New Structural Concept for Carbonized Coals

Anna Marzec

Institute of Coal Chemistry, Polish Academy of Sciences, 44-102 Gliwice, Sowinskiego 5, Poland

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The aim of this study was to present a model of structure for solid products of bituminous coal carbonization carried out at end temperatures (ETCs) in the 600−750 °C range. The products are of interest since they are used as raw materials for production of activated carbons. Moreover, a layer of such products occurring in coke ovens seems to play a crucial role in generation of excessive coking pressure in industrial coking. The experimental data used in modeling were derived from the following: carbonization studies of coals and individual aromatic hydrocarbons, X-ray diffraction, transmission electron microscopy, pyrolysis-field ionization mass spectrometry, and electrical resistivity measurements. The final step of model preparation relied on application of computational chemistry for search of stable conformers and for calculations of molecular orbitals. According to the model, semicokes contain two structural components: (i) oligomers that form nonplanar 3D networks of aromatic clusters (an extended system of conjugated π-orbitals unites clusters of the network despite the fact they are not coplanar) and (ii) planar aggregates that arise from products of dehydrocyclization reaction (the aggregates fill space between oligomeric networks). The two structural components represent optically isotropic and anisotropic phases, respectively.

Introduction

The objective of the paper is to model a structure of solid products of bituminous coal carbonization which is carried out to a final temperature in the 600−750 °C range. Occasionally, the short term "semicokes" is applied in the paper for such products, no matter whether they were derived from coking or not coking coals. The semicokes are of special interest since they are used as raw materials for the manufacture of activated carbons. Moreover, the semicoke layer plays an important role in generation of excessive coking pressure when some coals are being used for coke production in industrial coke ovens. It seems low permeability of the layer for vapor species is a critical property in generating the pressure.[1]

A chemical model of the carbonized coals was generated on the basis of information derived from the following:

(i) X-ray diffraction and transmission electron microscopy (TEM) carried out for coals carbonized at the carbonization end temperatures in question;

(ii) pyrolysis-field ionization mass spectrometry of bituminous coals;

(iii) carbonization studies of model aromatic hydrocarbons;

(iv) electrical resistivity measurements of carbonized coals as well as of individual aromatic hydrocarbons; and

(v) geometry optimization and molecular orbitals' calculations by application of computational chemistry (Hyperchem software).

X-ray data were already used in the 1950s and 1960s by R. Diamond and R. R. Franklin in modeling coal and coke structures; their works had been widely cited since that time and described in detail, for example, by van Krevelen.[2a] In the 1980s, the TEM technique was applied in modeling coal and coke structures by A. Oberlin and J. N. Rouzaud.[3−5]

Experimental Section

Structural Modeling, Geometry Optimization, and Calculating Molecular Orbitals. HyperChem software (Release 4.5 for Windows 3.11) was used for all these steps as well as for measuring torsion angles between aromatic planes and molecular dimensions of various aromatic hydrocarbons. In the present text main software commands are indicated in brackets.

Results

In this section, data are provided that were derived from a literature survey as well as from previous articles of the present author. Sources of information are indicated. The aim was to bring together all available analytical data obtained with the use of various experimental techniques that were related to the structure of semicokes.

X-ray Diffraction Data for Coals Carbonized up to 750 °C. The data derived from X-ray studies of semicokes were already summarized.[6a−8] The average

