DISCUSSION

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ON THE MECHANISM OF HEAVY ORGANIC RESIDUE LOW-TEMPERATURE CARBONIZATION

Abstract

Some ideas about low-temperature carbonization (LTC) of organic residues are presented in this paper. They base on the analysis of LTC intermediate and end products by means of capillary gas chromatography, ^1H NMR, EPR as well as on results from kinetic studies carried out under non-isothermal and isothermal conditions. It is shown that during LTC, practically no new aromatic structure is formed from non-aromatic one; for physical and physicochemical reasons only molecules similar in size and structure react together.

The changes in the asphaltene aromatic structure during the carbonization process at a constant temperature have been traced. It is shown that the size of individual molecules increases in stages rather than gradually. As for the studied residue, at first three molecules react together gradually or simultaneously and then the resulting molecule may rearrange and solidify. The newly-formed structure reacts only with another similar one. A threshold (critical) concentration of the corresponding reconstructed asphaltene structures of a definite size exists so as benzene-insoluble parts are formed. Six stages of LTC are proposed - from resins to quinoline-insoluble parts - illustrated by the estimated mean aromatic structures and their changes, respectively. It is proposed that isothermal inhibition is necessary during the formation of benzene-insoluble compounds to produce a high-quality coke from lower boiling residues.

One of the first ideas to explain the mechanism of LTC of heavy oil and other similar residues was the idea of a progressive conversion of their constituents from oils to resins, asphaltenes, carbenes, carboids and finally to coke [1, 2]. The proportion of these components in the carbonizing mixture is determined depending on their solvent solubility and hence, is presumably a physical characteristic. This idea has been supported by studies of the chemical composition of the components in the heavy residues. This was completed by examining the character of the chemical process that occurs either with groups of compounds available in the heavy residue or with model compounds [3]. The chain-radical mechanism of chemical process was proved to occur during coke-formation, especially at the initial degradation stages [4, 5].

Theoretical

The whole process of LTC of the heavy organic residue, from starting the thermal treatment to the formation of the structure of the resulting solid carbon product may be summarized as follows.

1. Initial partial degradation of the heavy residue molecules through rupture of the weakest chemical bonds resulting in the formation of chemically active radicals.

2. Interaction of radicals formed according to a chain-radical mechanism by consecutive and parallel-consecutive reactions forming high-molecular aromatic molecules as well as low-molecular liquid and gaseous compounds. It is established that this process is accompanied by aromatization, dehydrative polycondensation and removal of side substituents in the original and newly-formed aromatic structures.

3. Rearrangement and further growth of the high-molecular polycyclic compounds. These processes change their solubility in some solvents - benzene, pyridine, quinoline - defining the gradual transition of group components according to the above-mentioned order.

4. The enlarged and rearranged molecules form a mesophase (quinolin-insoluble material) and coalescence. This stage does not occur in some organic materials [6, 7].

5. Further structural changes at a higher temperature to form the final graphite-like texture with fixed physical characteristics.

We have decided to study the first, fourth and fifth of these stages most extensively. Generally, the first stage is related to thermal destruction during pyrolysis, cracking and coke formation. The last two stages are considered to be presumably of physical character. The second and third stages where the carbonization occurs by enlargement of the aromatic lattice remain greatly unclear (unexplained). Generally, studies on model compounds in a solution of thermally stable solvent or in melted stage are performed. ESR spectra are taken during their thermal treatment to determine the nature and the structure of the intermediate radicals. Later this method has been successfully combined with other physical methods as well - X-ray analysis, NMR spectra, mass spectroscopy, etc.

Different compounds have been used as models: acenapthylene [8, 9]; anthracene [10, 11]; 9,9-bianthryl [13]; 9,10-dibenzoanthracene [13]; periflanthene [12]; 7,12-dimethylbenzanthracene and naphthacene [13]; 3,4-benzpyrene [14], etc. Mostly, these studies have traced out the ESR spectra appearance and characteristics. Carbonization of model compounds of a higher molecular mass has also been studied from the point of view of coke output [15].

The initial stages of LTC were studied at first in numerous experiments with acenaphthylene. It was shown that the polymer undergoes destruction and rearrengements after the initial polymerization processes. A perinaphthyl radical was identified in the carbonizing mixture. Considering also the results of X-ray analysis, it was supposed that trimerized, acenaphthylene appears to be one of the main destruction products after structure enlargement to large aromatic lattices [8, 9].

We emphasize that the selection of acenaphthylene is not the most suitable one for LTC study. In this case still at a comparatively low temperature a polymer results from the destruction of double bonds with the temperature rise. Consequently, products of polymer destruction in the presence of unreacted acenaphthylene were examined. March et al. have studied LTC of anthracene [10]. It was shown that with the increase in temperature, the process runs through dimerization and trimerization of the starting anthracene molecules followed by both destruction and condensation of the intermediate products. Recent studies of LTC of anthracene as well as its mixture with phenanthrene include the examination of the intermediate products by means of mass spectroscopy [11]. The results obtained show at first processes of dimerization and trimerization followed by degradation to various products and their further condensation to coke. The role of hydrogen redistribution during the process has been pointed out.
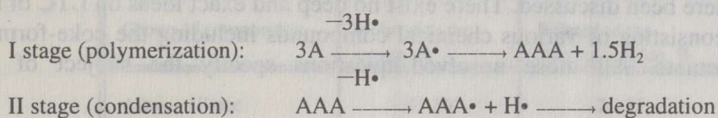
As seen so far these model compounds have enabled to study only the first stages of carbonization. As a rule, after the initial condensation of two or three molecules of the model compound, the enlarged molecule undergoes destruction and further condensation. But the latter has not been traced in details probably due to the difficulties in analysing the intermediate products produced during the carbonization. Though the

study of LTC of model compounds gives a picture of the processes taking place at the first carbonization stages, we consider that this process probably differs from that running under real conditions and with real raw materials. The main differences are as follows:

* when real raw materials and real conditions are used, there are a great number of compounds different in character that makes the reactions considerably more various;

* different types of aromatic structures undergo LTC more easily or with difficulties depending on their reactivity, e.g. peri-condensed as well as angular-linked (pheni) structures are of lesser reactivity than kata-condensed and linear-linked (aceni) ones, substituted aromatic compounds being of considerably greater reactivity than unsubstituted aromatic (condensed) rings;

* practically, the real raw materials contain no unsubstituted aromatic structures or their quantity present has no effect on LTC. As known from the literature, just unsubstituted aromatic structures are used as model compounds to study LTC.

