Change of chemical bonding of nitrogen of polymeric \( N \)-heterocyclic compounds during pyrolysis

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Abstract

Pyrolysis experiments were carried out with polymeric model compounds containing defined forms of bound nitrogen. The chosen compounds, polyvinylcarbazole, polyvinylpyridine and polyvinylpyrrolidone, were pyrolysed in a fixed bed annular reactor at 873 and 1173 K. The functionalities of the nitrogen in the precursors as well as that in the derived chars were determined by X-ray photoelectron spectroscopy (XPS). Additional information about the structure was received from FT-IR, solid-state \(^{13}\)C-NMR and, in part, X-ray absorption near edge structure (XANES) spectroscopy. The application of different analytical methods should result in a more reliable classification of the N 1s electron binding energies than is possible by the sole use of XPS. It is interesting to note that the nitrogen in five-membered rings (N-5) of the \( N \)-heterocyclic compounds remains in existence in the high temperature products. In the case of the carbazole system it is still the dominant bonding form. The high-temperature char from polyvinylpyridine contains nitrogen in both five- and six-membered rings. It may be concluded that the behaviour of the nitrogen during pyrolysis does not only depend on its functionality but also on its chemical environment. A comprehensible mechanism of the transformation of N-6 into N-5 nitrogen is discussed on the basis of the FT-IR and solid-state \(^{13}\)C-NMR spectra of the low temperature chars. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Special attention has been paid in recent years to the study of functional forms of nitrogen in coals and coal-derived products. Some research work has been done to explain the transformations of these functionalities occurring during pyrolysis, and to find some relation to the formation of nitrogen oxides from coal- and char-N under oxidizing conditions. The mechanisms causing changes in nitrogen functionalities in coals are manifold and only partly understood. This can be attributed to the molecular structure of coals and their relatively low content of nitrogen compared to that of other heteroatoms. From this point of view it can be seen that the substitution of the coal by model compounds in basic studies bears some advantages. The nitrogen content is much higher, in the case of the compounds used in this work about ten to 15 times higher than those of a local brown coal. The chemical environment of the nitrogen atoms is well-defined and the understanding of the proceeding mechanisms will be simplified.

Above all, X-ray photoelectron spectroscopy (XPS) and more recently X-ray absorption near edge structure (XANES) spectroscopy have been used to determine nitrogen bonding in coal, coal-related products and carbonaceous materials \([1–3]\). By the utilization of model compounds it should be possible to conclude more successfully on fundamental mechanisms of nitrogen retention in chars and its release during thermal treatment than by the utilization of coal.

The applicability of XPS as well as the spectra-fitting procedures with respect to the identification of nitrogen functionalities have been improved within the last years. It has been shown by several authors that the pyrrole and...
pyridine types are the most abundant forms in coals [1,2,4–7]. However, in most cases three components are required to achieve an acceptable fit of the N 1s spectra of coals and their pyrolysis chars. This additional peak at ~401.5 eV is assigned to quaternary nitrogen, N-Q [8–15].

There is still an uncertainty concerning the identity of the component at 401.5 eV. Kambara et al. [7] found a relation between quaternary nitrogen and NH yields due to pyrolysis, suggesting that this peak represents secondary amino groups. According to some experiments with different coals Boavida et al. [16] assumed protonated amines. Buckley [15] described not less than eight possible reasons for a component with such a binding energy, started from an excited final state satellite to an artefact of charging. Finally he suggested that this component must be assigned to protonated or oxidized pyridinic nitrogen. However, the appearance of oxidized pyridinic N at 401.5 eV is doubtful. Some high-severity pyrolysis chars of model compounds containing pyridine-N-oxide showed an additional peak in their N 1s-spectra near 403.5 eV [13,14,17]. Boavida and Zhu et al. [16,18] found, with some coals, a component at this binding energy and assigned it to N-oxide. An artefact due to surface preparation can also not be excluded. Later Nelson et al. [11] concluded from their investigations that the component near 401.5 eV must be closely related to pyridinic N in an environment of low electron density. Pels et al. [14] attributed N-Q to various forms of quaternary nitrogen as part of a larger aromatic structure, i.e. protonated pyridinic N in coals and six-membered ring nitrogen in graphene structures. Stanczyk et al. [13] concluded from their studies that N-5 can also be the origin of quaternary nitrogen.

