

Thermal Reaction Analysis of Coal Tar Pitch by Laser Desorption Ionization Mass Spectrometry[†]

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Abstract:

Laser Desorption Ionization Mass Spectrometry was applied for analysis of coal tar pitch and its thermal reaction. Pitch was found to consist of polycyclic aromatic hydrocarbons without alkyl side chains, ranging from $m/z^)=160$ to 6 000. Although compounds with molecular weights $m/z=500$ or more were observed only in TI (toluene insoluble) in the pitch, compounds below $m/z=500$ were found in both TS (toluene soluble) and TI. Heat treatment increased the peak intensity of the TI compounds. However, the molecular weight distribution of TS showed no significant change, suggesting that the compounds in TS randomly react with TS or TI to be transformed to TI through thermal reaction.*

1. Introduction

Coal tar pitch is derived from the distillation of coal tar, a byproduct in the steel manufacturing process, followed by heat treatment. Pitch is used as a binder for graphite electrodes and as a raw material for various carbon products. Since pitch contains many polycyclic aromatic hydrocarbons, the content of TI (toluene insoluble) or QI (quinoline insoluble) is often used as an important index to describe its composition, which relates to properties such as carbonization yield.

Instrumental analysis has also been applied to pitch in order to characterize its chemical structure. Nuclear magnetic resonance spectroscopy and infrared spectroscopy are used to determine the average structure of pitch¹⁾. The chemical constituents in pitch are analyzed by using gas chromatography and liquid chromatography, despite the analytical limitation of molecular weight^{1,2)}. Size exclusion chromatography and mass spectrometry are effective methods to determine the

molecular weight distribution¹⁻³⁾.

Several ionization methods have also been applied in analyses of pitch by mass spectrometry. While the methods of electron ionization⁴⁾, chemical ionization⁴⁾, and liquid ionization^{4,5)} are used for analysis of constituents with rather low molecular weights, methods such as fast atom bombardment⁶⁾, field desorption^{7,8)}, laser desorption ionization (LDI)^{2,3)}, and matrix assisted laser desorption ionization^{2,3)} are applied for analysis of constituents with high molecular weights. Since ionization methods influence the degree of fragmentation and detection sensitivity⁹⁾, the most suitable ionization method is chosen for the purpose of characterization.

In this report, LDI mass spectrometry was chosen to find out the chemical structure and thermal reaction scheme of pitch constituents, because it is suitable for analysis of solid samples.

2. Experimental

2.1 Preparation of Coal Tar Pitch

2.1.1 Distillation of coal tar

Pitch A was obtained by distillation of coal tar which produced by a commercial coke oven (operated at JFE Steel Corporation). The primary QI was removed before distillation. 2.0 kg of the QI-free tar was distilled in a glass flask at 320°C under flowing nitrogen (flow rate: 1.5 L/min) with a pressure of 31 kPa. The resulting Pitch A has a softening point (SP) of 77°C.

2.1.2 Heat treatment of pitch

Heat treatment of 200 g of Pitch A was heat-treated in a flask at 340°C for 10 h under ordinary pressure, and

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^{*}) Mass to charge ratio



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Table 1 Properties of pitch A and B

		Pitch A	Pitch B
Softening point	(°C)	77.4	83.0
Toluene insoluble (TI)	(mass%)	10.8	17.4
Quinoline insoluble	(mass%)	< 0.01	< 0.01
Fixed carbon	(mass%)	48.7	52.5
C*	(mass%)	92.2	92.6
H*	(mass%)	4.3	4.5
N*	(mass%)	1.2	1.2
O*	(mass%)	1.2	1.0
Mass loss of TI			
Room temperature (R. T.)-600°C**	(mass%)	12.9	9.3

*Elemental analysis (Thermo Fisher Scientific K. K., EA1110 CHNOS-O)

**Thermogravimetry (Shimadzu Corp., DTG60-AH), in N₂ at 600°C at a heating rate of 2°C/min

Pitch B was obtained with a yield of 97%. The properties of Pitch A and Pitch B are summarized in **Table 1**. As shown in Table 1, TI increased by 6.6% through the heat treatment.

2.2 Preparation of Sample for Analysis

The pitch was extracted by toluene under the standard compliant condition in JIS K 2425, and TS and TI were separated. The pitch and the separated TS and TI components were analyzed by mass spectrometry.