Based on ESR studies on behaviour of model compounds during LTC, mechanisms of the first stages of coke formation have been proposed, too. Simon et al. have proposed a scheme of coke formation during anthracene LTC through bisanthene to its trimer [16].These trimers condense further to a large aromatic lattice, building up the coke structure. This scheme cannot explain many of the observed points - there is not a radical mechanism, hydrogen and methane separation as well as the degradation processes and formation of low-molecular (light) products, including aromatics, remain unexplained.

Lewis and Singer propose more detailed and more complete mechanism of LTC [5]. We shall try to summarize it. Analysing a great number of ESR studies on the first LTC stages, they have supposed a great effect of the perinaphthyl radical on LTC. At that, formation and/or existence of aromatic hydrocarbons of odd-ordered structure is required for the formation of resonance-stabilized π-radicals. They suppose that condensed aromatic hydrocarbons of pitch and other carbonizing materials participating in LTC and forming coke, resp. the stable π-radicals, consist of an equal number of carbon atoms in phenalenyl-type odd-ordered aromatic structures. These molecules polymerize directly to form coke without residual ring degradation and rearrangement. Thus, LTC may be described mainly as a process of "free aromatic polymerization". It runs in two stages: polymerization and polycondensation, illustrated as follows:

$$I \text{ stage (polymerization):} \quad 3A \xrightarrow{-3H\bullet} 3A\bullet \longrightarrow AAA + 1.5H_2$$

$$II \text{ stage (condensation):} \quad AAA \xrightarrow{-H\bullet} AAA\bullet + H\bullet \longrightarrow degradation$$

The formation of intermediate reactive σ-radicals (A•) not noticed during the usual ESR studies on the process is included in the first stage. The second stage called polycondensation begins also with the separation of hydrogen. The resulted structure degrades to produce odd-ordered stable π-radicals that form big planar regions.

There are some disadvantages and unclear points in the proposed mechanism. We consider the presentation of a general LTC mechanism basing on only one method as too much idealized. In case of a real raw material it is less probable that a radical of perinaphthyl type plays a basic role in LTC, moreover, this radical being stable and low-molecular. It is hardly acceptable that the coke-forming structures of pitch are of the same number of atoms and all built up of phenalenyl-type odd-ordered units. The authors claim elsewhere that even during a uniform raw material degradation, various

intermediate radicals formed. We consider that the proposed mechanism explains the formation of resonance-stable π-radicals rather than the LTC process. But according to the authors, these stable radicals only weakly participate in the rearrangement processes. We consider both their role in LTC as well as the real run of the process after the formation of stable π-radicals to be practically not explained. Here we refer to the results of March et al. according to which there is no relation between the mesophase transformation during LTC and the concentration of radicals in the system [17].

The terminology proposed by the authors for the mechanism is not correct from the point of view of the polymer chemistry and can lead to some misunderstanding. A process where a great amount of a low-molecular product (stage I) separates could not be consioered a process of radical polymerization. Usually it is called polycondensation. In this case the macromolecule does not grow till the monomer is exhausted but only till a polymerization by a degree 3, followed by a degradation of the formed structure. There are no proves of the occurrence of this stage. It can be easily imagined if the separation of the respective amount of hydrogen (according to the equation for stage I) could be confirmed.

The second stage, called dehydrative polycondensation (though less hydrogen is removed and the first stage should rather be called polycondensation) is closer to the so-called block-copolymerization (block-copolycondensation, respectively). As a proof, the authors point out the increase in spin number per gram (i.e. of the stable π-radicals that could hardly be recombined) and the increase in the atomic C/H ratio with the temperature rise. But this ratio can change in the same direction also when methane and other low-molecular hydrocarbon gases are liberated which the authors have not checked experimentally. The probable liberation of these gases should also show a structural degradation that does not correspond to the mechanism proposed by the authors.

It can be said that the results from the investigations made on model compounds and the concepts based on them show that LTC runs through the following stages:

* formation of reactive σ-radicals from the starting molecules of model compounds;

* formation of an enlarged structure from two or three radicals;

* degradation of the structure to produce both low-molecular and high-molecular products.

The intermediate products are usually unknown. The next stages of structure growth (till mesophase formation starts) have not been elucidated and are only summarized. The problem why the model compounds are not polycondensed smoothly to coke during LTC has nowhere been discussed. There exist no deep and exact ideas on LTC of real raw material consisting of various chemical compounds including the coke-forming aromatic structures. All those unsolved questions specify the subject of our investigation.

Results

We used for our investigations a heavy residue from the distillation of shale oil. On the one hand, this residue is not as highly aromatic as the pitches of coal tar. On the other hand, it is not a mixture of various production residues or not of such a specific type as the petroleum raw materials for electrode coke. Due to the present of certain amounts of heteroelements and according to the chemical composition and structure, it may be considered to be an intermediate between the raw materials of petroleum and coal origin. This assumption makes the results from LTC investigation more universal.