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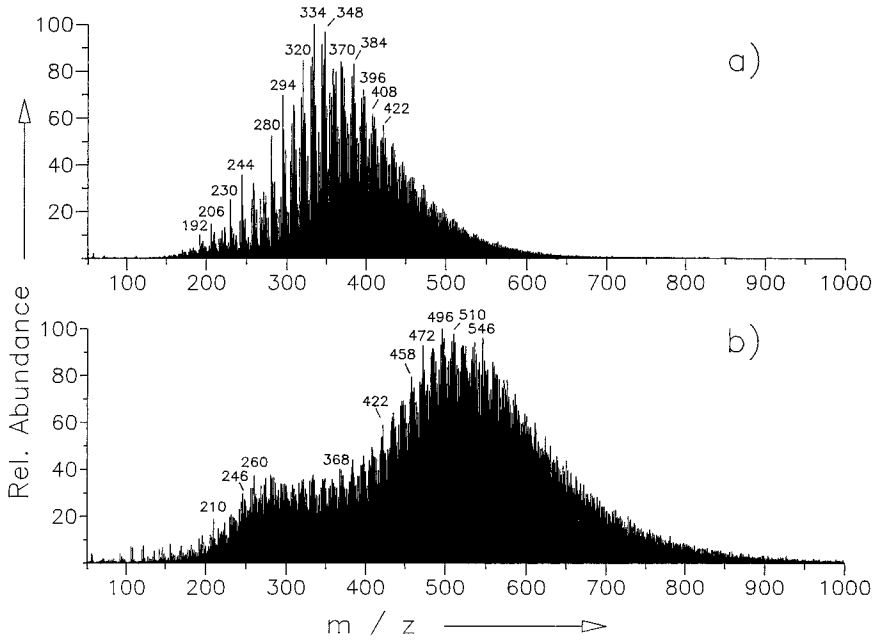

Figure 1. Typical pyrolysis–field ionization mass spectrum of bituminous coal. Molecular ions of thermal decomposition products: (upper) generated on heating coal up to Gieseler resolidification temperature T_R and (lower) on further heating, i.e., from T_R to 750 °C.

diameter of aromatic units (clusters) increases almost linearly with the end temperature of carbonization (ETC) from about 0.8 nm (this corresponds to 3–7 ring condensed units) for coals carbonized at 550–650 °C to about 1 nm at ETC = 750 °C. The dimension of 1 nm corresponds to a number of aromatic structures that contain 10–14 condensed rings. In contrast, the average height of crystallites displays a nonlinear dependence on the carbonization temperature. In general, a minimum of the height is observed in the 550–750 °C ETC range; the exact location of the minimum depends on the coal. The minimum height observed is equivalent to 1–4 aromatic layers per crystallite.

Transmission Electron Microscopy (TEM) of Carbonized Coals. The technique was extensively used for studying various carbonized materials.[3–5] The results showed that all coal cokes carbonized up to ETC = 1000–1200 °C contained aromatic clusters of dimensions <1 nm. The resolving power limit of the TEM technique is 1 nm. Thus, the sizes of <1 nm may correspond to aromatic clusters composed of 3–4 rings up to 10–14 rings. TEM revealed that the clusters occurred either singly or as stacks of two or three layers. For ETC < 1000–1200 °C, the stacks are not parallelly oriented to each other.

Aromatic and Aliphatic Structures in Carbonized Coals. Unfortunately, infrared spectrometry cannot be applied for determination of aliphatic and aromatic structures in coals carbonized at ETC > 600 °C. The carbonized coals show a continous increasing absorption in the 2000–3200 cm^{-1} range and in general do not have any absorption bands that are characteristic for aliphatic C–H (about 2900 cm^{-1}) and aromatic C–H (about 3030 cm^{-1}). A ^{13}C NMR technique using single-pulse excitation which was considered to give most reliable quantitative data for coals[9] as well as for carbonized material[10,11] could be much more useful in this respect. But scarce data are available. Measurements carried out with the use of this technique for a bituminous coal carbonized at various ETCs up to 612 °C indicated that for ETC > 500 °C the carbonized products contained less than 3% of aliphatic carbon atoms (f_a >0.97).[10,11] The ETC = 612 °C semicoke showed only 1% of aliphatic carbon.[10]

Elemental Composition of Carbonized Coals. Elemental composition of various ETC = 650 °C carbonized coals is in general in the range:[2b] %H = 2–2.5; H/C = 0.3–0.35; O/C = 0.01–0.04. For ETC = 750 °C carbonized coals, the data are %H = 1–1.5, H/C is about 0.15, and O/C < 0.02.