From the reviewed literature it can be concluded that quaternary nitrogen in coal does not occur in the same form as in its pyrolysis chars or in model compound chars. This finding was already stated by Pels et al. [14].

The assignment of components with a lower intensity than the above mentioned dominating forms is sometimes uncertain, too. Wojtowicz et al. [12] tried to fit XPS spectra using an additional binding energy of 399.4 corresponding to amino-type nitrogen. A reliable assignment of this peak between the pyridinic and the pyrrolic ones seems to be impossible. Besides this a slight shift of the spectra towards higher binding energies has to be considered with some samples. In these cases the component at 399.1 eV can also represent small amounts of pyridine. An N 1s value higher than 399.0 eV was determined by Beanmon and Briggs [19] for pyridine compounds. They measured 399.3 eV for two different polyvinylpyridines. Stanczyk et al. [13] found a peak at 399.1 eV assigned to CN groups with low temperature chars of 9-cyanoanthracene.

From analytical data it can be concluded that some nitrogen functionalities have similar binding energies. For example there are two possible structures with more than one nitrogen atom within the aromatic ring which can overlap the pyrrole peak: pyrimidinidine and pyrazine with binding energies of 400.0 and 400.9 eV, respectively [20]. In these cases the part of the five-membered ring nitrogen would be overestimated. Another compound containing two nitrogen atoms is pyridazine causing a peak at 401.3 eV in the N 1s spectra. This component could be a further explanation for the XPS signal at this binding energy. However, the probability of the occurrence of such structures in coals and coal-derived products as well as their formation due to pyrolysis and gasification of carbons is supposed to be too low to form distinct peaks within the spectra.

Special attention has been paid to pyridone and its tautomeric enol form – hydroxypyridine – as six-membered ring compounds with a binding energy near 400.3 eV. It is not distinguishable from pyrrole and can therefore not be identified convincingly by XPS N 1s spectra. This component was found by application of XANES spectroscopy by some researchers [1–3,18]. Stanczyk and Pels et al. [13,14] also assumed pyridone but they could not quantify its amount. Pyridone and pyridine-N-oxide are closely related because of the occurrence of oxygen in the organic ring structure [1]. Zhu et al. [21] assigned a peak at 401.5 eV to pyridone in their XANES studies of several carbonaceous materials. The occurrence of this peak was found to be closely related to partially gasified carbons, irrespective of the parent model compounds. The authors concluded that pyrrolic nitrogen has been converted to pyridinic and pyridone functionality during gasification.

The utilization of model compounds has been given a strong rise in the understanding of the stability and the mechanisms of transformation of nitrogen functionalities during carbonization and their incorporation within the carbon layer. It is acknowledged that during thermal treatment of nitrogen-containing carbon materials (acridine, polyvinylpyridine, carbazole) part of the pyrrolic and pyridinic N is converted into the quaternary form [12–14]. N-6 and N-Q are suggested to be the most stable forms of nitrogen binding. However, Kambara et al. [7,9] found N-5 to be more difficult to decompose than six-membered rings. Spracklin [22] and others observed also a thermal stability of the pyrrole system in carbazole up to 873 K.

To summarize, there are still some uncertainties regarding the occurring changes during pyrolysis in the chemical bonding of nitrogen in a polymeric or coal-related environment. Therefore the objective of this study has been a certain determination of different N-functionalities in model compounds and their chars by the use of other analytical methods (NMR, IR, XANES) beside XPS.

2. Experimental

2.1. Sample preparation

The model chars were prepared from the following
substances: polyvinylpyrrolidone (Mw 55 000, PVPO), poly-(N-vinylcarbazole) (Mw 1 100 000, PVCA) and poly-
(4-vinylpyridine) (25% cross-linked, PVPI). All polymers
were received from Aldrich, Germany.

