

# Preparation of Carbon fibers Derived from Quinoline and Isoquinoline Pitches by The Aid of HF/BF<sub>3</sub>

Kay Hyeok AN, Yozo KORAI, and Isao MOCHIDA  
Institute of Advanced Material Study, Kyushu University, Kasuga, Fukuoka 816, Japan

Takahumi YOSHIMURA and Takashi KOJIMA  
Mitsubishi Gas Chemical Company, Inc., Chiyoda-ku, Tokyo 100, Japan

## 1. INTRODUCTION

Heterocyclic nitrogen containing pitches have been recognized to serve a precursor for the interesting carbonaceous materials of high functionality(1). Nitrogen enriched pitches derived from quinoline and isoquinoline with the aid of AlCl<sub>3</sub> showed high basic property after the coking(2). Thus, such pitches can be an interesting precursor for activated carbon fiber with unique active surface area.

In the present study, heterocyclic nitrogen containing pitches from quinoline and isoquinoline synthesized with the aid of HF/BF<sub>3</sub>, and the resultant pitches were spun to prepare the fiber for conversion into activated carbon fiber of unique properties.

## 2. EXPERIMENTAL

Nitrogen containing pitches were prepared from commercially available quinoline and isoquinoline by aid of HF/BF<sub>3</sub> under 0.3 ~ 1Mpa of autogenous pressure in an autoclave. After the reaction, HF/BF<sub>3</sub> and unreacted quinoline or isoquinoline were distilled out. The yields and some properties of pitches are summarized in Table 1.

The pitches were fractionated by sequential soxhlet extraction using benzene and pyridine. Benzene soluble fractions(BS) were analyzed with <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and FD-MS. The whole pitches were analyzed with FT-IR and solid <sup>13</sup>C-NMR.

The nitrogen containing pitch was spun into fibers in 12 ~ 14 μm diameter under nitrogen pressure from a steel spinneret. The nitrogen containing pitch fibers were oxidatively stabilized at 280 ~ 300°C in the air containing 2 vol % of NO<sub>2</sub>. The stabilized fibers were activated with steam at 850°C for 7 ~ 15min. Surface area was measured according to the BET method.

## 3. RESULT AND DISCUSSION

### 3.1 Properties and structure of nitrogen containing pitches

Softening point, solubility, elemental analysis and optical texture of pitches are summarized in Table 1. Quinoline pitch(QP) and isoquinoline pitch(IQP) are nitrogen enriched isotropic pitches prepared from quinoline and isoquinoline, respectively. The N/C of QP was similar to that of the starting quinoline, indicating no denitrogenation during the condensation. QP showed higher H/C ratio and lower solubility in benzene and pyridine than IQP. Isoquinoline was found to lose its nitrogen during its condensations, reducing the N/C ratio from 0.11 to 0.07. The main fraction of IQP was BI-PS, while PI was very small. Higher reaction pressure and more amount of catalyst increased softening point and yield of the pitches.

<sup>1</sup>H-NMR spectra of BS in the QP-A,B and IQP-A,B are shown in Figure 1. Resonance peaks from 6 to 10 ppm are assigned to aromatic hydrogen, while those lower than 4.5 ppm are assigned to aliphatic hydrogens. The <sup>1</sup>H-NMR

spectra of QP-A,B exhibited intense peaks at 1.4 ~ 2.0 and 2.2 ~ 3.0 ppm which are ascribed to naphthenic β-hydrogen and α-hydrogen and the very intense peak at 1.6 ppm is ascribed to methylene groups, respectively. Such structural characteristics are also observable in spectra of FT-IR and solid <sup>13</sup>C-NMR. In a marked contrast, no resonance peak ascribed to the naphthenic structure was found in the spectra of BS in IQP-A,B, although the very intense peak ascribed to methylene groups at 1.6 ppm was observed.