Pyrolysis-Field Ionization Mass Spectrometry (Py–FIMS) of Coals. Py–FIMS studies of numerous bituminous coals[1,12,13] revealed that thermal decomposition products in the 100–800 Da range were continously generated on heating (at about 1 °C/s) coal up to 700–750 °C directly in the spectrometer at a high vacuum of about 10^{-4} Pa. Yields of the products on heating to the Gieseler temperatures of coal resolidification were in the 8–32 wt % range, and on further heating to 700–750 °C, the yields were 6–12 wt % (from ref 1 and yet unpublished results). The total yields for the whole temperature range, i.e., to 750 °C, were 11–50 wt %.[13] Py–FIMS high-resolution measurements and Py–GC–MS for the material evolved over the whole volatilization range led to the determination of major decomposition products. The species represented a great variety of hydrocarbons such as nonalkylated and alkylated aromatics with two up to eight rings, OH derivatives of the aromatics, and some hydroaromatics (from refs 1, 12, 13, and unpublished results).

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As an example, Figure 1 shows Py–FI mass spectrum of a bituminous coal; molecular ions of the decomposition products generated on heating coal to its resolidification temperature and on further heating from this temperature up to 750 °C are separately displayed.

Carbonization of Individual Aromatic Hydrocarbons. Studies carried out on carbonization of individual aromatic hydrocarbons for example, perylene,[14,15] showed that major reaction products were (i) oligomers (biaryls) of the substrates and (ii) compounds arising from dehydrocyclization. The latter refers to intermolecular condensation of two aromatic molecules as well as to intramolecular condensation of biaryls. The intramolecular condensation is a commonly proposed route for thermal formation of polycyclic aromatics under carbonization conditions.[16]

Electrical Resistivity of Individual Aromatic Hydrocarbons. As reported by Ouchi,[17] Zander,[18] and Meier,[19] hydrocarbons containing three to six aromatic condensed rings (anthracene, chrysene, pyrene, naphthacene, pentacene, and hexacene) showed at 25 °C a specific resistivity (r_s) on the order of 10^{19}–10^{10} ohm·cm. The resistivity r_s of hydrocarbons composed of 7–11 condensed aromatic rings was in the 10^{17}–10^{8} ohm·cm range. In general, a decrease of resistivity was observed on increasing number of condensed aromatic rings, although types of the structures (peri or kata) had also some influence on the resistivity.

Carbonization of Coals and Electrical Resistivity of Resultant Semicokes. Twenty-seven bituminous coals of different rank were carbonized at various ETCs which were in the 650–850 °C range. Electrical resistivities of the semicoke rods were measured at room temperature. Details of the carbonization procedure as well as of the resistivity measurements are described elsewhere.[8] Resistivities r_s of the semicoke rods obtained at ETC = 650 °C were in the 1×10^3 to 23×10^3 ohm·cm range; r_s of those obtained at ETC = 750 °C were in 1–4 ohm·cm range. It is noteworthy to point out that no relationship was found between the resistivities of the rods and their ash content or their optical anisotropy content.[8]

Discussion

Application of information derived from Py–FIMS of coals and from carbonization data for individual hydrocarbons to modeling coal carbonization may be described as follows. It is assumed that the decomposition products detected by Py–FIMS are also generated during carbonization of coals. In a coal being carbonized, the products undergo further thermal decomposition; aromatic molecules are stripped off the majority of alkyl substituents. Some of the molecules escape from the system as gas or tar components. However, the majority of them remain in the system (no vacuum is applied in carbonization processes) and undergo complex reactions (among themselves as well as the nonvolatile part of the material) that result in material

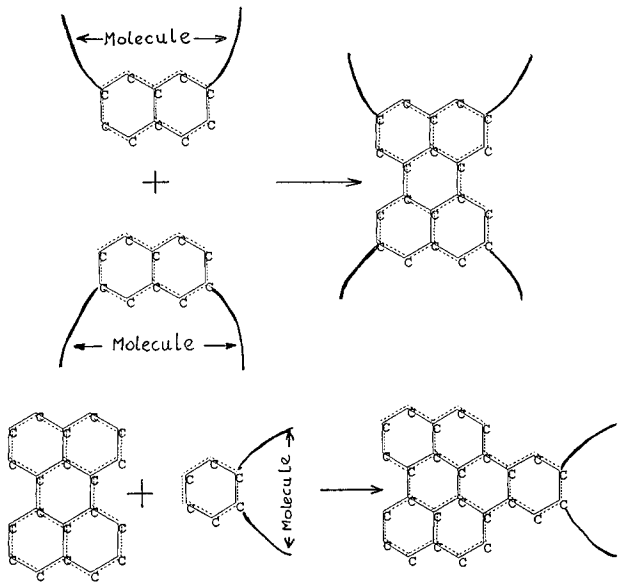

Figure 2. Aromatic structures that can produce planar dehydrocyclization products. (upper) Each of the reacting molecules has a "bay" structure composed of three C atoms. (lower) One of the reacting molecule has a "bay" structure composed of four C atoms; the other molecule has an edge composed of two C atoms.

