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Effect of Hydrogenation on Solubility of Carbonized Pitch

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The effect of hydrogenation of carbonized pitch on its solubility in quinoline was investigated in connection with structural changes of the pitch during carbonization. Naphtha-tar pitch (NTP) and acenaphthylene were carbonized at 673 and 703 K, respectively, for various periods of time. The pitches thus heat-treated were hydrogenated by BenKeser reaction and the amount of quinoline insolubles (QI) in the hydrogenated pitch was determined. An acenaphthylene pitch (ACP) heat-treated for 24 h was rendered completely soluble into quinoline by the hydrogenation, whereas a considerable amount of insolubles was left in the case of NTP treated for longer residence times than 8 h. This can be explained in terms of the difference in interaction among aromatic molecules constituting the QI components derived from NTP and ACP. ACPs doped with elemental sulfur left a significant quantity of QI after the hydrogenation. The addition of sulfur is considered to form crosslinking bonds between aromatic molecules through hydrogen abstraction by the sulfur. When QI separated from carbonized NTP was hydrogenated, the degree of conversion into quinoline solubles (QS) was low as compared with that for the whole sample of the same NTP. The presence of QS in the pitch plays a very important role for the hydrogenation.

Since mesophase transformation occurring in the early stage of carbonization of pitch is a key step to determine physical and chemical properties of resultant coke and carbon products, much attention has so far been focused on the carbonization behavior of various pitches and related materials. The texture of optically anisotropic mesophase formed during the carbonization process is influenced by various factors, *e.g.*, molecular structures, their distribution in starting materials, and the fluidity of the system.[1] One of procedures controlling mesophase textures is modification by means of hydrogenation of pitch.[2,3] The effect of the hydrogenation is considered as increasing the fluidity of the system in the temperature range where mesophase is formed and thereby developing optical textures.

Hydrogenation under severe conditions such as high temperature and high pressure of hydrogen induces cracking and consequently, gives products different from original constituents. On the other hand, a mild reaction using lithium in ethylenediamine, *i.e.*, the BenKeser reduction, is suitable for modification of pitch[4] because aromatic rings in molecules are converted mainly to hydroaromatics in which hydrogens attached to naphthenic rings are transferrable during the carbonization. Such a hydrogenation of heat-treated pitch which contains partly anisotropic textures in an isotropic matrix, is also effective for controlling the development of mesophase by converting all anisotropic textures into isotropic ones.[5]

In this study, in order to obtain structural information on mesophase, pitches have been subjected to heat-treatment to different degrees prior to hydrogenation and then hydrogenated by the BenKeser reaction. The solubility of pitches thus obtained was determined for quinoline. In addition, influences on the hydrogenation have been investigated of sulfur doped in acenaphthylene pitch and of quinoline-soluble components in naphtha-tar pitch.

Experimental

Carbonization. Naphtha-tar pitch (NTP) obtained by thermal cracking of naphtha was supplied from Kureha Chemical Industry. Acenaphthylene of reagent grade was commercially available from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. NTP and acenaphthylene were carbonized at 673 and 703 K, respectively, at a heating rate of 3 K min^{-1} and maintained at each temperature for 1—24 h in a nitrogen stream. Sumatora Light (Minas) vacuum residue (SL) treated at 703 K for 1—24 h[6] was used for comparison.

Doping of sulfur into acenaphthylene pitch (ACP) was carried out in the following way: Elemental sulfur was added to acenaphthylene with a ratio of 1:5 by weight and the mixture was heat-treated at 623 K for 3 h in a nitrogen atmosphere in an autoclave with a magnetic stirrer. After the treatment unreacted sulfur was removed by washing with ethanol. The pitch obtained was carbonized in a similar procedure as described above.