The used model compounds were thermally quite un-
stable. They depolymerized nearly completely at tempera-
tures well below the required ones for pyrolysis. To obtain
significant amounts of residual chars the samples were
pre-treated under low temperature conditions in an air
stream at a heating rate of 1 K/min. The objective of the
pre-treatment was to include oxygen into the organic
structure principally to form cross linkings to stabilize the
macromolecules and to avoid early depolymerization. The
success of this procedure was detected by elementary and
thermogravimetric analyses. In Table 1 the chemical
analyses of the parent and the pre-treated samples are
given. The calculated values from the empirical formulas
and those obtained from analyses are compared. The
results agree very well. In the case of PVPI a part of 25
Ma. % divinylbenzene added for crosslinking purposes has
been considered in the calculations. During the preparation
procedure up to 573 K the amounts of oxygen which were
additionally incorporated into the polymers vary from 1.7
to 6.8 wt. % (dry basis). The air treatment at elevated
temperatures leads to a stabilization of the molecule
structure. The DTA/DTG-data of the original and the
pre-treated samples are presented in Fig. 1. The solids
were analysed with a ‘vario EL’ elemental analyser. Espe-
sially for PVPO the effect of oxygen incorporation
into the organic structure is obvious. The low-temperature
oxidation of the model compounds results in a more
gradual mass loss over a wider temperature range than
those recorded for the original sample. The total sample
mass loss at 1173 K is the same or lower for the oxidized
samples compared to that of the original ones.

The pyrolysis experiments were carried out in a fixed-
bed annular reactor. A schematic of the testing installa-
tion is shown in Fig. 2. The pre-treated samples were carbon-
ized under high purity (99.999 vol. %) nitrogen atmos-
phere at temperatures of 873 and 1173 K, respectively,
practising a heating rate of 15 K/min and a soak time of
15 min. The gas was passed from the top of the reactor
through the inner tube and with inverse direction of flow
through the sample placed within the annulus. Liquid
devolatilization products were condensed in the tar trap
and the gas was passed through washing bottles with
H₂SO₄ and NaOH, respectively, to detect the release of the
nitrogen containing gases, ammonia and hydrogen cyanide.
The amounts of these components were determined by
argentometric and alcalimetric titration. The analytical data
of the obtained chars are also given in Table 1.

### 2.2. Analytical methods

The XPS measurements were performed on a VG
ESCALAB 220i XL spectrometer with Mg Kα radiation
(12 kV and 20 mA). Spectra of C 1s, N 1s and O 1s core
levels were recorded (pass energy 10 eV). The energy scale

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**Table 1**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Char yield</th>
<th>Original (calculated)</th>
<th>Original (elementary analysis)</th>
<th>Thermal treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 K/min; air</td>
<td>15 K/min; N₂</td>
</tr>
<tr>
<td>PVCA</td>
<td>Char yield</td>
<td>C 87.01</td>
<td>87.42</td>
<td>85.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H 5.74</td>
<td>5.68</td>
<td>5.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 7.25</td>
<td>7.23</td>
<td>6.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 14.40</td>
<td>14.54</td>
<td>16.26</td>
</tr>
<tr>
<td>PVPO</td>
<td>Char yield</td>
<td>C 64.82</td>
<td>64.82</td>
<td>66.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H 8.17</td>
<td>8.08</td>
<td>4.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 12.61</td>
<td>12.56</td>
<td>12.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 14.40</td>
<td>14.54</td>
<td>16.26</td>
</tr>
<tr>
<td>PVPI</td>
<td>Char yield</td>
<td>C 84.03</td>
<td>84.07</td>
<td>80.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H 7.05</td>
<td>6.95</td>
<td>5.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 8.91</td>
<td>9.13</td>
<td>7.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 14.40</td>
<td>14.54</td>
<td>16.26</td>
</tr>
</tbody>
</table>