that is aromatic already at ETCs in the 550–600 °C range. No doubt, the aromatic material undergoes some "condensation" reactions which contribute to formation of a new solid phase (semicoke). Types of these "condensation" reactions may be deduced from data on carbonization of individual aromatic hydrocarbons. The data indicate that oligomerization and dehydrocyclization of aromatic molecules are dominant reactions. The same reaction types were also postulated in kinetics interpretation of H_2 emission from carbonized coals.[6b]

Dehydrocyclization Reaction; Structural Restrictions. A scheme is presented in Figure 2 of the formation of some dehydrocyclization products. A new benzenoid aromatic ring may be formed under two conditions: (i) each of the reacting molecules has a "bay" structure composed of three C atoms or (ii) one of the reacting molecule shows the "bay" composed of four C atoms while the other molecule has an accessible edge of two C atoms. The products are planar aromatic clusters. The two restrictions referring to formation of planar aromatic molecules are valid, no matter whether the molecules were formed by intermolecular condensation of two aromatics or by intramolecular condensation of a biaryl molecule. The methyl substituent on the C atom vicinal to the "bay" structures or to the edge may prevent dehydrocyclization (this restriction is valid for temperatures below 750 °C, i.e., as long as methyl groups are still thermally stable[16]).

The resulting planar aromatic species are able to form liquid crystals during carbonization and finally yield an anisotropic phase in the carbonized material. The anisotropic phase formation (i.e., mesophase fromation) was already extensively studied and described.[20] The present data just point out that the dehydrocyclization plays an important role in its formation.

In another case (not shown here), dehydrocyclization may result in formation of five-membered aromatic rings. Such newly formed aromatic molecules would deviate from planarity.

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(16) Poutsma, M. L. *Energy Fuels* **1990**, *4*, 114–131.
(17) Ouchi, K. *Fuel* **1967**, *46*, 71–85
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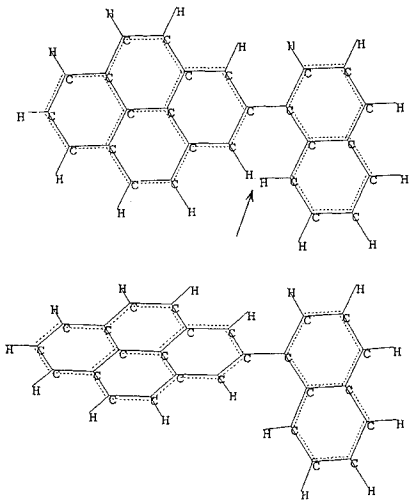

Figure 3. Dimer of pyrene and naphthalene as an example of oligomerization products. (upper) Planar conformer: torsion angle $T = 0°$; the distance between two H atoms (indicated by an arrow) is 0.055 nm; its calculated energy E is 330 kcal·mol^{-1}. (lower) Nonplanar conformer: $T = 49.4°$; the distance of the two H atoms is 0.25 nm; $E = 14$ kcal·mol^{-1}.

Oligomerization Reaction. In contrast to the dehydrocyclization, there are no special structural requirements for the oligomerization reaction. Any aromatic structure may undergo oligomerization, no matter how the molecules juxtapose themselves. In other words, there are more sites on aromatic rings available for oligomerization than for dehydrocyclization. An example of an oligomerization product (dimer of pyrene and naphthalene) is shown in Figure 3.

Rotational Conformers of Oligomers. Calculations of potential energies (MM; single point) for dimers and trimers of various aromatic structures were performed for their planar (model built) and energy-minimized conformers (geometry optimization/Polak–Ribiere algorithm followed by molecular dynamics). The results showed that the planar oligomers had the highest energies and were the least stable compared with nonplanar conformers (an example is shown in Figure 3). This is mostly due to strong repulsive forces between H atoms (indicated by an arrow in the figure) in planar conformers.