Hydrogenation. These pitches carbonized as above were hydrogenated by a method reported by Brooks and Silberman:[7] Lithium was added in small portions to a stirred suspension of a finely ground sample in anhydrous ethylenediamine in a nitrogen atmosphere. The weight of lithium was equal to that of the pitch. After 3 h reaction, the mixture was cooled and hydrolyzed with ice and water. The reaction product was recovered by centrifugation and washed repeatedly with water until lithium ion was removed. The product was dried below 383 K for 24 h in an oven.

Determination of Quinoline Insolubles (QI) and Elemental Analysis. The amount of QI was determined according to the filtration method of JIS-K2425. Analysis of carbon, hydrogen, and nitrogen was carried out with a Yanaco MT-3 CHN Corder and sulfur content was measured by using a LECO Corporation IR-33.

X-Ray Diffraction. The average size of molecules for carbonized pitches was calculated from the (11) band of X-ray diffraction profile according to Diamond's method.[8]

Results

Structural Change with Carbonization. Amounts

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of quinoline insolubles in NTP and ACP carbonized at 673 and 703 K, respectively, are plotted against carbonization time in Fig. 1, together with those for hydrogenated pitches described in the next section. NTP forms easily QI at a higher rate than ACP does in spite of its lower carbonization temperature. Both pitches consist of almost all QI components at longer residence times. In order to obtain structural information on heat-treated pitches, the average size of molecules, *La*, was calculated from the (11) band of X-ray diffraction pattern (Table 1). It seems that the molecular size increases with residence time although the values listed in Table 1 somewhat scatter. An obvious difference between NTP and ACP is that NTP before carbonization is composed of larger molecules (10.2 Å). This is because the original pitch was subjected to thermal treatment at a higher temperature.[9] The number of stacking units as obtained from the (002) band of X-ray profile for the carbonized pitches of NTP ranges from 2.4 to 2.8 under these experimental conditions.[*1]

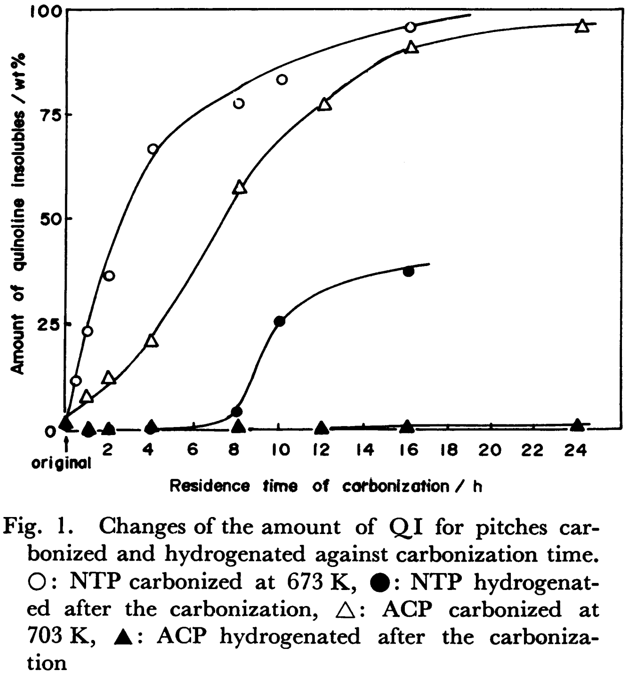

Fig. 1. Changes of the amount of QI for pitches carbonized and hydrogenated against carbonization time. ○: NTP carbonized at 673 K, ●: NTP hydrogenated after the carbonization, △: ACP carbonized at 703 K, ▲: ACP hydrogenated after the carbonization

TABLE 1. AVERAGE SIZES (*La*) OF MOLECULES FOR NTP AND ACP CARBONIZED AT 673 AND 703 K, RESPECTIVELY, FOR VARIOUS HOURS

Residence time	*La*/Å	
h	NTP	ACP
original	10.2	—
0.5	10.6	—
1	10.3	9.6
2	11.7	9.8
4	11.1	9.8
6	—	9.8
8	11.4	10.8
10	11.2	—
12	—	10.4
16	11.1	—
24	—	11.4

