exact mass. Boundary parameters were defined as $2 \leq c \leq 100$, $2 \leq h \leq 100$, $n \leq 2$, $o \leq 2$ and $s \leq 1$ and an error of 5 ppm was allowed. Furthermore, only compounds with a maximum number of three heteroatoms, an H/C ratio within the interval [0.4, 2.4] and a number of double bond equivalents within the interval [0, 50] were allowed for comparison. All peaks were checked against the NIST 02 MS library. The minimum spectra similarity was set to 850.

DIP-HRMS data were processed using the ChromaTOF software (Leco, St. Joseph, MI, USA) and home-built Matlab-scripts (R2020b, the Mathworks Inc., Massachusetts, USA). All features with less than 100 counts and PFTBA-specific fragments with an error window of 5 ppm were removed. Sum formula assignment was then performed for all features according to smallest mass difference and lowest heteroatomic content. The used parameters are analogous to those described above.

RESULTS AND DISCUSSION

The results of the elemental analyses, solvent extractions and thermogravimetric measurements are summarized in Tab. I. The elemental compositions of both samples are similar with carbon and hydrogen as main components. However, the heteroatom content is slightly higher in P compared to F, which is particularly due to the higher oxygen content. The lower H/C ratio in P indicates a lower degree of saturation. This is consistent with the lower solubility in heptane and toluene and the higher residual carbon content that could be observed in the thermogravimetric measurements. Together with significant differences in the softening points, the volatile, low molecular weight fraction seems to be larger in F than in P.

Tab. I. Elemental composition, weight percentages of solvent-separated fractions and coke residue after heating up to 1500 °C

	P	F
C in wt %	91.02	91.79
H in wt %	4.07	4.80
N in wt %	0.93	0.84
O* in wt %	3.03	1.48
S in wt %	0.50	0.52
Others in wt %	0.45	0.57
H/C atomic ratio	0.53	0.62
HS in wt %	0.9	8.2
HI/TS in wt %	42.4	40.3
HI/TI in wt %	56.7	51.5
TG residue (1500 °C, Ar) in %	63.3	52.1

* by difference

Fig. 1 shows the results of the GC x GC experiments. By hyphenating mass spectrometry to GC x GC, a mass spectrum of the corresponding separated compound is available for each peak in the chromatogram. These mass spectra can then be used for matching against the NIST database on the one hand. On the other hand, a molecular formula can be assigned to each base peak, which allows to draw conclusions about the structure of the compound, such as ring size or elemental composition. A comparison of sum formulas and retention times shows that the ring size of the base peaks increases with increasing retention time in the first dimension (RT1). The maximum number of double bond equivalents (DBE) is reached at $DBE = 17$ for both samples, corresponding to 6-ring aromatics such as benzo[ghi]perylene. However, the molecular mass distribution within this range differs significantly between the two samples which is consistent with the results from thermogravimetric analyses and solubility. While P is composed entirely of aromatic compounds, a small fraction of saturated hydrocarbons with chain lengths between 10 and 15 can be observed in

F. Moreover, F shows intense peaks in the region of 3- and 4-ring aromatics, which are particularly due to phenanthrene and anthracene ($C_{14}H_{10}$) as well as pyrene and fluoranthene ($C_{16}H_{10}$). Intense oxygen heteroaromatics such as dibenzofuran ($C_{12}H_8O$) and xanthene ($C_{13}H_9O$) also occur in the same range. Nitrogen-containing intense compounds are 9H-carbazole-9-methanol ($C_{13}H_{11}NO$) and acridine ($C_{13}H_9N$). Dibenzothiophene ($C_{12}H_8S$) represents the most intense sulphur compound.