Thus, the calculation results indicate oligomers in semicokes cannot be planar structures.

Comparison of Elemental Analysis Results with TEM Data for Carbonized Coals. Let us consider the following two cases. One of them is that among various aromatic clusters producing the characteristic average number of rings per cluster (five rings/cluster for HTT = 650 °C and about nine rings/cluster for HTT = 750 °C) the material contains some amount of clusters that have dimensions close to 1 nm (see the Results; according to the TEM data, clusters of >1 nm are not present in carbonized coals obtained at HTT < 1000 °C). Calculation of the hydrogen content for various aromatic hydrocarbons of molecular dimensions (HyperChem calculated) of about 0.9 nm indicates that the hydrocarbons have H content in the 3–3.7% range (their number of aromatic rings is from 14 to 10, respectively). Thus, any combination of various clusters whose molecular dimensions are below 1 nm must show H content of >3%. This is definitely higher compared with the experimental H contents for the carbonized coals in question which are 2–2.5% H (ETC = 650 °C) and 1–1.5% H (750 °C).

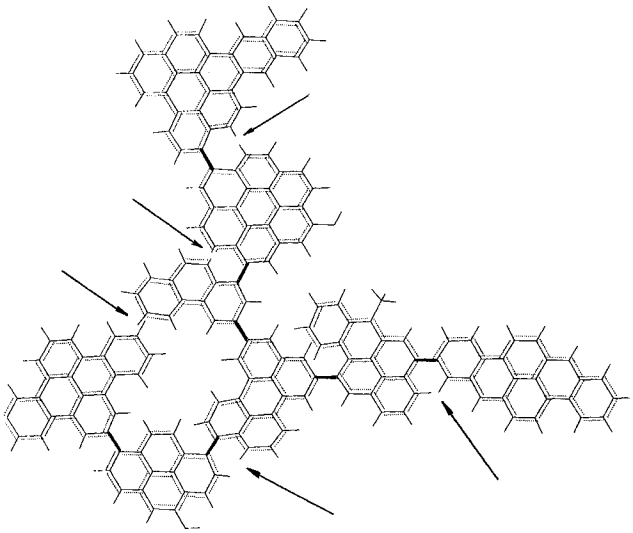

Figure 4. Oligomeric $C_{173}H_{88}O_2$ macromolecule constructed on the basis of available analytical data for low-temperature carbonized coals (ETC = 650 °C). It is composed of eight aromatic clusters that contain three, four, five, six, and seven aromatic condensed rings. Bold lines indicate seven aryl bonds connecting the clusters. Arrows indicate H atoms that are less than 0.1 nm apart; strong repulsive forces between them make the planar conformer unstable.

Referring now to the next case, one can calculate H content and molecular dimensions for various aromatic structures with an increasing number of rings. The calculations clearly indicate that a hydrocarbon showing 2.5% H content consists of 25 condensed aromatic rings and its dimension is 1.96 × 1.22 nm. Such a structure could be easily detected by TEM, not saying about much larger structures that show H contents below 2.5%. In fact, however, they were not detected by TEM (see the Results) in coals carbonized at ETC < 1000 °C.

The above considerations led to the following conclusion: results of elemental analyses of carbonized coals and their TEM and X-ray data are not in accord.

Building Large Oligomeric Molecule. A molecule is displayed in Figure 4 which was assumed to represent an oligomeric part of ETC = 650 °C semicokes. The molecule was constructed in such way that its properties present some compromise between the experimental data (referring to H content on one hand and X-ray and TEM on the other) for the ETC = 650 °C semicokes. An average number of rings/cluster has been made higher with the aim to decrease H content. Due to restrictions of H content (which should be as close as possible to the experimental value of 2.5%) and the negligible amount of aliphatic carbon indicated by ^{13}C NMR (see the Results), no more than one methyl group was assumed to be present. For the same reason, no other linkages between aromatic clusters, except aryl bonds, are included in the molecule.