* Char yield, related to 573 K sample.
* Oxygen by difference.
* PVPI, crosslinked with 25% divinylbenzene.
was calibrated to reproduce the binding energies of Cu 2p_{1/2} (932.65 eV) and Au 4f_{7/2} (84.00 eV). Sample charging was corrected by the C 1s peak: EB (C 1s) = 284.8 eV. The energy resolution of the instrument was 0.8 eV (FWHM for Ag 3d_{5/2} at a pass energy of 10 eV). The core-level spectra were fitted with the software UNIFIT2.1 for Windows [23] using a least-squares procedure. An analytical model of the peak shape (Gaussian multiplied by Lorentzian) with a mixing ratio of 0.5 and 0.7, respectively (pure Lorentzian peak: 1; pure Gaussian peak: 0) was used. The fitting procedure was based on the FWHM of N 1s which was fixed to 1.8 eV. The samples were prepared on a carbon tape.

FT-IR spectra were recorded by diffuse reflection using a NICOLET 510 analyser. The samples were not penetrated by the infrared-radiation, only the state at the surface was considered in accordance with the XPS spectra. The spectral dispersion of this facility was about 2 cm\(^{-1}\).

Solid-state \(^{13}\)C nuclear magnetic resonance (NMR) spectroscopy has been also widely used in recent years to identify functional forms of carbon within the macromolecule of the coal. Nevertheless, there is still a poor...
knowledge concerning the application of the NMR technique for other elements in coal. The obtained results with $^{15}$N-NMR have been considerably unsatisfactory [24]. There is a great uncertainty about the direct evidence of nitrogen functionalities with NMR. Nevertheless, this technique was used to verify the changes in the organic structure of the polymers occurring during pyrolysis. Above all, the detection of oxygen incorporated into the char matrix due to low-temperature oxidation has been of interest.

The $^{13}$C NMR spectra were recorded with a BRUKER MSL 300 spectrometer using a recording frequency of 75.47 MHz. The TOSS (total suppression of sidebands) sequence with four 180° carbon pulses of 8.8 µs width and a proton pulse width of 5.4 µs was used (contact time 3 ms) to obtain highly resolved spectra.

All parent carbon materials and medium temperature char samples were analysed by these three spectrometric methods. XANES was only used with the char samples of PVPI to enable a comprehensive discussion and clear distinction especially between pyrrole and pyridone. With the applied techniques it should be possible to get more information than by the single use of XPS.

3. Results and discussion

X-ray photoelectron spectroscopy is a surface technique and therefore sensitive to chemical changes in a thin layer on the sample surface. To be able to attribute the information obtained by XPS to the whole sample the O/C and N/C atomic ratios of bulk – determined by elementary analysis – and surface – determined by XPS – were compared. As it is shown in Fig. 3(a) and (b) there is a good agreement between the values obtained by both techniques. The N/C ratios of all samples are in the range of bulk-surface parity indicated by the solid line. Due to these results, the achieved spectra which will be discussed in the following are supposed to represent the state in the
adsorption of H₂O molecules during sample transfer to the spectrometer could not be prevented completely.

Depending on the parent polymeric structure, three to six different nitrogen functionalities were found either as intermediates or in the finally obtained char at 1173 K. The peaks in the fitted XPS spectra were assigned to the functionalities according to the binding energies (Table 2). Additional information was obtained by FT-IR and solid-state ¹³C-NMR spectra.

### 3.1. Polyvinylcarbazole

The XPS-spectrum of the PVCA sample treated in an air stream at 573 K shows a strong peak at 400.4 eV assigned to pyrrolic nitrogen (N-5) and a somewhat smaller peak at 398.0 eV (Fig. 4). This peak corresponds to pyridinic nitrogen (N-6). There is no difference between the spectra

![N 1s XPS spectra of polyvinylcarbazole and its chars obtained at various temperatures.](image)