The studied heavy residue of oil, resulted from thermal destruction of oil shale has the following physicochemical characteristics:

Density, kg/m^3	0.9739
Coke number (by Conradson), wt.%	9.1
Average molecular mass	370
Elemental composition, DAF, wt.%:	
carbon	85.44
hydrogen	10.88
sulphur	0.50
nitrogen	0.67
oxygen (by difference)	2.51
Composition by groups of components, wt%:	
oils	60.0
resins	30.0
asphaltenes	10.0
benzene insolubles	absent

The asphaltenes are obtained through double sedimentation with n-pentane. The oils and resins are separated on silica gel by eluation with an alcohol-benzene mixture. The lack of benzene-insoluble materials shows the absence of high-condensed structures. By ESR spectra the spin concentration in the starting heavy residue has been determined - 28.7×10^{16} spin/gr - a high value, in general typical for all carbon-containing materials having undergone thermal treatment to some extent [18]. It is shown that the spin concentration is slightly changed after the thermal treatment of the residue for 5 hours [19].

For tracing the condensation process in the studied real raw material, its composition was analysed in details. For this purpose different physical and chemical methods of analysis have been applied [20]. The following data have been obtained.

Oils. Their average molecular mass is 320. They have been analysed by means of adsorption, column, gas, gel and other types of chromatography combined with IR and UV spectra. The oils appear to be a mixture of the main groups of compounds listed in Table 1.

Table 1. **Contents of the Main Groups of Components in Oils**

Group of components	Related to the group, %	Related to the starting residue, %
Alkane-alkene	43.86	26.32
Monoaromatic	8.87	5.32
Biaromatic	31.11	18.70
Triaromatic	7.10	4.26
Resins	9.06	5.43

It is shown that the alkane-alkene part consists of straight-chain compounds of the length C_{16}-C_{33}, the maximum being C_{21}-C_{23}. The monoaromatic part has in average one side substituent of an average length C_{17}. The biaromatic part has in average two side chains of the length C_7-C_{10} [20].

Resins. They have an average molecular mass 430. By means of chromatography 2 % of biaromatic compounds and 13 % of triaromatic compounds similar to those in oils

were separated. A certain quantity of phenol and carbonyl groups was identified by means of IR spectra, UV spectra and chemical methods. The structure of the rest of resins was characterized by means of ^{1}H NMR spectra. Based on the spectral data, the elemental composition and molecular mass, the mean molecule building up the resins was determined by a method proposed by William and modified by Smith et al. for lower condensed structures [21, 22]. Parallelly, a method proposed ealier by Corbett was applied [23].

It is known that modern methods of determination of an average structure based on C^{13} NMR have already been developed. They were used successfully to determine the structure of coal and derivatives. We selected these methods as they are simpler and more suitable for our investigations. The structure of an average resin molecule obtained by these methods is shown in Fig. 1a.
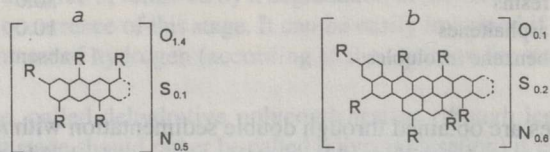
Fig. 1. Calculated structure of an average molecule of (a) resins (R = C_3H_7) and (b) asphaltenes (R = C_2H_2)

Asphaltenes. They build up the high-molecular part of the residue. An average molecular mass is 610. By means of liquid chromatography it was shown that they contain practically no unsubstituted aromatic (condensed) compounds. The structure of the average molecule shown in Fig. 1b was determined on the basis of Smith and Corbett methods [22, 23].

In the figure it is seen that the average structure of asphaltene is built up of 8 or 9 condensed aromatic rings. The linearly condensed molecules cannot be distinguished from the angularly condensed ones by the applied methods but the peri-condensed molecules are well distinguishable from kata-condensed ones.

The number of the side substituents is not small - 7 of an average length C_2. In the example their probable locations are given. The content of heteroelements is small. The structures shown in Fig. 1 may have different isomeric forms. Some possible structures have been used to illustrate further proposed LTC mechanism. The main condition was to retain the total number of C-atoms and the definite ratio between the peripheric and 12 - condensed aromatic carbon atoms in the structure. For that purpose in our calculations a computer was used.

This examined starting residue from distillation of the shale oil has been subjected to LTC. The equipment used permits heating, as well as catching and removing of the obtained products and a smooth regulation of material balance tests. Each of the resulting products - gas, distillate and coke - was analysed. The average material balance of LTC is as follows, %:

	Yield of:	
	coke	18.5
	distillate	68.8
	gas	12.0

Separation of water - 0.7 % - was observed as well. During the investigation, it was established that the maximum quantity of distillate appears at 420 °C and the maximum liberation of gas is observed at 440 °C. At 460 °C, only gas liberates, the carbonizing matter solidifies and swells. The LTC end temperature is 550 °C.

It was established that there are no asphaltenes and resins as well as practically no high-boiling (over 410 °C) part in the coke distillate. But the type of aromatic compounds (mono-, bi- and triaromatic) as well as their ratio actually remain the same as in the starting oils. By means of capillary chromatography, the chemical composition of the benzene fraction (up to 180 °C) was determined. Summarizing the individual compounds by chemical groups, the generalized composition is as follows, %:

n-Alkanes	25.95
i-Alkanes	12.68
Alkenes	34.13
Aromatics (monoaromatic with short side	
substituents C_1-C_4)	25.60
Unidentified	1.38

The ratio between the individual groups of compounds is similar in the next fraction of coke distillate as well. The most general conclusion is that the resins, asphaltenes and the high-boiling part of the starting heavy residue have been transformed into coke during LTC. Parallelly, a degradative rupturing process of the side substituents in aromatic rings and mono-, bi- and trinucleic structures has occurred. They are transferred to the coke distillate. The compounds identified during the study of the benzene fraction of the coke distillate are the end products of degradation. The same applies to those of a boiling temperature up to 350 °C.