Thus, the properties of the molecule are %H = 4.0, H/C = 0.5, and the average number of aromatic rings/cluster = 5.6. Other data are $C_{173}H_{88}O_2$, 2196 mol weight, O/C = 0.01, and C unprotonated/C total = 0.50. A further decrease of H content could be realized by a significant increase of the aromatic clusters' dimensions; this, however, would be entirely inconsistent with X-ray and TEM data (see the Results). The H content of the oligomeric part of semicokes does not have to exactly correspond with the experimental H content for semicokes since other components of semicokes, i.e., dehy-

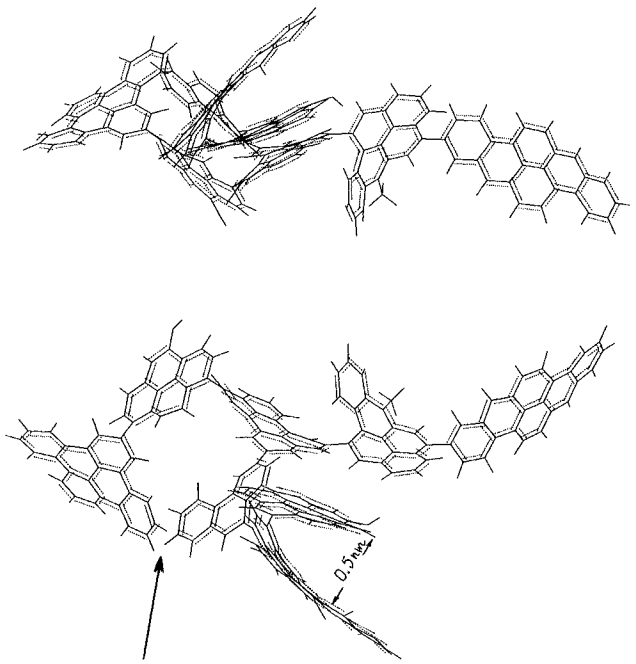

Figure 5. Model of oligomeric structures in low-temperature carbonized coals. The model was obtained by (HyperChem) energy optimization of the structure presented in Figure 4. Two different views of the structure are displayed. Torsion angles between the neighbor aromatic clusters are from 37° to 80°. An arrow indicates a slit (0.38 nm width) leading to a void (0.87 × 0.58 nm) between branches of the oligomeric macromolecule.

drocyclization products, may show lower H content. In referring to the molecular weight of the oligomeric macromolecule, it should be pointed out there are no experimental data available that could provide such information. Nevertheless, one should assume that oligomeric macromolecules show a wide range of molecular weights. The weights, however, cannot be below 700–900 units since in such case semicokes could be vaporized under high vacuum. The molecular weight of the oligomeric molecule has been arbitrarily assigned at about 2200 units level. A change of the weight by combining a higher or lower number of the aromatic clusters would not result in any meaningful change of H content nor in the results presented in the next section.

Figure 4 displays an unoptimized (model built) conformer of the oligomeric macromolecule. The total energy of the molecular system (MM; single point), $E =$ 10916 kcal·mol^{-1}, is high due to strong repulsive forces between H atoms on neighbor clusters. The forces make the molecule unstable.

Geometry Optimization of the Oligomeric Macromolecule. For minimizing the total energy of the molecular system and thus increasing the stability of its conformation, step-by-step instructions given by HyperChem were applied (MM; geometry optimization/Polak–Ribiere algorithm; followed by molecular dynamics).

Figure 5 displays one of the stable conformers resulting from these calculations. The total energy of the system (MM; single point) was minimized to $E = 250$ kcal·mol^{-1} (compared to $E = 10\,916$ kcal·mol^{-1} for the unoptimized conformer). Torsion angles between the planes of neighbor aromatic clusters were in the 37–80 °C range.

Next, an aggregate composed of five oligomeric macromolecules was investigated. The aggregate was built by adding (merge) step by step one macromolecule (the same as in Figure 5) after another and carrying energy optimization (MM; geometry optimization/Polak–Ribiere algorithm; molecular dynamics). Figure 6 shows the energy-optimized system composed of the five macromolecules. As the figure displays, the oligomeric macromolecules can hardly be arranged to each other in such way that they would form crystallites of parallel aromatic layers. It is concluded, therefore, that an ETC temperature for semicokes corresponding to a minimum number of layers per crystallite (which is the 550–750 °C range; see the Results) indicates the temperatures at which a maximum amount of the oligomeric macromolecules is formed.