Hydrogenation of Carbonized Pitch, QI of NTP, and ACP Containing Sulfur. Hydrogen to carbon atomic ratios for pitches carbonized and hydrogenated

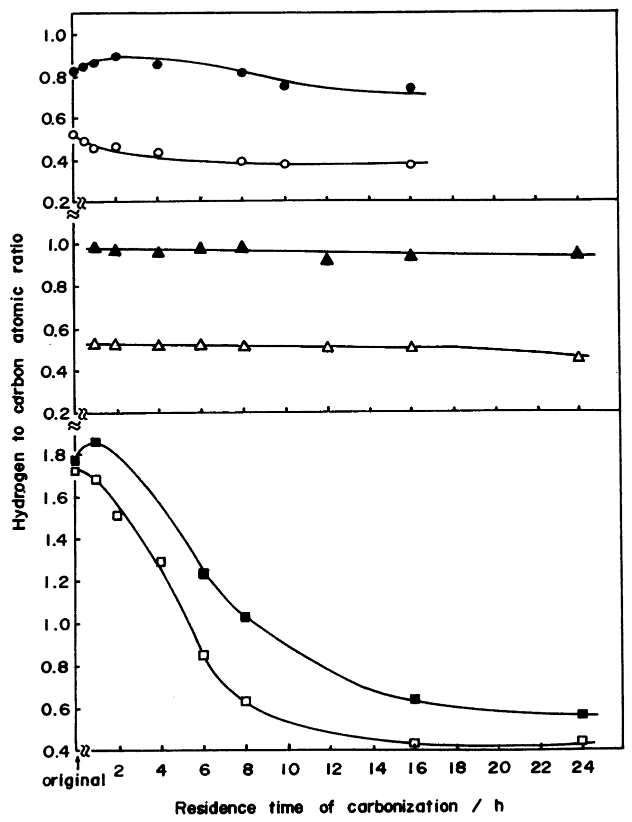

Fig. 2. Changes of hydrogen to carbon atomic ratio against carbonization time.
○: NTP carbonized at 673 K, △: ACP carbonized at 703 K, □: SL carbonized at 703 K, ●: Hydrogenated product of NTP carbonized at 673 K for various periods, ▲: Hydrogenated product of ACP carbonized at 703 K for various periods, ■: Hydrogenated product of SL carbonized at 703 K for various periods.

TABLE 2. AMOUNTS OF QI FOR NTP AND HYDROGENATED NTP (NTP-BK)

Carbonization time at 673 K before hydrogenation	QI/wt%	
h	NTP	NTP-BK
4	66.9	0.4(25.7)[a]
8	76.3	3.9(44.1)[a]
10	83.3	26.6(28.1)[a]
16	95.7	38.7(37.5)[a]

a) Values were obtained when QI isolated from NTP was hydrogenated.

[*1] Reliable values could not be obtained in the case of an ACP due to the presence of an additional band at a lower diffraction angle.

Table 3. Changes in H/C atomic ratio and sulfur content for ACP containing sulfur (ACP-S) and hydrogenated ACP-S (ACP-S-BK)

Sample	Treatment	Residence time at 703 K/h	H/C atomic ratio	Sulfur content
				wt%
ACP-S	Carbonization	4	0.501	1.00
		8	0.487	1.55
		12	0.484	1.72
ACP-S-BK	Carbonization/ Hydrogenation	4	0.816	0.39
		8	0.761	0.47
		12	0.740	0.49