Table 2

<table>
<thead>
<tr>
<th>N-functionality</th>
<th>Symbol</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridinic</td>
<td>N-6</td>
<td>398.5±0.4</td>
</tr>
<tr>
<td>Pyrolic</td>
<td>N-5</td>
<td>400.5±0.3</td>
</tr>
<tr>
<td>Pyridonic</td>
<td>N-6(O)</td>
<td>400.5</td>
</tr>
<tr>
<td>Pyridonic</td>
<td>N-5(O)</td>
<td>399.6±0.2</td>
</tr>
<tr>
<td>Quaternary</td>
<td>N-Q</td>
<td>401.1±0.3</td>
</tr>
<tr>
<td>N-oxide</td>
<td>N-Ox</td>
<td>402.5–403.7</td>
</tr>
</tbody>
</table>

bulk as well. The O/C ratios deviate with all samples more from the parity line than the N/C ratios. This phenomenon can be explained by surface reaction with residual oxygen in the experimental set-up or adsorption of water molecules after sample preparation. Although the pyrolysis chars were ground and stored under inert atmosphere the
of the residue obtained at 573 K and the chars after further pyrolysis under nitrogen at 873 K. The fraction of pyridinic N-6 increases only at a pyrolysis temperature of 1173 K and an additional peak occurs at 401.2 eV suggesting to represent quaternary nitrogen (N-Q). The conversion of N-5 to N-6 and N-Q under pyrolysis and gasification conditions has been already shown by Pels and Zhu et al. [14,21]. Despite the proposed conversion mechanisms the majority of the original N-5 survives and it remains the dominant form of bond. If the char yield is taken into consideration a high degree of depolymerization has to be noticed. This mass loss is assigned to devolatilization of complete carbazole molecules caused by cleavage of vinylgroups.

3.2. Polyvinylpyrrolidone

Some greater changes occurred during the carbonization of PVPO. The XPS spectrum of the 573 K product has to be decomposed into three peaks to achieve an acceptable fit (Fig. 5). The major component at 399.5 eV is assigned to the nitrogen in the pyrrolidone system (N-5(O)). The two smaller peaks correspond to pyridinic nitrogen and a component at 400.3 eV indicating a secondary product of PVPO (described as N-5(O)'). Because of the five-membered ring origin of this component it is suggested to represent pyrrole-type nitrogen. At a temperature of 873 K the pyrrolidone peak disappears completely whereas the fraction of the two other components increases to nearly

![Fig. 5. N 1s XPS spectra of polyvinylpyrrolidone and its chars obtained at various temperatures.](image-url)
50% each. A component at a high binding energy of 403.7 eV was required within the fitting procedure. This component is assigned to pyridine-N-oxide (N-Ox). The char obtained at 1173 K contains, besides these three functionalities, also a component at 401.4 eV corresponding to N-Q.

Diffuse reflection infra-red spectroscopy was used to improve the peak assignment and to receive additional information about structural changes during the thermal treatment (Fig. 6). The characteristic amide band of the pyrrolidone system at 1660 cm\(^{-1}\) is still in existence with the 573 K sample and disappears during pyrolysis up to 873 K. In accordance with the XPS spectra it is confirmed that the pyrrolidone system is completely converted to other nitrogen-containing compounds. The bands of the methylene groups in the range of 1430–1470 cm\(^{-1}\) appear with a decreased relative intensity compared to the amide band of the pre-oxidized parent polymer. These bands cannot be detected in the 873 K sample. A new band at 1580 cm\(^{-1}\) occurs in the spectra of the pyrolysed PVPO firstly detected as a shoulder of the amide band and as the predominant peak in the high-temperature chars. This band is suggested to be caused by C=O double bonds both in heteroaromatics and in polymer chains. The occurrence of this band in connection with the decrease in intensity of the CH\(_2\) band confirms the beginning of dehydration and aromatization at low temperature sample treatment. However, a definite proof of heteroaromatic substances beside olefinic structures is not possible with the IR spectra. Therefore, solid-state \(^{13}\)C-NMR spectra of the parent PVPO and the char obtained at 573 K were recorded (Fig. 7). The spectrum of the original polymer shows the peaks of carbonyl carbon of the amide group at 177 ppm and of aliphatic carbon both in saturated heterocyclic structures and in side chains at 44, 32 and 19 ppm. In contrast, the spectrum of the pre-oxidized sample contains an additional peak in the range of 95–150 ppm. The maximum of this wide peak lies at about 130 ppm. It can be distinguished between the predominant olefinic double bonds in the peak maximum and the resonance values of the pyridine system at 148 ppm and of the pyrrole system at 120 ppm, located in wide shoulders. The obtained results correspond with those of the XPS spectra. The assignment of the small side peaks in the XPS spectrum of the thermally pre-treated PVPO to N-5 and N-6 therefore has been confirmed. A direct evidence of the formation of pyrrol, which should cause a strong peak in the range of 3400–3500 cm\(^{-1}\) (N–H resonance), is not possible using the diffuse reflec-