Table 2. **Composition of the Gas (vol%) Formed at LTC of the Starting Residue and its Group Components - Oils, Resins and Asphaltenes**

Compound	Starting residue	Asphaltenes	Resins	Oils
Hydrogen	16.75	12.79	7.81	11.43
Methane	60.40	54.45	51.28	55.20
Ethane	10.98	15.80	19.18	14.09
Ethylene	1.98	1.50	1.57	2.12
Propane	3.08	3.97	7.36	7.27
Propylene	2.21	1.38	2.13	2.80
Butanes	1.01	absent	1.08	1.81
Butenes	0.67	0.57	1.05	1.36
Carbon oxide	1.47	3.33	4.34	1.13
Carbon dioxide	1.33	6.21	3.20	2.80
Hydrogen sulphide	0.28	traces	traces	traces

The gas composition presented in Table 2 was determined by means of gas chromatography. It can be seen that methane and hydrogen of 60.40 vol%, and 16.75 vol% respectively, are dominating. The same Table shows the composition of coke gas from LTC of the single group components which will be discussed later. A comparatively good presentation of the character of the process could be obtained from the change in the gas composition during carbonization (Table 3). It is shown that the amount of hydrogen separating during the first stages is comparatively low and sharply increases above 440 °C; practically half of it separates above 460 °C when the carbonizing matter is already solid, i.e. during the main stages of LTC a low separation of hydrogen is observed. We emphasize this fact as it disagrees with the mechanisms proposed for LTC of model compounds. It is characteristic that methane continues to separate during the first LTC stages and its quantity remains close by this

value within the whole LTC temperature range. The separation of methane is weakest in the interval when the coke distillate is removed. But in this interval the quantity of C_2-C_4 gases passes a maximum. From the Table it is seen that the larger part of oxygen is liberated in the form of CO and CO_2 during the first stages of the process.

Table 3. A Change in the Gas Composition during LTC
         of the Starting Heavy Residue

Compound, vol%	Temperature range, °C				
	370-405	405-440	440-460	460-490	490-530
Hydrogen	7.4	6.7	12.2	19.5	27.2
Methane	46.7	38.2	57.9	62.0	56.4
C_2-C_4-unsaturated totally	13.5	25.3	13.0	8.9	7.9
C_2-C_4-saturated totally	24.8	28.5	15.1	9.0	6.4
Carbon monoxide	4.8	1.0	0.9	0.6	0.6
Carbon dioxide	2.8	0.7	0.9	0.6	0.6

For collecting other data on the mechanism, LTC of each group component individually - oils, resins, asphaltenes - was carried out. The material balance of the process is shown in Table 4. It is seen that most of the coke and gas result from LTC of asphaltenes. The formation of coke distillate highly dominates in oils. The composition of the liberated gas is presented in Table 2. The quantities of the separating hydrogen and methane are very close for the LTC of three group components. This shows an equality of their separation during degradation of both aromatic and aliphatic structures.

Table 4. Material Balance of LTC
         of the Group Components

Product, wt. %	Asphaltenes	Resins	Oils
Coke	58.6	43.1	10.5
Coke distillate	27.4	45.7	83.8
Coke gas	14.0	11.2	5.7

From the numbers for gas composition, material balance and molecular mass, it can be calculated that during carbonization of each of the group components respective amounts of gases were separated: from 1 mol asphaltenes - 2 mols methane and 0.5 mol hydrogen; from 1 mol resins - 1 mol methane and 0.3 mols hydrogen; from 1 mol oils - 0.5 mol methane and 0.1 mol hydrogen. Thus, during LTC the amount of liberating hydrogen is significantly less than that which should be liberating according to the mechanisms proposed so far for LTC of model compounds. The quantity of methane allows to assume that reactions of rupturing of side substituents dominate during reaction of asphaltenes. At that, it is not considered that a great part of hydrogen separates after solidification of the carbonizing matter.

During LTC of single group components, the individual composition of the coke distillate was also examined by means of gas chromatography [25, 26, 30]. All distillate products of the resins and asphaltenes result from the degradation process. The most typical feature is that the major quantity of the coke distillate represents different alkane-alkane compounds, i.e. rupture of side substituents or non-aromatic cycles. The quantity of aromatics removed during LTC of resins is about 15 % and during LTC of asphaltenes - about 30 %. This fact allows to assume that during LTC of asphaltenes, the

degradation of the aromatic part of the molecule is more extensive than in the resins. Concerning the latter it is noticed that the condensation process leading to the growth of the molecule into an asphaltene one dominates.

During carbonization of resins also the changes occurring at a lower temperature were investigated. It was established that some amount of gas and light distillate is separated up to 320 °C and they were analysed as well. The main compounds are n- and i-pentane, n-hexane, 1,4-dimethylcyclohexane [26]. It was also found that about 37 % of resins were already transformed to asphaltenes. By means of the above-mentioned method based on NMR, it was established that the newly-formed mean asphaltene molecule is built up of at least 6 condensed aromatic rings. We consider this fact a proof that the first stage of resins conversion under LTC is their conversion to asphaltenes.

Another subject of the studies was the examination of LTC kinetics. The kinetic studies were carried out under non-isothermal [27] and isothermal [28] conditions. The kinetic data for non-isothermal conditions were derived for LTC of the individual group components by means of derivatography of oils, resins and asphaltenes. Kinetic data for isothermal conditions were derived for LTC of the starting heavy residue at three temperatures - 400, 420 and 440 °C determining the changes in the concentrations of the group components. This range was chosen according to the established run of LTC of the heavy residue. The obtained kinetic data are presented in Table 5. They show that the reactions of transformation of oils, resins, asphaltenes, benzene-insolubles are of first order. The lowest value of E_{act} is determined for asphaltenes - a value very close to E_{act} for the diffusion in case of similar systems - 50 kJ/kg [3]. Comparing the results from the kinetics examination carried out parallelly under isothermal and non-isothermal conditions for asphaltenes and resins, practically similar values of E_{act} of their transformation during LTC were obtained. We accept this as a proof that their behaviour under LTC is not influenced by whether they are carbonized in a mixture or individually, i.e. it seems that during LTC the resins in the carbonizing system react only with resins and the asphaltenes - only with asphaltenes. Especially for the oils it was shown that the kinetic values are strongly affected by evaporation processes and therefore it was not possible to interprete them.