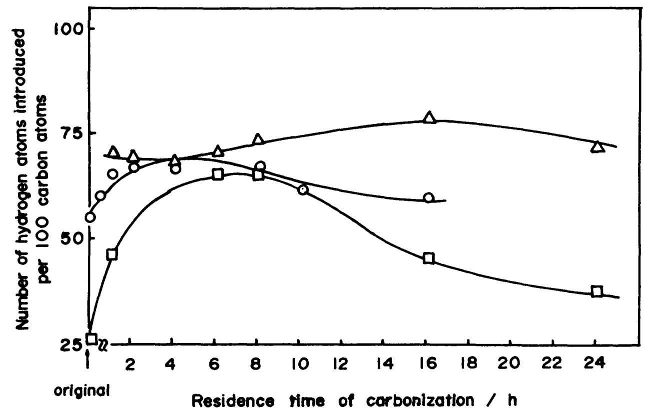

Fig. 3. Changes of hydrogen addition for carbonized pitches of NTP, ACP, and SL with carbonization time.
○: NTP carbonized at 673 K, △: ACP carbonized at 703 K, □: SL carbonized at 703 K.

Table 4. Amounts of QI for ACP containing sulfur (ACP-S) and hydrogenated ACP-S (ACP-S-BK)

Carbonization time at 703 K before hydrogenation	QI/wt%	
h	ACP-S	ACP-S-BK
4	51.4	8.0
8	67.7	21.7
12	78.9	32.7

samples are plotted against residence time in Fig. 2. Values for SL pitch obtained in the same procedure are added there for comparison. When carbonized pitches of NTP and ACP were hydrogenated, the H/C ratio increased from 0.5 to 0.8—1.0. The number of hydrogen atoms introduced per 100 carbon atoms can be calculated from the difference between measurements of elemental analysis. The data are shown in Fig. 3. ACP maintains almost a constant value over the ranges of residence time adopted. On the other hand, the hydrogenation susceptivity of NTP is different from that of ACP; a remarkable hydrogen addition for NTP was recognized with its pitches produced in the early stage of carbonization. After a maximum was reached near 4 h carbonization, the number of hydrogens introduced was caused to decrease with residence time. SL exhibits a similar curve with a steeper slope than NTP.

When a series of ACPs heat-treated for various periods of time was hydrogenated, all carbonization products were completely converted to QS even in the case of the ACP carbonized at 703 K for 24 h, which consisted entirely of quinoline-insoluble fractions (Fig. 1). On the other hand, the whole components of the NTP samples carbonized at shorter residence times than 4 h were made soluble in quinoline by the hydrogenation, but further heat-treatment left a considerable amount of QI in the hydrogenated pitches, as can be seen in Fig. 1 and Table 2. The values designated in parentheses in Table 2 represent the amounts of QI when the insolubles isolated from NTP pitches were hydrogenated. When the whole NTP pitch treated for 10 or 16 h and the QI separated from the corresponding sample were hydrogenated, there was no significant difference between them. In the case of NTP carbonized for 4 or 8 h, however, a considerable difference is recognized between them (Table 2).

The ACP containing sulfur was prepared in order to investigate the effect of sulfur doping on carbonization. The amount of residual sulfur in the pitch is given in the last column of Table 3. The amount of the sulfur remaining increased with residence time, but after the hydrogenation the sulfur content in the pitch decreased because part of the sulfur had reacted with hydrogen to produce hydrogen sulfide. Values of QI for these pitches are given in Table 4. In contrast to the data of ACPs without sulfur (Fig. 1), ACPs containing sulfur left a large amount of QI after the hydrogenation.

Discussion

The structure and reactivity of insolubles present in original pitches have been investigated in detail by Mochida *et al.*[10,11] They found that the QI fraction with optical isotropy is different in chemical structure from the other fractions and can be modified by means of reductive alkylation and hydrogenation. Since the QI matters generated in the carbonization process of pitch are anisotropic in optical texture, they are fundamentally different from QIs involved in pitches without heat-treatment. Therefore, it is interesting to consider structural changes associated with the increase in QI on the basis of the extent of hydrogenation of NTP and ACP carbonized to different degrees.