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Fig. 6. Diffuse reflectance IR spectra of polyvinylpyrrolidone and its chars obtained by air oxidation at 573 K and subsequent pyrolysis at 873 K.
There is still an uncertainty concerning the interpretation of the peak at 400.5 eV as N-5. The narrowing of aromatic pyridine rings to pyrrole is inconsistent with the thermal stability of pyridine systems. Moreover, there are some other functionalities which might be responsible for the peak around 400 eV. In the case of the used model compound the component in question could possibly also be pyridone. Because of the doubts about the origin of this peak it has been indicated as N-6 representing a daughter product of pyridine.

FT-IR and solid-state $^{13}$C-NMR spectra were recorded to clarify the problem of correct assignment. The IR spectra of the parent PVPI, the product after air pre-treatment at 573 K and the char obtained at 873 K are shown in Fig. 9. In the pre-oxidized sample occurs a peak at 1660 cm$^{-1}$ representing the amide group. This band disappears after further pyrolysis at 873 K. The major peaks of the $^{13}$C-NMR spectrum of the 573 K sample at 150 and 126 ppm are assigned to pyridine (Fig. 10). There is no evidence for the presence of pyrrolic structures with expected bands at 121 and 108 ppm. Moreover, the shoulder on the left-hand side of the peak at 150 ppm and the decreasing intensity of the peak itself ($\alpha$-position of the pyrrole-type nitrogen). This can be attributed to the type of pyrrol, which is not occurring as a single molecule but in close relation to the vinyl group (N–C bond).

The peak shapes in most of the recorded spectra are not well-defined, so it could not be excluded that part of the component at 400.3 eV is caused by pyridone. The formation of pyridine as another six-membered ring structure in the course of the rearrangement indicates also the possibility of occurrence of N-6(O). Undergoing further pyrolysis to the maximum heat treatment temperature, pyridone is unlikely to survive. An explanation for this assumption will be given in the next section. The peak at 400.3 eV in the 1173 K sample is therefore assigned to pyrrole-type nitrogen.

3.3. Polyvinylpyridine

The XPS spectrum of PVPI obtained after 573 K air treatment shows a major peak at 399.5 eV assigned to pyridinic nitrogen and a smaller peak at 400.5 eV which might represent pyrolic nitrogen (see Fig. 8). The part of the component at 400.5 eV increases due to pyrolysis at 873 K. The spectrum of the PVPI char obtained from pyrolysis at 1173 K contains also components at 400.8 and 402.5 eV corresponding to N-Q and N-Ox, respectively.

This reaction was verified by Brent et al. [25] by means of pyrolysis experiments. The carbocyclic analogue to the above mentioned chemical equation represents the pyrolytic elimination of CO from phenol to form cyclopentadiene, reaction (2) [26]:

\[
\text{(1)}
\]

Another elimination reaction can be drawn up to explain...
the transformation of the N-5(O) to the N-5 system, reaction (3):

$$\text{N} = O \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{N}$$  (3)

This process begins at temperatures below 573 K and is completed at 873 K.