Table 5. **Kinetic Data on LTC under Isothermal ($1 - T = \text{const}$)**
and Non-Isothermal ($2 - T \neq \text{const}$) Conditions

Index	Oils		Resins		Asphaltenes		Benzene insolubles	
	1	*2*	*1*	*2*	*1*	*2*	*1*	*2*
Activation energy E_{act}, kJ/kg	172	63	121	146	63	63	168	—
Velocity constant $K_{420} \cdot 10^{-5}$	11.1	—	38.9	—	11.7	—	111	—

Further data on LTC mechanism were obtained by investigating the change in the structure of asphaltenes during isothermal heating at the temperatures already mentioned - 400, 420 and 440 °C. The isothermal heating was carried out in specially constructed small metal test tubes immersed in a metal bath for maintaining the proper temperature [29]. At definite time intervals (0 to 180 min.), the test tubes were taken out one by one and the contents were removed and analysed. The change in the amount of the group components with the time at 420 °C is shown in Fig. 2.
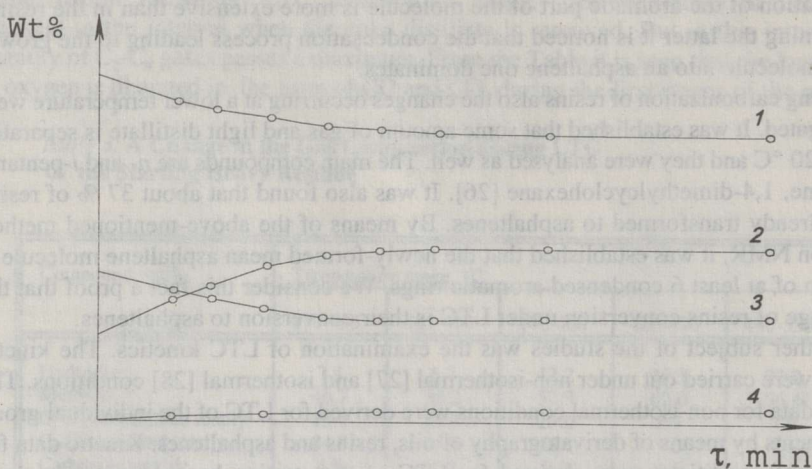
Fig. 2. Change in the quantities of the group components at isothermal heating of the starting residue at 420 °C: *1* - oils; *2* - resins; *3* - asphaltenes; *4* - benzene insolubles

The curves obtained for other two temperatures are of a similar character - after the initial change in the amount of group components, an equilibrium of the system is established during the examination. ESR and NMR spectra have been taken and the molecular mass and elemental composition of the removed asphaltenes were determined. On this base, by means of the above mentioned methods, the mean asphaltene molecule at a different period of thermal treatment (heating) has been determined. The changes in the molecular mass and spin concentration at certain time intervals (0 to 180 min) are presented in Table 6. It is seen that the molecular mass passes a maximum corresponding to the minimum of the spin concentration. The changes in the indexes of asphaltene structures are presented in Table 7. There is a good coincidence in values defined by both methods. During the last interval, the removed products appear to be asphaltenes as they are benzene-insoluble/pyridine-soluble (BI/PyrS). We have calculated their structural unit by Corbett as, because of the difficulties in dissoluting the sample, the molecular mass could not be determined.

Table 6. Change in the Molecular Mass and Spin Concentration of Asphaltenes during Isothermal Heating at 420 °C at Equal Time Intervals

Characteristics	Time intervals (min)					
	τ_0	τ_1	τ_2	τ_3	τ_4	τ_5
Molecular mass	610	1100	1570	1400	800	—
Spin concentration $\times 10^{19}$, spin/g	80	550	170	500	400	—

Table 7. **Structural Changes in Asphaltenes during Isothermal Treatment at 420 °C**

Indexes	Starting resins	asphal-tenes	Asphaltenes isolated after isothermal treatment of resins at certain time intervals (min)				
	τ_0	τ_0	τ_1	τ_2	τ_3	τ_4	τ_5
According to Smith et al. [22]							
Arom. rings/mol, R_A	3.5	8.2	15.8	24.2	20.5	14.6	–
Aromatization degree, F_A	0.573	0.722	0.750	0.750	0.735	0.785	–
Condensation degree	0.289	0.451	0.491	0.535	0.519	0.543	–
Number of side substituents per mol, R_S	4.8	6.6	8.9	13.3	10.3	5.1	–
According to Corbett [23]							
Arom. rings/mol, R_A	3.5	7.5	15.0	22.7	19.7	15.0	32.0
Aromatization degree, F_A	0.523	0.721	0.770	0.800	0.820	0.850	0.911
Ring condensation index, CI	0.250	0.353	0.364	0.379	0.372	0.372	0.391

Discussion

The subject of the studies, as mentioned already, is to explain some stages of LTC of heavy organic residues and at the same time to explain completely some of the observed facts during LTC under real conditions - liberation of gas, its composition and change during the process of coke distillate removal, the changes in the molecular mass and spin concentration. Based on the results, a mechanism of LTC process when LTC is in an advanced stage will be proposed and compared with such for LTC of model compounds.

Based on the observed effects and the results obtained from other investigations, mainly the kinetic ones, we have established that the molecules of the group components react in the reactive mixture only with similar ones - i.e. resin molecules with resinous ones, asphaltenic with asphaltenic ones, etc. At that, E_{act} of asphaltenes is close to E_{act} for diffusion of similar systems, i.e. their reaction velocity is defined by diffusion. Comparing the data in Fig. 1, and Tables 6 and 7, we conclude that LTC process begins with a consecutive reaction of 3 resin molecules to form an asphaltene molecule (experimentally confirmed).