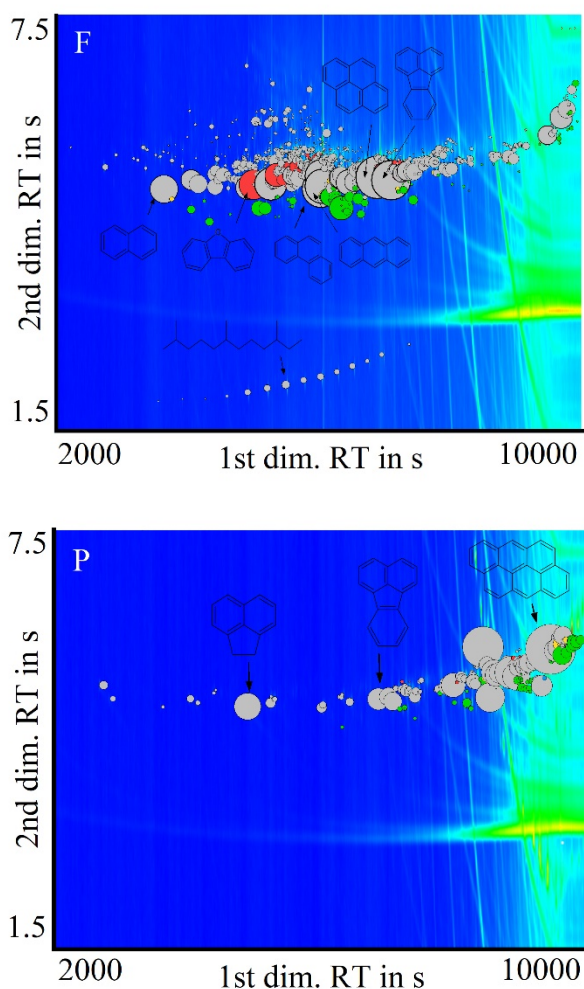


Fig. 1. GC x GC-chromatograms after peak picking and classification of base peaks into the four classes: CH (grey), N (green), O (red) and S (yellow). Chromatograms are shifted 1.5 s in the second dimension to adjust wrap-around. Peak areas are represented by bubble sizes.

Intense areas from 9000 seconds are due to column bleeding.

In comparison, the compounds in P are clearly shifted towards higher molecular weights. The 5- and 6-ring aromatics predominate, such as benzo[k]fluoranthene ($C_{20}H_{12}$), indeno[1.2.3-cd]pyrene ($C_{22}H_{12}$) and indeno[1.2.3-fg]naphthacene ($C_{24}H_{14}$). The amount of heteroatomic compounds is very low in this fraction. However, some intense nitrogen compounds can be detected, mainly attributable to dibenzocarbazoles and naphthocarbazoles ($C_{20}H_{13}N$).

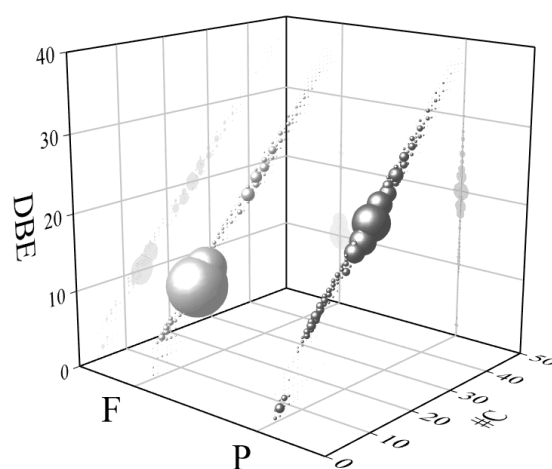


Fig. 2. 3D-Isoabundance plots of double bond equivalents (DBE) vs. carbon number (#C) for the compound class of hydrocarbons detected by DIP-HRMS. Bubble sizes represent normalized peak areas.

Due to limited temperature range of GC x GC in combination with a large semi- and non-volatile fraction of CTP-binders, additional DIP-HRMS experiments were performed. Because of the reduced pressure inside the ion source, the boiling points of the compounds are shifted to lower temperatures⁹. This allows the investigation of the semi-volatile fraction. The gradual increase in temperature results in a slight separation of the sample based on different boiling points.