The suggested mechanisms point to the improbability of the occurrence of pyridone in high-temperature residues of inert pyrolysis. However, they result from the interpretation of experimental data and from comparison with the reviewed literature. There remain some doubts whether the component at 400.5 eV in the high temperature char originates from pyrrole as a matter of fact. To bring on a definite clarification, XANES spectra were recorded for the series of PVPI chars (Fig. 11). In the pre-oxidized sample no evidence was obtained of formation of pyridone structures. Beside the prevalent peak at 398.9 eV assigned to pyridine-type nitrogen no other component could be determined. This is in contrast to the results obtained from IR analyses. The spectra of the chars obtained from inert pyrolysis at 873 and 1173 K, respectively, show a decrease in the peak intensity of pyridine and a new peak at 401.9 eV which might represent pyridone. However, it should not be possible to produce this type of nitrogen functionality in the oxygen-free atmosphere during the high temperature carbonization. The interpretation of the XANES spectra is of great uncertainty because of the shift in the base line of the 873 K sample and the not well resolved peaks in the 1173 K sample. The latter one might also contain pyrrolic.
Fig. 9. Diffuse reflectance IR spectra of polyvinylpyridine and its chars obtained by air oxidation at 573 K and subsequent pyrolysis at 873 K.

Fig. 10. Solid-state $^{13}$C-NMR spectra of polyvinylpyridine (a) and its char obtained by air oxidation at 573 K (b).

From the pyrolysis experiments one can conclude that the heteroaromatic pyrrole system is considerably stable in carbonized model polymers. It has to be considered in the spectra interpretation of high-temperature residues. Although the fraction of N-5 in the chars of PVCA and PVPO decreases with rising pyrolysis temperature, it remains always the dominant form of bonding in the temperature range studied (Table 3). The fraction of pyrrole-type nitrogen has been somewhat more difficult to determine within the char samples of PVPI. However, some evidence of pyrrole has been found in all chars produced. Pyridone has been detected in pre-oxidized products of polyvinylpyridine. Compared with that, there is a strong decrease of the part of N-6 in the residual chars of PVPO and PVPI in the temperature range from 873 to 1173 K. Simultaneously, N-Q occurs in the XPS spectra. According to Pels and Grant et al. [14,27] it is suggested that the pyridinic ring is preferentially incorporated into the pre-graphitic carbon structure in the form of quaternary nitrogen.

Only with the pyrolysis chars of PVCA no oxidized nitrogen was detected. This phenomenon is attributed to
Table 3
Distribution of nitrogen functionalities in the pyrolysis chars (by XPS) [% N]

<table>
<thead>
<tr>
<th>T [K]/atm</th>
<th>Pyridinic</th>
<th>Pyrrolic</th>
<th>Pyrrolidonic</th>
<th>Pyridonic</th>
<th>Quaternary</th>
<th>N-Oxide</th>
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<tbody>
<tr>
<td>PVCA</td>
<td>573/air</td>
<td>6</td>
<td>94</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>873/N₂</td>
<td>7</td>
<td>93</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1173/N₂</td>
<td>18</td>
<td>61</td>
<td>–</td>
<td>–</td>
<td>21</td>
</tr>
<tr>
<td>PVPO</td>
<td>573/air</td>
<td>18</td>
<td>61</td>
<td>45</td>
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<td>–</td>
</tr>
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<td></td>
<td>873/N₂</td>
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<td>49</td>
<td>–</td>
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<td>4</td>
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<tr>
<td></td>
<td>1173/N₂</td>
<td>32</td>
<td>42</td>
<td>–</td>
<td>–</td>
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<tr>
<td>PVPI</td>
<td>573/air</td>
<td>71</td>
<td>–</td>
<td>–</td>
<td>29</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>873/N₂</td>
<td>70</td>
<td>30</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1173/N₂</td>
<td>32</td>
<td>28</td>
<td>–</td>
<td>–</td>
<td>33</td>
</tr>
</tbody>
</table>

Fig. 11. Nitrogen XANES spectra of PVPI chars.
the small fraction of pyridinic nitrogen formed during pyrolysis. Solely the pyridine system is able to be oxidized to N-oxide.