According to the pyrolysis scheme of acenaphthylene reported by Singer and Lewis[12] and others,[13,14] acenaphthylene polymerizes when subjected to heat-treatment at lower temperatures than 503 K, and then decomposes to produce fluorocyclene, decacyclene, *etc.* when heated over a temperature range of 600 to 650 K. As the temperature is raised further, zethrene which has a unit structure favorable for formation of higher aromatic sheet molecules, appears from 703 to 723 K. It was found from the X-ray result (Table 1) that a series of ACPs carbonized at 703 K for various periods of time has average sizes of 9.6—11.4 Å, which are roughly comparable to the size of zethrene-like molecules ($\approx$10.6 Å). The hydrogen to carbon atomic ratios are kept at almost the same values (Fig. 2), whereas the QI content steadily increases with residence time (Fig. 1). These results suggest that the treatment for a prolonged period at this temperature does not bring about any drastic structural change in the constituent molecules of QI.[15] When the carbonized pitches of ACP were hydrogenated, the number of hydrogens introduced into aromatic molecules was almost constant over the carbonization-time range of 1—24 h and the whole samples were completely rendered soluble in quinoline. The above evidence suggests that the arrangement of aromatic molecules would be destroyed by the hydrogenation due to a reduction in the interaction among the molecules. Thus, it seems that the QI matters of ACP consist of components with such smaller molecular weights as to get dissolved into quinoline by the BenKeser reaction.

In contrast, hydrogenated NTP and SL behave in a manner different from that of ACP described above. Since both samples originate from petroleum oil, they contain alkyl chains attached to hydroaromatic rings before the carbonization. The less degree of hydrogenation on the pitches without heat-treatment might result from the presence of the alkyl groups inhibiting the effective hydrogenation of aromatic ring molecules.[7] When they are heat-treated, elimination and/or cyclization of the alkyl groups occur and at the same time the resultant molecules become more aromatic.

It is well known that the BenKeser reaction mainly converts aromatic hydrocarbons into partially hydrogenated ones without cleavage of rings.[4,7] However, the stronger the interaction between aromatic layers becomes, the lower the degree of hydrogenation is rendered because of the decrease in the dispersibility of molecules in solvent. Therefore, the considerable decrease in the ratio H/C of NTP and SL for longer residence times (Fig. 2) may suggest the presence of such a strong intermolecular force among aromatic layers in QI. In fact, the aromaticity of NTP carbonized at 673 K for 16 h was estimated to be roughly unity from data of H/C and helium density.[16] This value is higher than that obtained for ACP treated at 703 K for 24 h (0.95). Therefore, as the residence time becomes longer, NTP is considered to produce matters with high contents of QI, in which the interaction among stacked molecules is strong enough to prevent the solvent penetration. In other words, the degree of solubility in quinoline after the hydrogenation may reflect the quality of QI in pitch before the hydrogenation.

The influence of the sulfur present in the original NTP was taken into account as another factor in order to understand the difference in hydrogenation behavior between NTP and ACP. As already described, the result in Table 4 reveals that the sulfur addition to ACP produces residues which leave some amounts of QI after the hydrogenation. It may be associated with formation of crosslinkages during carbonization.[17]

Marsh and Crawford[18] reported that mesophase spherules formed in the early stage of carbonization include small soluble molecules between lamellae. When the carbonized pitch is treated with quinoline, the small molecules incorporated between mesophase layers are considered to get dissolved into quinoline. Consequently, it is expected that the interaction between the layers becomes stronger and that the solvent such as ethylenediamine cannot penetrate into these layers on the hydrogenation. Hydrogenation of only the QI fraction from NTP carbonized for 4 or 8 h left a considerable amount of insolubles (Table 2). Thus, the result supports the above assumption and furthermore, suggests that the soluble components in the present system contribute to the solubility of QI after the hydrogenation, as pointed out by Mochida *et al.*[11]

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