The second stage of a consecutive reaction between 3 asphaltene molecules and the distillate leads to a macrostructure built up of 24 aromatic rings (still benzene-insoluble - BI), parallelly decreasing the spin concentration. This is followed by a gradual rupture of the obtained structure leading to the decrease in the ring number, increase in the degree of aromatization and the index of ring condensation as well as the number of the side substituents (this is observed during LTC of model compounds as well). Gas and light distillate are separating during these stages. The gas consists mainly of methane. This shows that during the LTC stages the side substituents but not the hydrogen atoms are ruptured (according to Table 3). The latter separate mostly at the end of the process - during the rearrangement of the already solidified matter. Moreover, according to

Table 6, the spin concentration passes extremes and then shows a tendency to stay at a constant value, not depending on the period of heating at the indicated temperature.

According to the theory proposed by Levis and Singer [5] identifying carbonization with a polymerizing system, we could suppose that the processes of copolycondensation of starting monomer molecules run to form an average trimer oligomer.
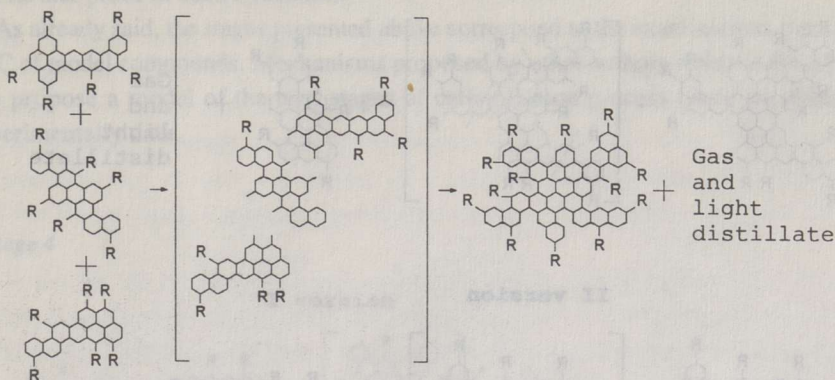
These stages can be illustrated as follows:

Stage 1: A Consecutive Reaction of Three Resin Molecules

| Starting asphaltene molecules | Supposed intermediate stage | Identified asphaltene structure |
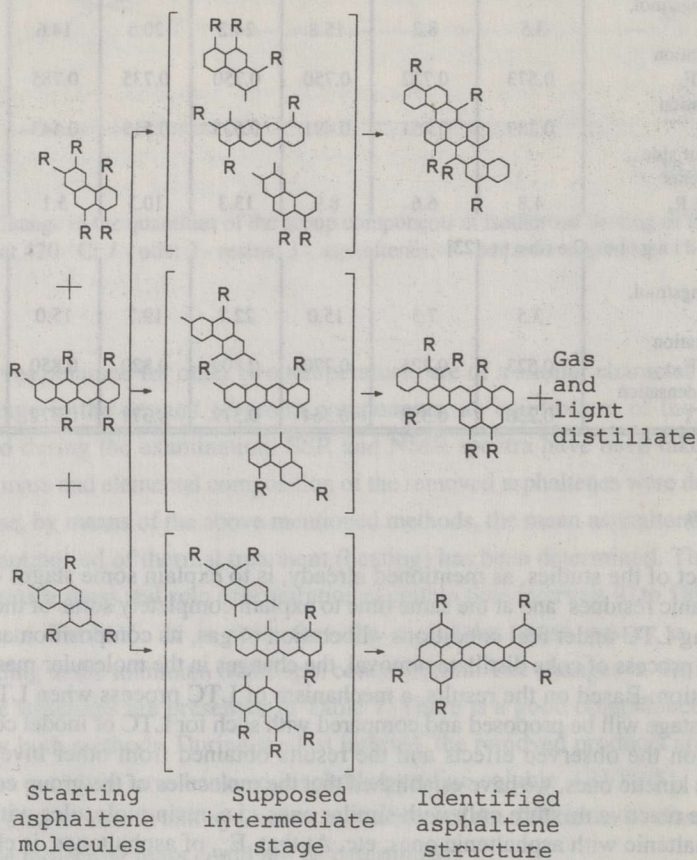
There exist numerous isomeric forms of asphaltene structures (molecules). We have considered the present ones to be the basic types.

Stage 2: A Consecutive Reaction between Three Average Asphaltenic Molecules
to Form an Enlarged Asphaltene Molecule

I version

Gas
and
light
distillate

II version

Gas
and
light
distillate

Starting	Supposed	Identified
asphaltene	intermediate	asphaltene
molecules	stage	structure

Two versions for this case are given — a reaction between starting asphaltene molecules
different in structure and similar in structure.