2.3 Mass Spectrometry

The LDI mass spectrum was acquired with an AXIMA Performance mass spectrometer (Shimadzu). The measurement mode was linear-positive using a nitrogen pulsed laser (wave length 337.1 nm), and the laser power was adjusted to 30–42% of the maximum power. The mass range was set from $m/z=1$ to 10 000.

The TS sample was dropped on a sample plate and dried in air to remove the solvent toluene. The pitch and its TI were ground in an agate mortar and fixed on a sample plate by a conductive tape.

3. Results

3.1 Constituents in Pitch

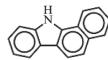
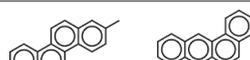
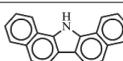
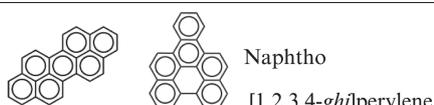
3.1.1 Pitch

The mass spectrum of Pitch A is shown in **Fig. 1**. More than 20 strong peaks, which seem to be molecular ion peaks, were observed, along with neighboring peaks of low intensity. The low intensity peaks are estimated to be isotropic ions. The m/z values of the molecular ions are also shown in the spectrum for easy understand-

ing. The smallest m/z value among the strong peaks is 167, and the largest is 500. A regular increase in molecular weight by $\Delta m/z=24$ was observed in the main peaks, for example, $m/z=228$, 252, 276 and $m/z=302$, 326, 350.

Since coal tar pitch is composed of atoms of C, H, and small amounts of O and N (see Table 1) and its main constituents are polycyclic aromatic hydrocarbons without alkyl side chains⁷⁾, it is possible to estimate the chemical structure corresponding to the molecular weight. **Table 2** presents the m/z values of the main peaks and their estimated structures. Most of the peaks are possibly explained by the structure of the poly-condensed aromatic hydrocarbons without side chains, even though some of these hydrocarbons have nitrogen atoms in their structures. According to these structures, the regular increase of $\Delta m/z=24$ can be convincingly explained by the increase of peri-type condensation, such as from perylene (252) to benzo [*ghi*] perylene (276). On the other hand, the increase of aromatic rings caused by cata-type condensation shows the pattern of $\Delta m/z=50$, as in the example of the change from benzo

Table 2 Estimated structure of polycyclic aromatic hydrocarbons in pitch

m/z	Structure
217	
228	
242	
252	 Perylene
267	
276	 Benzo[<i>ghi</i>]perylene
292	
302	
326	 Naphtho [1,2,3,4- <i>ghi</i>]perylene
350	

[ghi] perylene (276) to naphtho [1, 2, 3, 4-ghi] perylene (326)⁸.

3.1.2 TS and TI of pitch

In order to observe the high molecular weight constituents, both TS and TI were examined by LDI mass spectrometry, since peaks of high molecular weight ions were not found in the spectrum of the whole Pitch A. The spectra are shown in **Fig. 2** for TS and in **Fig. 3** (a)

for TI.

In comparison with the whole pitch (see Fig. 1), the TS shows a very similar spectrum to the pitch, while the TI shows a wider molecular distribution, which ranges from $m/z=167$ to around 5 000 or 6 000. Figure 3 (b) presents the mass spectra of TI in a narrow m/z range for an easy comparison between TS and TI. As in the TS, constituents having m/z from 167 to 500 were found. Whereas TS shows the highest intensity at around $m/$