Fig. 2 shows the molecular-weight-distribution of the hydrocarbons. It is shown that the highest intensities for F are obtained at 10 DBE and 12 DBE, whereas the most intense peaks in P are at 18 DBE and 20 DBE. In general, ions with up to 50 DBE could be detected in both samples. The low fragmentation is caused by the stability of polycyclic aromatic hydrocarbons due to their delocalized π -electrons and the resulting stabilization of the charge. In contrast, alkyl side chains tend to fragment. The resulting fragment ions always have 0.5 DBE due to the absence of rings or double bonds and the typical elimination of one hydrogen. The low intensity of these ions together with the strong orientation of the remaining ions along a diagonal in the isoabundance plots suggests a very low degree of alkylation for both samples (Fig. 2).

For the investigation of different heteroatomic species, all detected ions were assigned to a substance class based on their exact masses. The elemental composition of the samples can then be calculated based on these results.

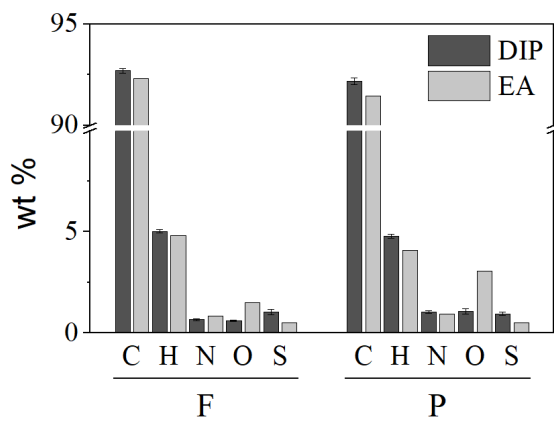


Fig. 3. Comparison of elemental compositions of both CTP-binders. The light grey bars represent the results of elemental analyses, whereas the dark grey bars represent calculated elemental composition using DIP-HRMS data. Error bars represent the standard deviation through triple determination.

A comparison with the elemental analyses is shown in Fig. 3. The results of these two analyses agree very well. In both cases, carbon and hydrogen represent the largest mass fraction. In addition, the amount of oxygen and nitrogen is greater in P than in F, while the amount of sulphur is slightly lower. The variance in the absolute values can be explained by the limitations of the DIP analysis. While in elemental analysis the entire sample is examined, in mass spectrometry the transfer of the components into the gas phase is a necessary criterion. Therefore, very high molecular weight compounds are underrepresented in this method. Nevertheless, DIP analysis offers a reliable possibility for the investigation of the semi-volatile fraction.

The amount of different compound classes is even more interesting than the elemental composition of the samples (Fig. 4). In both samples the compound classes N, S, O, NO and NS are the most abundant ones along with the class of hydrocarbons. It can be observed that all heteroatomic compound classes, except for S and SO, have a higher relative abundance in P than in F.

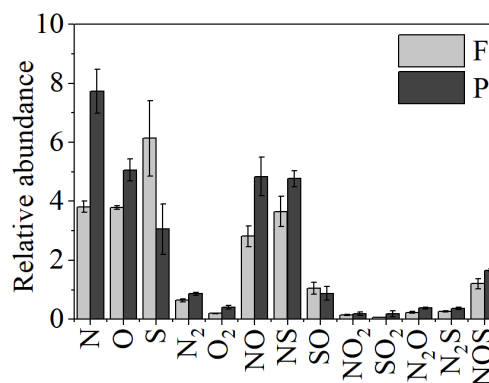


Fig. 4. Normalized abundances of all assigned compound classes with a minimum of one heteroatom detected by DIP-HRMS measurements.