Figure 2 illustrates FD-MS spectra of the BS fractions in the QP-A and IQP-B. The molecular weight of the constituents in the QP distributed from m/z 141 to 1300 with maximum abundance at m/z 397 and 524, exhibiting major peaks around m/z 255, 397, 524, 651, 778, 879 and 1047. These peaks are ascribed to dimers, trimers, tetramers, pentamers, hexamers of quinoline retained naphthenic structure, respectively. It is noted that they were observed at regular intervals of molecular weight of 127, suggesting that the degradation of pyridine ring hardly took place during the cationic polymerization with HF/BF<sub>3</sub>. The BS fraction in the IQP was distributed from m/z 128 to 1300 with major peaks at m/z 256, 383, 510, 626, 741, and 865. These major peaks didn't show regular intervals such the major peaks of QP, indicating some degradation of the heterocyclic ring during the synthesis.

### 3-2 Properties and activation of nitrogen enriched carbon fibers

QP-A and IQP-B were spun smoothly into thin fibers of about 12 ~ 14 μm in diameter at 315 and 310°C, respectively. The pitch fiber derived from QP-A was stabilized at 300°C (QP-CF). The fiber from IQP-A was stabilized different temperature of 280°C (IQP-CF-280) and 300°C (IQP-CF-300). The elemental analysis of stabilized fibers are summarized Table 3. The stabilized fibers from QP-A and IQP-A retained 11.5% and 7.6 ~ 8.5% of nitrogen. QP-CF showed higher content of nitrogen than IQP-CF. It is noted that IQP-CF-300 stabilized at higher temperature contained higher content of nitrogen than IQP-CF-280. Table 2 summarizes mechanical properties of nitrogen containing carbon fibers carbonized at 950°C. The carbon fiber derived from QP-A showed higher tensile strength and modulus than that from IQP-A. The stabilized fibers were activated with steam at 850°C for 7 ~ 15min. Figure 3 illustrates the surface area as a function of burn-off rate for the three series of activated carbon fibers prepared. Surface area increased with degree of burn-off. The surface area of IQP-CF increased more rapidly at low burn-off than that of IQP-CF-280 and 300, although the increase of surface area in IQP-CF-300 became drastically fast at high burn-off. The surface area of IQP-CF-280 increased continuously with burn-off.

Table 3 summarizes some properties of the activated carbon fibers with the similar degree of burn-off about 50%. The surface areas of activated carbon fibers were 740 ~ 860 m<sup>2</sup>/g, with IQP-CF-300 showing the highest surface area among the activated carbon fibers of the present study. The nitrogen content of IQP-CF-300 higher than that of IQP-CF-280, although lower than that of QP-CF by 1%.

## REFERENCES

1. A. Otani, Tanso(carbon) **127**, 33(1988)
2. I. Mochida, K.H. An and Y. Korai, Carbon in press.

Table 1. Some properties of QPs and IQPs

Run. No.	Preparation conditions (°C-hr-Mpa)	S.P. (°C)	Yield (wt%)	Elemental Analyses(wt%)					Solubility(wt%)			O.T.
				C	H	N	H/C	N/C	BS	BI-PS	PI	
QP-A	230-4-0.3	216	44	83.84	4.32	10.35	0.618	0.106	20.0	50.0	30.0	Isotropic
QP-B	230-4-0.2	282	53	81.96	4.28	9.82	0.627	0.103	1.7	62.6	35.7	Isotropic
IQP-A	340-4-0.7	230	45	84.22	4.02	6.76	0.573	0.069	28.8	68.4	2.8	Isotropic
IQP-B	340-4-1.0	274	67	81.52	4.08	5.94	0.601	0.062	15.9	80.4	3.7	Isotropic

O.T.: Optical texture

Table 2. Some properties of carbonized fibers at 950 °C

CF	Diameter (μm)	T.S. (kg/mm <sup>2</sup> )	Y.M. (Ton/mm <sup>2</sup> )	E (%)
QP-CF	13.8	106	6.96	1.5
IQP-CF-280	13.6	78	4.18	1.8
IQP-CF-300	11.9	92	4.18	2.2

T.S.: tensile strength, Y.M.: Young's modulus, E: elongation

Table 3. Some properties of stabilized fibers and activated fibers derived from QP and IQP