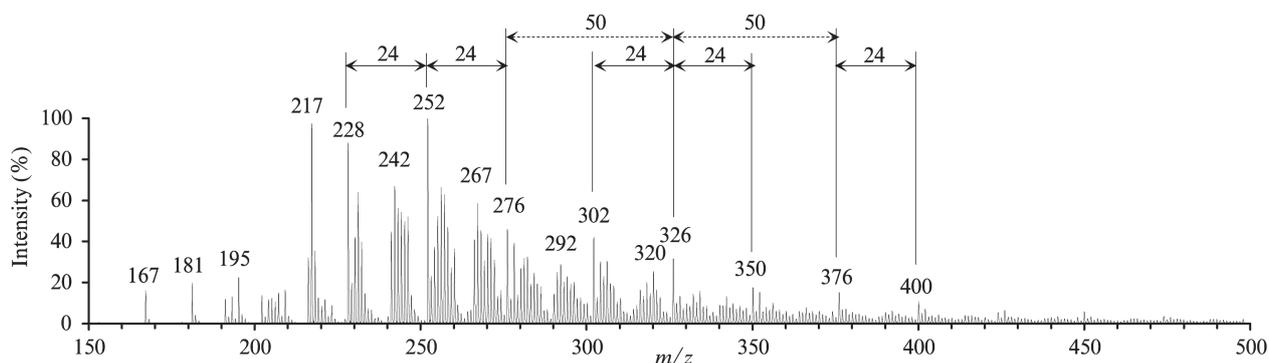


Fig. 1 LDI Mass spectrum of pitch A

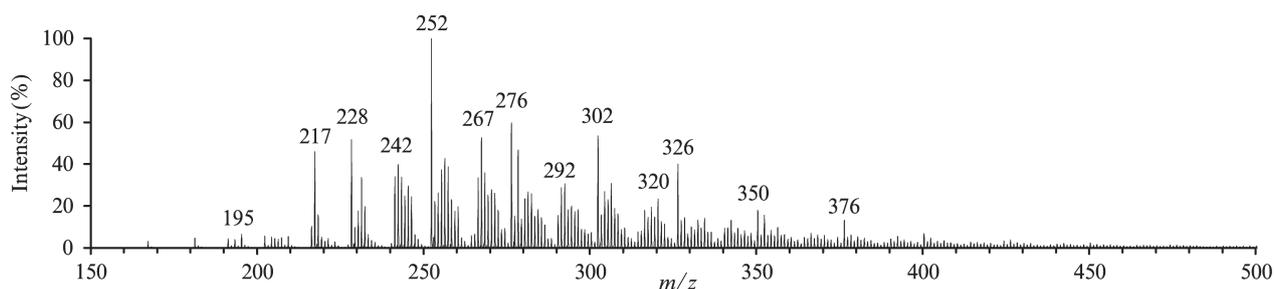
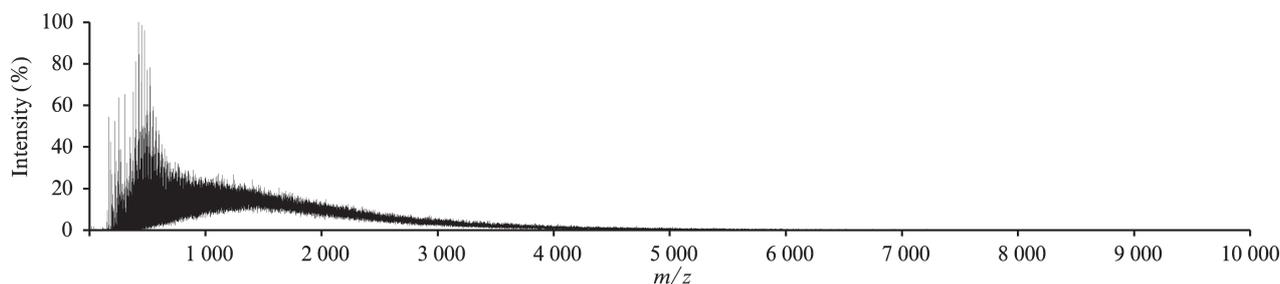