The two samples can already be distinguished from each other by their different relative abundances of substance classes. However, more significant differences are revealed by

molecular weight distribution analysis (Fig. 5). F shows the most intense signal at 9 DBE for the compound classes N, O and S. This is due to the 3-ring aromatics $C_{12}H_9N$, $C_{12}H_8O$ and $C_{12}H_8S$, which are very intense heteroatomic compounds in the GC x GC experiments, too. It is also observed that almost no ions are detected in the range of 5-ring aromatics within these three compound classes. It is only from 17 DBE that more intense compounds appear again. In the case of P intense signals of the classes O, N, S, and NS appear only for higher molecular weight compounds of 17 DBE and above. This is noticeable because this mass range can no longer be investigated by GC x GC experiments. This proves the potential of the direct inlet measurements especially for samples with a large fraction of semi-volatile compounds. In contrast to the substance classes with one heteroatom, the substance classes with several heteroatoms such as NS, NO and NOS behave similarly in both samples. The compounds of these classes are more evenly distributed over a certain mass range than it was the case especially for F. But here, again, the shift into a higher mass range is clearly visible for P in contrast to F.

Another interesting observation is the strong orientation on a diagonal line for all compound classes as already seen for the class of hydrocarbons. The slope of this planar limit is an indication for the growth of the aromatic ring system. The linear and nonlinear integration of benzene rings to an existing aromatic system leads to slopes of 0.75 and 1, respectively. In contrast, the integration of saturated rings leads to a slope of 0.25¹⁰. Zhang showed that the planar limit of hydrocarbons in CTP has a slope of 0.78, indicating that linear and nonlinear addition of benzene rings is the dominant mechanism¹¹. For these samples, the slopes for all compound classes range from 0.75 to 0.85, suggesting that this mechanism is also prevalent for heteroaromatic compounds.

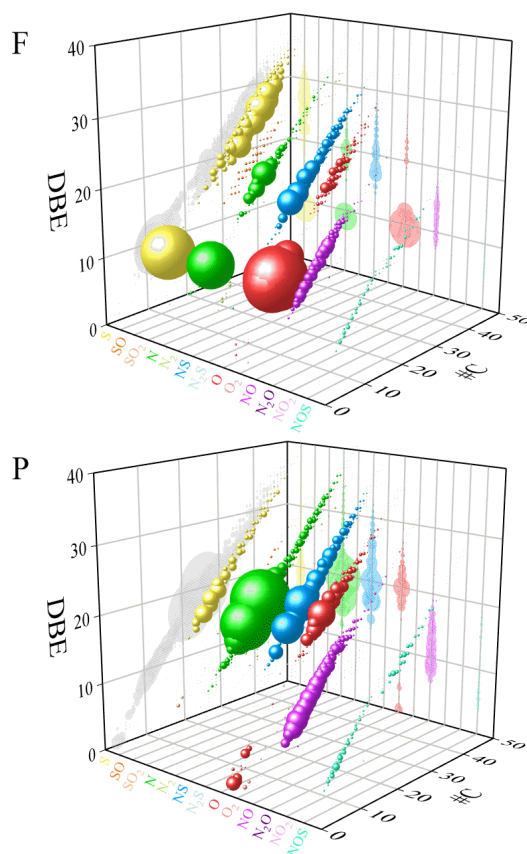


Fig. 5. 3D-Isoabundance plots of double bond equivalents (DBE) vs. carbon number (#C) for all compound classes with a minimum of one heteroatom detected by DIP-HRMS. Bubble sizes represent normalized peak areas.

CONCLUSIONS

Different analytical methods were conducted to investigate two organic binders in terms of their elemental composition and molecular structure. Significant differences in their molecular weight distribution were observed. In this context, it was shown that DIP-HRMS proved to be extremely useful, especially for the higher molecular weight sample P. With respect to the study of heteroatomic compounds, mass spectrometric analysis was shown to be a robust method to separate different classes of compounds. Thus, the rule of planar limits known for hydrocarbons could be adapted to heteroatomic compound classes in CTP.

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