Run No.	Stabilized Carbon Fiber							Activated Carbon Fiber <sup>1)</sup>								
	Elemental analysis(wt%)							W.L. (wt%)	S.A. (m <sup>2</sup> /g)	Elemental analysis(wt%)						
	C	H	N	O(dif.)	H/C	N/C	O/C			C	H	N	O(dif.)	H/C	N/C	O/C
QP-CF	71.76	3.03	11.49	13.38	0.507	0.137	0.140	46.6	738	80.78	1.65	5.59	11.98	0.245	0.059	0.111
IQP-CF-280	72.92	2.89	7.62	15.28	0.475	0.089	0.157	49.6	862	79.00	1.83	3.85	15.32	0.278	0.042	0.145
IQP-CF-300	70.19	2.63	8.51	17.25	0.449	0.104	0.184	52.1	750	76.30	1.95	4.49	17.26	0.307	0.051	0.170

1) activated with steam/nitrogen at 850°C for 15min(QP-CF, IQP-CF-280) or 7min(IQP-CF-300).

W.L.: weight loss, S.A.: surface area

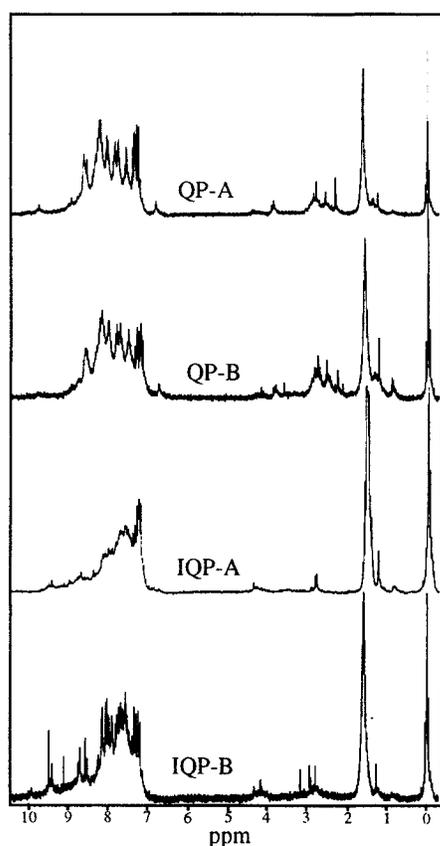


Fig. 1. <sup>1</sup>H-NMR spectra of BS in QPs and IQPs

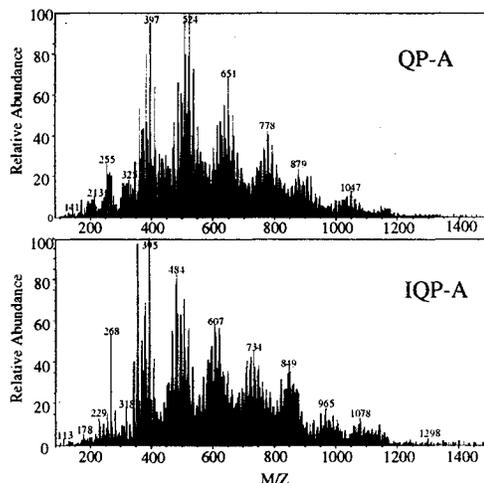


Fig. 2. FD-MS spectra of BS in QP-A and IQP-A

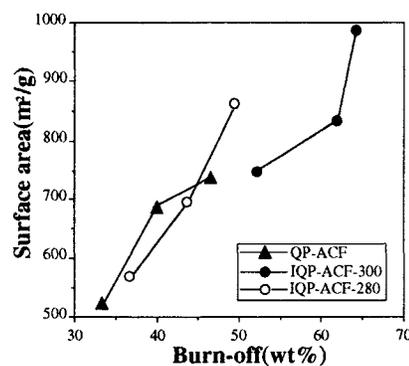


Fig. 3. Surface area as a function of burn-off at 850°C.