Fig. 2 LDI Mass spectrum of TS in pitch A

(a) m/z 1–10 000



(b) m/z 160–500

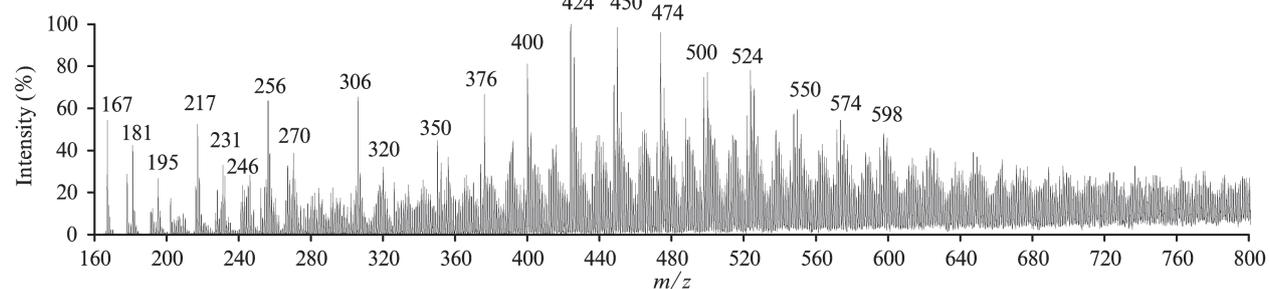


Fig. 3 LDI Mass spectrum of TI in pitch A

$z=250$, the highest peak in TI is at $m/z=424$. On closer examination, TI has different constituents from TS, such as $m/z=231, 246, 256, 270, 306$. However, the regular increases in m/z (increments of 24 and 50) were found in the spectrum for the main peaks in TI.

Although main peaks become less distinguishable from their isomer peaks in the high-mass region ($m/z=650$ or more), the regularity of $\Delta m/z=24$ is still found for the distinguishable main peaks ($m/z=550, 574, 598$).

3.2 Effect of Heat Treatment

3.2.1 Heat-treated pitch

Figure 4 shows the mass spectrum of heat-treated Pitch B. Comparing with Pitch A (see Fig. 1), most constituents are the same despite slight differences in peak intensity. Although TI increased by 6.6% through the heat treatment as described in the experimental section, there were no changes in the spectrum profile, and no increases or decreases of specific constituents were found.