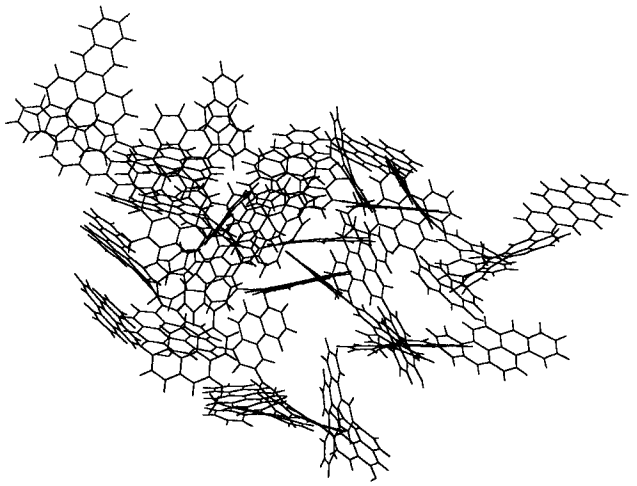

Figure 6. Model of optical isotropic phase in low-temperature carbonized coals. The model was obtained by (HyperChem) energy optimization of an aggregate composed of five oligomeric macromolecules (the same as presented in Figure 5).

Planar dehydrocyclization products (not shown in the two figures) forming stacks of parallel aromatic layers are expected to fill space between the oligomeric networks.

A model for the ETC = 750 °C semicokes (not shown) also includes oligomeric networks as well as planar aggregates of dehydrocyclization products, representing optical isotropic and anisotropic phases, respectively. However, dimensions of aromatic clusters in both phases are larger. They are about 0.9 nm which corresponds to 10–14 condensed rings/cluster. The growth of aromatic clusters on heating from 650 to 750 °C may be viewed (in a purely speculative way) as occurring via intramolecular dehydrocyclization of outer clusters in oligomeric networks. Higher temperature may supply enough energy for crossing the energy barrier of rotation to make the intramolecular reaction possible. Another option is that some thermal degradation products can be attached to outer aromatic rings of the two phases.

Comparison of Electrical Resistivities of the Semicokes and Individual Aromatic Hydrocarbons. Electrical resistivities r_s of numerous semicokes (see the Results) are on the order of 10^3 and 1–4 ohm·cm for ETC = 650 and 750 °C, respectively. The r_s values of individual hydrocarbons that correspond to aromatic clusters in the semicokes are in the 10^{19}–10^8 ohm·cm range (see the Results). Thus, the resistivities of the individual hydrocarbons that represent various clusters in the semicokes are higher by many orders (i.e., by the factors 10^{16}–10^8) compared with r_s values

