

Reflux Pretreatment of Hydropyrene and Its Chemistry

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The reflux pretreatment of oxidized hydropyrene was examined in order to increase its coke yield. The pretreatment between 350 and 380 °C was effective to increase the yield by 8 %. The chemical constituents in the pitches derived from hydropyrene were analysed by means of the solvent fractionation, gas chromatography and FD-Mass spectroscopy to reveal the chemical change during the pretreatment. The increase of the coke yield is ascribed to the dehydrogenative condensation of trimers and tetramers of pyrene units.

INTRODUCTION

In the carbonization technology, it is most desirable to find procedures for the appreciable increase of coke yield without deterioration of anisotropic development.

The present authors reported the carbonization reactivity of pyrene hydrogenated with Li-ethylene diamine. Its oxidation increased the coke yield to ca.20 % maintaining the development of excellent anisotropic flow texture (1).

In the present report, the reflux pretreatment of the oxidized hydropyrene was studied to increase its coke yield. The oxidized hydropyrene still carried naphthenic hydrogens.

The chemical constituents in the pitches from the hydropyrenes are analyzed to discuss the condensation scheme.

EXPERIMENTAL

Hydropyrene (Table 1) which was obtained by hydrogenation of commercial pyrene using Li and ethylenediamine at 80-100 °C was oxidized in air at 150 °C for 24 hr. The oxidized hydropyrene (O.H.P) was heat-treated in a flask with a condensor at the temperature of 300, 350 and 380 °C for 40 hr under stirring of 400 rpm.

The resulting pitches (Pitch-300, Pitch-350, Pitch-380) were carbonized under flowing nitrogen at 600 °C for 24 hr by the heating rate of 600 °C/hr. The pitch was also carbonized at 400 °C for variable times to prepare the mesophase pitch of intermediate state in the carbonization.

RESULTS AND DISCUSSION

All of the cokes obtained at 600 °C exhibited anisotropic flow domain textures similar to those from the original hydropyrene and O.H.P regardless of the refluxing heat-treatment (Fig. 1). The

Table 1. Elemental Analyses of Hydropyrene

C	H	N	diff.
90.30	6.58	0.24	1.47



Fig. 1 Optical micrograph of coke from Pitch-350.
HTT: 600°C-2hr.

influence of the reflux heat-treatment on the coke yield (starting hydropyrene base) is shown in Fig. 2. Although the coke yield of Pitch-300 was same to that of O.H.P, the coke yield of Pitch-350 and Pitch-380 were 32 %, which was about 8 % higher than those of O.H.P and Pitch-300.

Solubilities of O.H.P and pitches are shown in Fig. 3. The HS fraction, the major part of which consisted of pyrene and hydropyrene (ca 85 % of HS in O.H.P), increased from 30 % of O.H.P to 70 % of the pitches during the reflux heat-treatment, regardless of the temperatures. Pyrene and hydropyrenes were also dominant in HS of the pitches. The BI fraction which was not found in C.H.P was produced during reflux heat treatment, the amount increasing at the expense of the HI-BS fraction with the severity of the refluxing treatment conditions. The BI fraction in Pitch-350 and Pitch-380 contained some PI fractions.

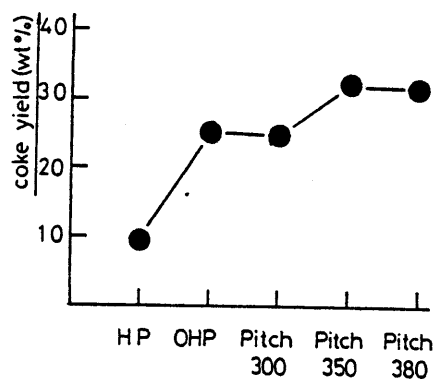


Fig. 2 Coke yields of HP, OHP and pitches
HTT: 600°C/hr, 600°C-2hr
HP: hydropyrene
OHP: oxidized hydropyrene
(hydropyrene base)