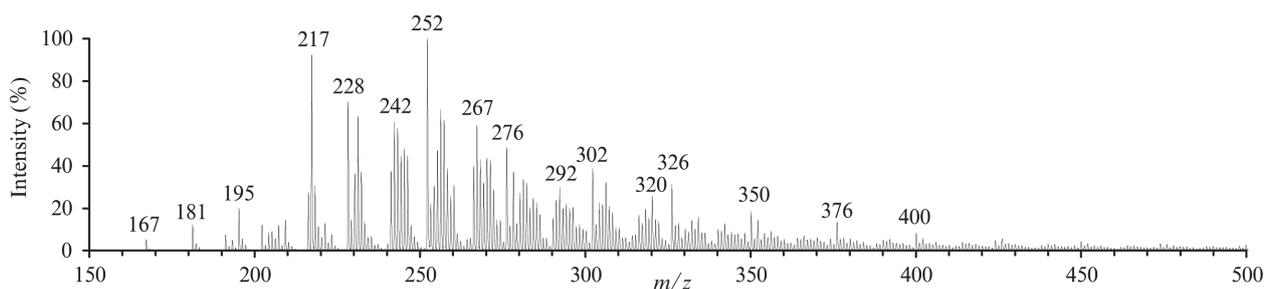


Fig. 4 LDI Mass spectrum of pitch B

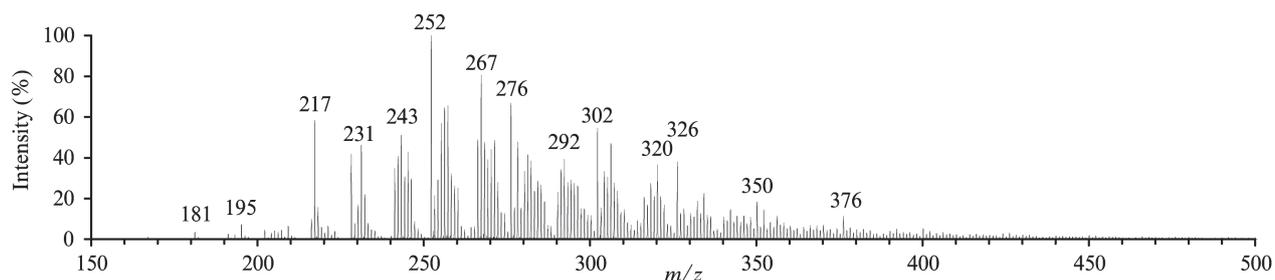


Fig. 5 LDI Mass spectrum of TS in pitch B

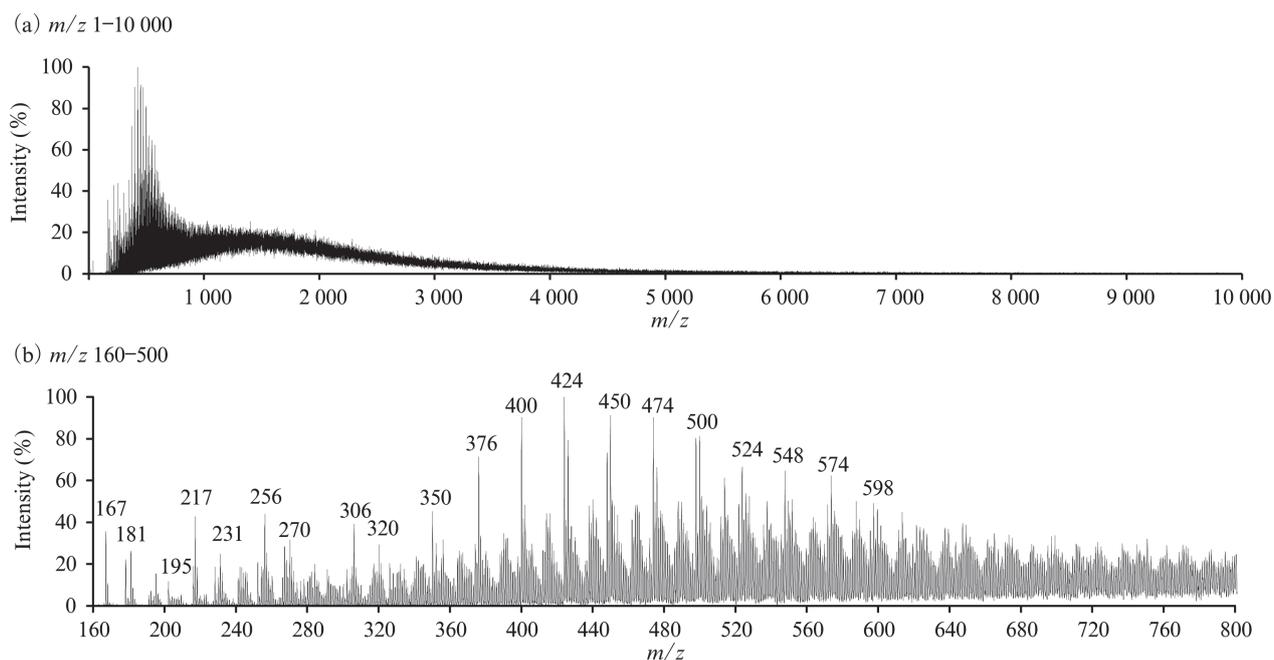


Fig. 6 LDI Mass spectrum of TI in pitch B

3.2.2 TS of heat-treated pitch

LDI-MS was carried out on TS of Pitch B in order to analyze the influence of heat treatment in greater detail. The mass spectrum of the TS is shown in Fig. 5. The molecular weight distribution and constituents are almost the same as those of the TS of Pitch A (see Fig. 2), although there are slight differences in peak intensity such as a peak at $m/z=231$ having higher intensity than 228. While TI increased (in other words, TS decreased) as a result of the heat treatment, no specific increases or decreases of the constituents were observed, and no new main peaks were found after heat treatment.

3.2.3 TI of heat-treated pitch

Figure 6 (a) shows the TI spectrum of Pitch B. Compared with the TI in Pitch A (see Fig. 3 (a)), the TI in Pitch B has the same constituents, which range from $m/z=167$ to around 5 000 or 6 000, but the constituents with $m/z=1\ 500$ or more have slightly higher peak intensities.

Figure 6 (b) shows an enlarged spectrum of the lower mass region. The pattern of the molecular weight distribution is almost the same as that of the TI in Pitch A (see Fig. 3 (a)) under $m/z=500$ and in the range of $m/z=500-800$.

4. Discussion

4.1 Chemical Structure of Constituents in Pitch

The chemical structures of the constituents in coal tar pitch and petroleum pitch have been estimated from the molecular weight obtained by the mass spectrum. It has been reported that petroleum pitch shows an interval of $\Delta m/z=14$, which corresponds to the methylene side chain ($-\text{CH}_2-$)⁷. Coal tar pitch has also been reported to contain polycyclic aromatic hydrocarbons without alkyl side chains^{3,5,7,8}. The results of this paper indicate that coal tar pitch has the same structural characteristics as reported, and based on the fact that coal tar pitch has no side chains, it can be estimated that it is more thermally stable than petroleum pitch, since constituents having alkyl side chains are thermally unstable and initiate thermal reactions.