Stage 3: Partial Degradation of the Enlarged Molecule

I version

II version

| Starting asphaltene molecules | Supposed intermediate stage | Identified asphaltene structure |
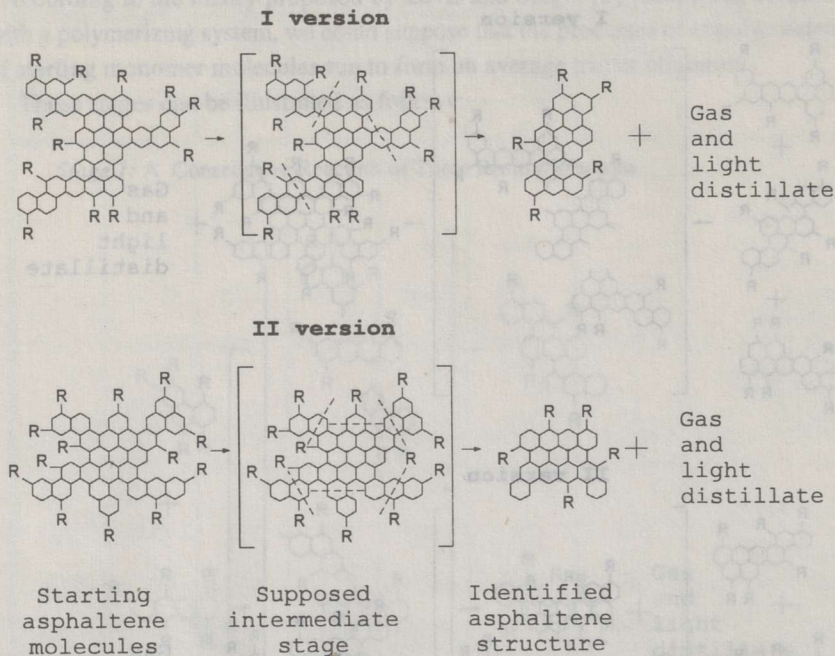
After reaching the final size during Stage 2 (data from Table 7 and the illustration on p. 353), the resulting large structure (still benzene-soluble) does not grow any more. It undergoes destruction and rearrangements - its molecular mass decreases, the degree of aromatization and the index of ring aromatization increase, the number of side substituents diminishes. The coke distillate removed during the process also forms at this stage. Gas continues to liberate as well. The spin concentration increases again - probably as a result of the formation of new and stabilized π-radicals.

These stages were also observed studying the stages of LTC of model compounds but the reason for rupture and rearrangement of these compounds was not explained. We consider that by increasing the starting molecule, mobile and reactive (probably with the intermediately formed σ-radicals), an enlarged structure of unfavourable (from the thermodynamic point of view) configuration results in a system still of low viscosity. In such structures, the deformation stresses together with the heat fluctuations due to the high temperature that cause the rupture of a specific part of the chemical bonds also increase. The complex effect of these reasons causes the processes of rupture and rearrangement observed by many authors and leads to the formation of a thermodynamically favourable (probably a planar) configuration of the structures. We suppose some role in this process to be played by a radical stabilization process by the formation of an odd-ordered structure, like that proposed by Lewis and Singer [5].

The further reaction of the obtained condensed planar structures could probably be realized only between molecules of a suitable configuration at the linking points

(attachments). Otherwise, the chemical bond formed will be quickly ruptured due to the mechanical stresses and heat fluctuations mentioned above. The value obtained for E_{act} of the transformation of the asphaltene molecules, close to that for the diffusion process, is a further proof of such a reaction.

As already said, the stages presented above correspond to the examinations made for LTC of model compounds. Mechanisms proposed by other authors finish at this point. We propose a model of the next stages of carbonization process based on obtained experimentally data.

Stage 4

I version

II version

Starting	Supposed	Identified
asphaltene	intermediate	asphaltene
molecules	stage	structure
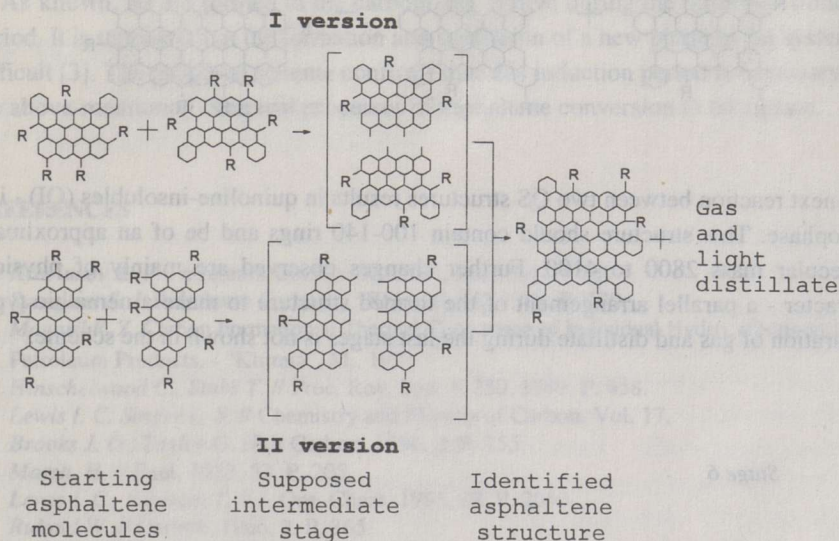
As the mechanism of the previous stages has revealed, similar structures react with similar ones. At that n-pentane-solubles (resins) transform into in n-pentane-insoluble but benzene-soluble compounds (asphaltenes). Basing on the theories expressed so far it is possible to suppose the run of the next stages. We propose a reaction between further two structures, similar in construction and size, and being of suitable configuration to form larger structures already benzene-insoluble (BI) but pyridine-soluble (PyrS).

The resulted structure cannot be examined by the method of Smith et al. [22] but it is possible to do by Corbett method [23]. As shown in Table 7, the structure estimated by this method coincides with the proposed one formed as a result of the reaction between two BS structures and one BI structure, consisting of about 30 aromatic condensed rings. The number of the side substituents is hypothetical. An indication of their existence at this and next stages is the established separation of methane, C_2-C_4 hydrocarbons as well as of hydrogen (from a methyl group) during heating.