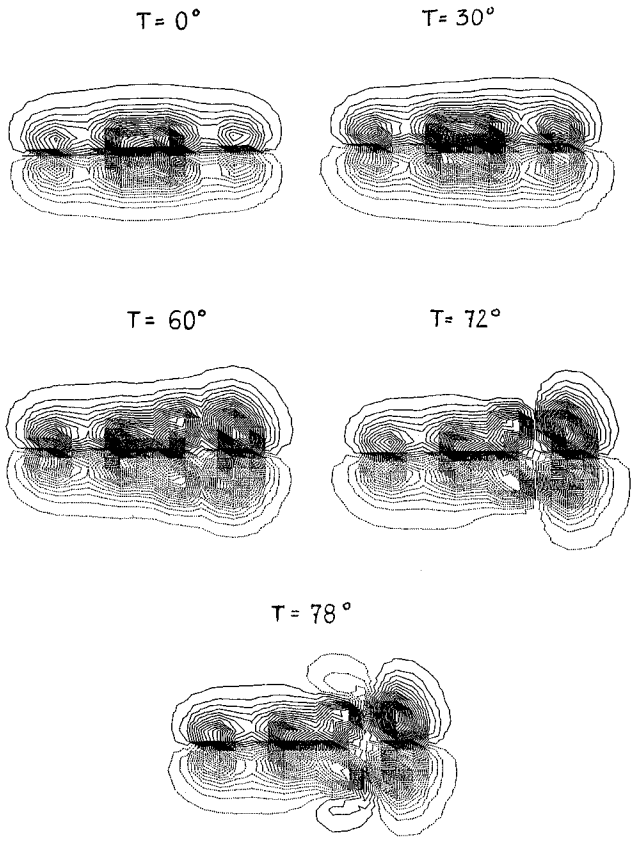

Figure 7. Influence of torsion angle T between aromatic planes of oligomeric molecule on π-orbitals; an example for diphenyl. The π-orbital is surrounding the whole molecule for torsion angles of $\leq 72°$.

of the semicokes. Let us assume now that the resistivity of a complex mixture of various types of aromatic structures is determined by their low resistance constituents (the assumption from ref 17). In this case, one should expect that the resistivities of the semicokes would be about 10^8 ohm·cm. But, in fact, the semicokes' resistivities are lower by many orders of magnitude. This is even more curious if one takes into account that the semicokes are porous materials and porosity is known to enhance electrical resistivity.

The comparison indicates two options: either (i) aromatic clusters in semicokes are much larger than those shown by X-ray and TEM measurements or (ii) the clusters form an extensive system of conjugated π-orbitals, despite the fact the clusters are not coplanar. The latter has been verified with the use of HyperChem software.

Influence of Torsion Angle in Oligomers on Their π-Orbitals. Calculations of π-orbitals (semiempirical/CNDO; single-point calculated MO) were carried out for numerous di-, tri-, and tetramers of various individual aromatic hydrocarbons with various torsion angles. Figure 7 displays an example for diphenyl. The example shows that a conjugated π-orbital is expanded over the whole molecule for torsion angles between the benzene planes that are $\leq 72°$. Further increase of the angle ruins the conjugation between the clusters.

The results indicate that conjugation of π-orbitals between nonplanar aromatic clusters in semicokes may occur and may be extended over a large part of the oligomeric network. This conjugation provides an explanation for the extremely low electrical resistivity of the semicokes compared with the resistivities of the individual aromatic hydrocarbons which reflect the semicoke clusters.

Summary

A literature survey has been prepared on (i) various analytical data (elemental composition; X-ray; TEM; ^{13}C NMR SPE technique) referring to solid products of bituminous coal carbonization carried out at 600–750 °C ETC range; (ii) electrical resistivity of the carbonized coals as well as of individual aromatic hydrocarbons which reflect structures of aromatic clusters detected by X-ray and TEM in the carbonized coals (the resistivities of the carbonized coals appeared to be lower by many orders of magnitude compared with those of the individual aromatic hydrocarbons); and (iii) carbonization studies of individual aromatic hydrocarbons; the studies pointed out two reactions, i.e., oligomerization and dehydrocyclization, should be considered as major pathways resulting in formation of solid carbonization products.

Molecular mechanics calculations carried out for various bi-, tri-, and tetraaryls (oligomers) composed of the aromatic clusters in question revealed that nonplanar conformers of the oligomers are much more stable compared with planar ones.

Semiempirical calculations of molecular orbitals of the nonplanar conformers showed that the clusters are united by an extended system of conjugated π-orbitals despite the fact the clusters are not coplanar.

Taking into account the analytical data for the coal carbonization products, an oligomeric macromolecule was constructed and subjected to an energy optimization procedure. The results showed the macromolecule formed a 3D network of nonplanar clusters with wide range of torsion angles between the planes of the clusters.

Conclusions

Low-temperature carbonized coals consist of two differently organized components, i.e., oligomers and planar dehydrocyclization products.

Oligomers create 3D nonplanar networks of aromatic clusters. The networks form the optical isotropic phase of the carbonized coals. An extended system of conjugated π-orbitals occurring in the networks makes the semicokes electrical semiconductors.

Planar dehydrocyclization products generated during carbonization constitute components of optical anisotropic phase. The products fill space between the oligomeric networks.

The ETC temperature corresponding to a minimum number of aromatic layers per crystallite in carbonized material, usually observed in the 550–750 °C range, indicates the temperature that is favorable for extensive formation of oligomeric structures.

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