4.2 Solvent Extraction

As described in the previous section, coal tar pitch consists of many poly-aromatic hydrocarbons and each constituent is mutually dissolved. When toluene is added to pitch, toluene dissolves the constituents of lower molecular weight, and this liquid mixture then dissolves the constituents of higher molecular weight. The amount of soluble constituents depends on the solubility of the

pitch by the liquid mixture, and the excess amount over its solubility will precipitate as TI¹⁰.

The same constituents were found in both TS and TI in the spectrum ranging from $m/z=167$ to 500 (see Fig. 2 and Fig. 3 (b)). These constituents are considered to exist in pitch in a larger concentration than its solubility, and for this reason, the constituents will be found both in TS and in TI. Since molecular weight is one of the major determining factors of solubility, the constituents of high molecular weight with $m/z=500$ or more are found only in TI. However, the amounts of some constituents such as $m/z=256$, 270, 306 are larger in TI than in TS, which means that the solubility will be affected not only by the molecular weight but also by other factors such as polarity.

4.3 Reaction of Pitch in Heat Treatment

In the heat treatment of pitch, dehydrogenation of polycyclic aromatic hydrocarbons causes the poly-condensation reaction, and the molecular weight of the constituents in the pitch becomes higher than before heat treatment. This reaction converts TS constituents to TI, and as a result of this conversion, the amount of TI increases. As described in the results section, there was almost no difference in the molecular weight distribution in the TS spectra before and after heat treatment (see Fig. 2 and Fig. 5). This fact implies that the specific constituents in TS do not react and are transformed to TI constituents, but they randomly react to form TI constituents. In contrast, the molecular weight distribution of TI changes as a result of heat treatment, displaying some increase in the higher molecular weight region (see Fig. 3 (a) and Fig. 6 (a)). This means that heavier constituents are produced during heat treatment. This change will result in less mass loss of TI in the heat-treated pitch, as shown in Table 1.

From the discussion above, the reaction schemes during heat treatment of pitch are estimated to be as follows:

- (1) TS constituent+TS constituent→TI constituent
- (2) TS constituent+TI constituent→TI constituent
- (3) TI constituent+TI constituent→TI constituent.

The plausible reaction schemes for (1) and (2) are summarized in Fig. 7.

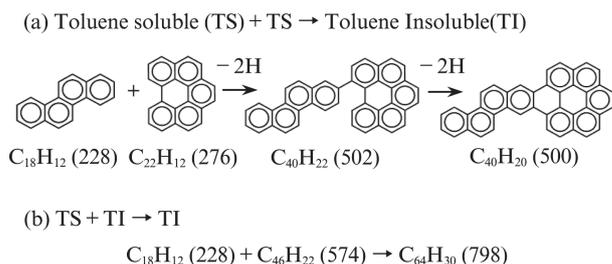


Fig. 7 Plausible scheme of thermal reaction in pitch

Through these reactions, the molecular weight of the constituents in pitch will become higher, and the number of aromatic rings will increase. When the aromatic rings in polycyclic hydrocarbons are large enough, the molecules will begin to stack by interaction between the rings, generating optically anisotropic mesophase in the coal tar pitch.

4.4 Limitation of Mass Spectrometric Analysis of Pitch

In this study, LDI mass spectrometry was applied for analysis of pitch constituents up to $m/z=6\ 000$, and the results were discussed. Although LDI mass spectrometry is an excellent analytical method for mixtures such as coal tar pitch, there are two major problems which can be commonly found in every mass spectrometry technique. The first is the upper limitation of molecular weight, and the second is poor quantitativity caused by the difference in the ionization efficiencies of molecules.

However, when LDI mass spectrometry is used with an understanding of these limitations, it will be a useful method for obtaining information about the chemical structure of constituents in pitch and estimating the reaction mechanism.

5. Conclusions

As discussed above, LDI mass spectrometry has some limitations when used for analysis of pitch, but it is still an effective method for obtaining various types of useful information. In this report, LDI mass spectrometry was applied to analyze the molecular weight distribution of TS and TI in pitch before and after heat treatment. The chemical structures were estimated from the

spectra, and the reaction schemes were also discussed.

JFE Chemical Corporation has been producing pitch products such as binders and impregnation pitches by a production process developed over the course of many years. We will continue to produce products which meet customers' needs by carrying out basic analysis and developing production technologies.

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