From the scheme of the previous stages there follows a reaction between two BI/PyrS parts to form pyridine-insolubles (PyrI) but quinoline-solubles (QS). The resulting structure may involve 50 to 70 rings (average 60) and may have a mass of 1500 to 2200 (average 1800):

Stage 5
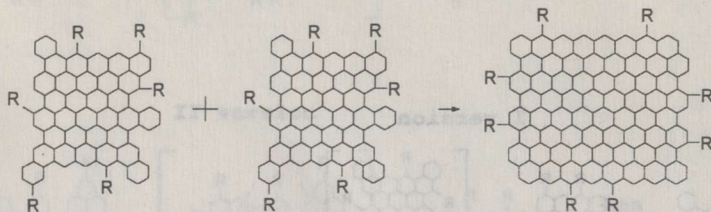
The next reaction between two QS structures results in quinoline-insolubles (QI) - i.e. mesophase. This structure should contain 100-140 rings and be of an approximate molecular mass 2800 to 4100. Further changes observed are mainly of physical character - a parallel arrangement of the formed structure to make a nemathic type. Separation of gas and distillate during the last stages is not shown in the scheme.

Stage 6
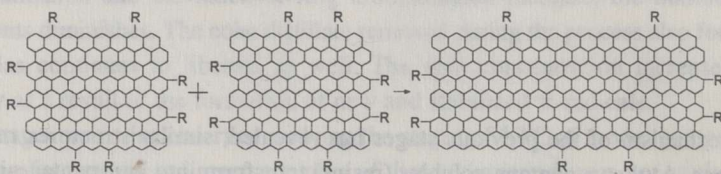
The resulting wide aromatic lattices explain the increase in the quantity of π-radicals during the process of mesophase conversion. Their formation could be explained by a detachment of H atom or side substituent followed by a resonance stabilization. Moreover, the formation of other structures e.g. biradicals could also be expected. Probably, during this stage the physical processes - orientation through diffusion and arrangement of crystals to form the nemathic type prevail over the chemical ones. In this aspect, the lack of a dependence between the mesophase conversion and the spin concentration could be explained - the behaviour of the wide plane structure is less affected, regardless of whether it is a radical or not.

Conclusions

The mechanism proposed for LTC brings the facts observed at LTC of model compound close to those observed during LTC of actual materials. The results from the investigations on this mechanism show that for producing a high-quality anisotropic electrode coke, the carbonizing systems have to be heated slowly (almost isothermally) not only within the range of mesophase transformation but also within the preceding temperature range - to give a possibility for a gradual reaction between the asphaltenes and for the required changes in the enlarged structure to take place before its further growth.

As known, BI are formed in the carbonizing system during the induction (hidden) period. It is supposed that the formation and separation of a new phase in the system is difficult [3]. The proposed scheme confirms that this induction period is necessary for the above-mentioned chemical processes of asphaltene conversion to take place.

REFERENCES

1. *Krasiukov A. F.* Petroleum Coke. - "Khimia", M., 1966. P. 180.
2. *Syunyaev S. J.* Petroleum Carbon. - "Khimia", M., 1980. P. 220.
3. *Magaril R. Z.* Carbon Formation at Thermal Conversion of Individual Hydrocarbons and Petroleum Products. - "Khimia", M., 1973.
4. *Hinschelwood C., Stubs T.* // Proc. Roy. Soc. A 250, 1949. P. 458.
5. *Lewis I. C. Singer L. S.* // Chemistry and Physics of Carbon. Vol. 17.
6. *Brooks J. O., Taylor G. H.* // Carbon. 1966, 2. P. 155.
7. *Marsh, H.* // Fuel. 1973, 52. P. 205.
8. *Lewis I. C., Edstrom T.* // J. Org. Chem. 1963, 28. P. 2050.
9. *Ruland W.* // Carbon. 1966, 2. P. 365.
10. *Marsh H., Akitt Y. V., Hurley J. M., Melvin J.* // J. Appl. Chem. 1971, 21. P. 251.
11. *Kubiza Cr., Jastembski J.* // Koks, smola, gas. 1987, 32(9). P. 211.
12. *Edstrom T., Lewis I. C.* // Carbon. 1969, 7. P. 85.
13. *Lewis I. C., Singer L. C.* // Carbon. 1967, 5. P. 373.
14. *Forbes W. F., Robinson J. C.* // Nature. 1967, 214. P. 80.
15. *Ruschev D.* // J. Therm. Anal. 1970, 2. P. 337.
16. *Simon C., Estrade H., Tchoubar D., Konrad J.* // Carbon. 1977, 15. P. 211.
17. *Marsh H., Akitt J. W., Hurley J. M., Melvin J., Warbuton A. P.* // J. Appl. Chem. Biotechnol. 1971, 21. P. 251.
18. *Ingram D. J.* // Proc. 3rd Carbon Conf. 1957. Pergamon, New York, 1959. P. 93.
19. *Georgiev I. B.* Thesis of Ph. D., 1983. - Technological University, Sofia, Bulgaria.
20. *Georgiev I. B., Angelova G. A., Dimitrova Z.* // Communications of the Departm. of Chemistry, Bulgarian Acad. of Science. Sofia, 1985, 18, 3. P. 376.
21. *Wolliams R. B.* // Spectrochem. Acta. 1959, 14. P. 24.
22. *Smith W. E., Mapier, B. P., Horne O. J.* // Petroleum Derived Carbon. ACS Symp. Series, Washington D. C., 1976, 21. P. 63.
23. *Corbett B. A.* // Anal. Chem. 1964, 36, 0, 1967.
24. *Georgiev I. B.* // Solid Fuel Chemistry. 1990, 3. P. 32.
25. *Georgiev I. B., Kaloyancheva K., Andonova K.* // Oil Shale. 1989, 6, 4. P. 349.
26. *Georgiev I. B., Kaloyancheva K., Andonova K.* // Oil Shale. 1988, 6, 4. P. 425.
27. *Georgiev I. B.* // J. Appl. Chem. - in press.

28. *Georgiev I. B., Dimitrova Z., Angelova G.* // Annuaire de L'Ecole Superieure de Chimie Technologique. Sofia, XXIX, 1983, 2. P. 350.
29. *Georgiev I. B., Kaloyancheva K., Andonova K.* // Solid Fuel Chem. 1990, 2. P. 76.

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