The quantitative distribution of the nitrogen functionalities in the pyrolysis chars is highly differentiated and it depends strongly on the parent substances. There is no evidence of a leveling of the several spectra even at the highest chosen temperature. These results are in contrast to those obtained by Stanczyk et al. [13]. The outstanding thermal stability of the pyrrole system within a polymer combination was recently shown by Konno et al. [28,29]. The forms of nitrogen bonding of a polymer carbon derived from high-temperature treatment of the polyimide kapton were analysed by XPS. The authors found that pyridine and pyrrole systems were formed. The pyrrolic structures were observed to be predominant at a temperature range from 1100 to 1500 K, and to be in existence up to about 2500 K. The results agree also very well with those obtained by Kambara et al. [7]. The authors concluded from their study the pyrrole-type structures being more difficult to decompose due to pyrolysis than N-6 structures for many coals. However, this is in marked contrast to the results obtained by other researchers [12–14,21]

The determination of the nitrogen-containing gaseous products NH₃ and HCN showed a strong dependence on the parent polymeric structure. PVCA seems again to be the most stable N-heterocyclic polymeric system because only small amounts of ammonia or hydrogen cyanide were detected (Fig. 12). The ring fragments form HCN in a primary step, and ammonia after further reactions with hydrogen or water. The high conversion ratio of the organic bound nitrogen to ammonia is attributed to the soak time of a few seconds in the reactor. Model chars with a higher content of pyridinic structures tend to rupture more easily than those with prevalent five-membered ring systems. So far the obtained results correspond to those found by Kambara et al. [9]. However, one should be careful with a comparison of the several model compounds. The chemical environment of the pyrrole system in carbazole differs from that of the other polymers. The condensed benzene rings cause a higher thermal stability compared to a single pyrrole molecule.

The results of the present paper deviate from those of most other studies dealing with the same subject. It is the authors opinion that the determination of nitrogen functionalities is still difficult, and the peak assignment must be improved by application of other analytical methods.

5. Conclusions

- The identification of several nitrogen functionalities by application of the XPS technique only is complicated and in some cases ambiguous. A better assignment to different types could be possible by combining XPS with XANES and, in the case of model compound studies, with solid-state ¹³C-NMR and FT-IR spectroscopy.
- XANES was used in the case of PVPI to resolve the origin of the XPS peak at 400.5 eV. However, in spite of the application of this technique a clear peak assignment is not really possible.
- Part of the pyridinic N is converted to pyridone due to low-temperature oxidation (up to 573 K) in an air stream. The transformation of the pyridone ring to pyrrole is supposed to be a result of elimination of CO. The obtained IR and NMR spectra indicate that this ring narrowing of a part of the six-membered ring nitrogen occurs in a temperature range from 573 to 873 K.
- Because of the existence of pyrrole-type nitrogen even in high temperature chars [28,29] and the carbonization of pre-oxidized samples in high purity nitrogen atmosphere a formation of pyridone structures seems to be unlikely. Moreover, the occurrence of this functionality at high temperatures does not correspond to reaction (1).
- Pyrrole-type structures within the polymers were found to be more stable in the studied temperature range than expected from the reviewed literature. N-5 is the dominant form of bonding in the high temperature chars of the five-membered ring heterocyclic compounds. In comparison with previous studies it can be assumed that the pyrolysis conditions were too mild to cause a ring expansion of N-5 to form pyridine (N-6).
- There was no N-oxide observed with the pyrolysed PVCA samples. It concluded that the formation of N-Ox is closely related to pyridinic-type nitrogen, which was found to a minor extent in PVCA as compared with the other model chars.

![Fig. 12. Conversion of organic bound nitrogen to NH₃ and HCN during pyrolysis at 873 and 1173 K.](image-url)
The conversion of nitrogen functionalities to N-Q depends on the parent polymer structure. N-6 is converted to a higher extent to quaternary N in the PVPI and PVPO chars whereas N-5 seems to be the main source of N-Q with the PVCA samples.

Further research work is needed to understand the conversion mechanisms of the several nitrogen functionalities. One aspect to be examined in the future should be the influence of pyrolysis conditions on nitrogen bonding and the char yield. As it is shown in this paper, most of the carbonaceous material is volatilised during thermal treatment. Special attention should be paid therefore to nitrogen species in the high-molecular fractions which are released into the gas phase during pyrolysis. Volatiles should be the main shuttles of nitrogen with most of the used model compounds.

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References