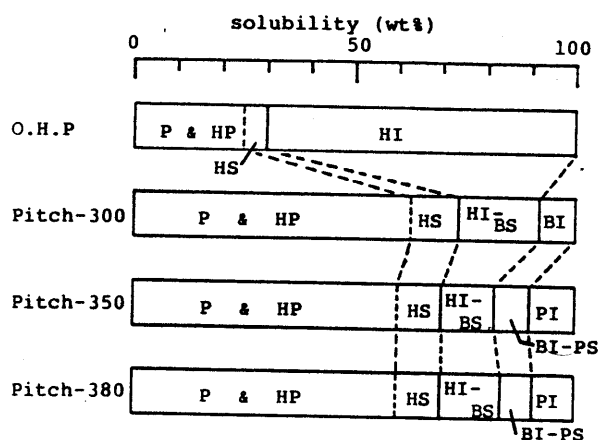


Fig. 3 Solubilities of O.H.P and pitches
P = pyrene HP = hydropyrene

Gel-permeation chromatograms of the HI-BS and BI fractions in the pitches are illustrated in Fig. 4. The chromatogram of the BI fraction in Pitch-300 had single-distribution profile, the retention time ranging from 26 to 34 min. The same fractions in Pitch-350 and Pitch-380 exhibited different profiles from that of Pitch-300. The chromatograms of the HI-BS and BI fractions overlapped each other, especially for Pitch-350 and Pitch-380, indicating that molecular weight is not the major factor differentiating the solubility.

The major mass numbers observed in the fractions of O.H.P and Pitch-350 are summarized in Table 2. The HI-BS fraction of Pitch-350 consisted of dimers, trimers and tetramers which contained less hydrogen and were more aromatic than those of O.H.P. The components of the BI fraction observed were dimers and trimers which had lost more hydrogens to become essentially aromatic, indicating that the extent of dehydrogenation or aromaticity, not the extent of oligomerization, was the principal determinant of solubility in benzene.

During the carbonization at 400 °C red coloured matter sublimed on to the cool wall of the glass tube. Fig. 5 shows optical micrographs of this matter after annealing at 380 °C for 5 min. There present anisotropic needles. The elemental analyses and molecular weight by FD-MS of the matter suggest dibenzoperopyrene a condensed dimer of pyrene unit. The increase of the coke yield was

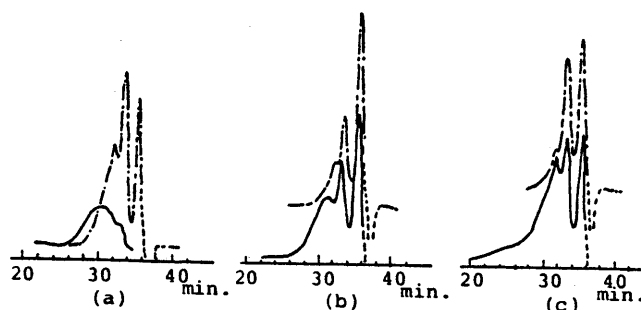


Fig. 4 G.P.C. of fractions of pitches after the reflux heat-treatment
(a) Pitch-300 (b) Pitch-350
(c) Pitch-380
— BI — — — HI-BS

Table 2. Major Peaks of Mass Spectra

O.H.P	Pitch-350	
HI	HI-BS	BI
(m/e)	(m/e)	(m/e)
202	a 200	a 200
208	a 302	a 299
b 220	400	400
406	406	c 598
408	414	
414	600	
424	c 604	
440	804	
612		
614		
818		

a: molecular ion of double charge
b: molecule caused by cleavage of peroxide
c: very strong peak



Fig. 5 Optical micrograph of sublimed matter annealed at 380°C for 5 min. (cooling rate: 1°C/min.)

ascribed to the dehydrogenative condensation of trimers, tetramers of pyrene units.

(1) I.Mochida, K.Tamaru, Y.Korai, H.Fujitsu Carbon 20 231 (1982)