

Characterization of Heat Reformed Naphtha Cracking Bottom Oil Extracts

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(Received November 13, 2008; Accepted December 12, 2008)

Abstract

Naphtha Cracking Bottom (NCB) oil was heat reformed at various reforming temperature and time, and the volatile extracts were characterized including yields, molecular weight distributions, and representative compounds. The yield of extract increased as the increase of reforming temperature (360~420°C) and time (1~4 hr). Molecular weight of the as-received NCB oil was under 200, and those of extracts were distributed in the range of 100-250, and far smaller than those of precursor pitches of 380-550. Naphthalene-based compounds were more than 70% in the as-received NCB oil, and most of them were isomers of compounds bonding functional groups, such as methyl (CH₃-) and ethyl (C₂H₅-). When the as-received NCB oil was reformed at 360°C for 1 hr, the most prominent compound was 1,2-Butadiene, 3-phenyl- (24.57%), while naphthalene became main component again as increasing the reforming temperature.

Keywords : NCB oil, pitch, extract analysis, heat reforming

1. Introduction

860 million barrel per year of petroleum oil was refined in Korea, 2004 [1]. About 155 million barrel per year of naphtha, the raw material of petrochemical products is producing by steam cracking the refined petroleum, and approximately 3 wt%, 5 million barrel per year of bottom oil is producing as a by product from the cracking process. Only a little part of naphtha cracking bottom oil is using as boiler fuel, and most of them is discarded as unuseful waste because of containing water. However, reformed NCB oil is known as one of precursor pitch for pitch-based carbon fiber [2-4]. Recently, the demand of pitch-based carbon fiber is being increased as increasing the demand of PAN-based carbon fiber. Pitch-based carbon fiber is preparing from precursor pitch spinning, oxidation and carbonization of the spun fiber. Otani and Sanada [5] reported that pitch based carbon fiber has superiority to elasticity rate, electrical conductivity and thermal conductivity, compared with other precursor carbon fiber. On the other hand, the yield of precursor pitch is below 20 wt% of NCB oil [6]. Most of NCB oil is vaporized to volatile extracts. Up to now, there is no report on the characterization and application of this extract. The volatile extracts need to be characterized for further usages.

In this research, volatile extracts were obtained from condensation of heat reformed NCB oil during the

preparation of precursor pitch for pitch-based carbon fiber. The extracts were characterized to investigate the molecular weight distribution, representative compounds, yield, and other properties as following different heat reforming conditions.

2. Experimental

The NCB oil used in this study is, dark-brown bottom oil generated as waste liquid in naphtha cracking progress, supplied by SK Co., Korea. The extract preparation was identical to precursor pitch preparation [6]. Batch reactor was filled up 4 kg NCB oil. The as-received NCB oil was reformed at 360, 380, 400, and 420°C for 1, 2, 3, and 4 hr in 0.5 vvm nitrogen flow rate. The volatile extracts were obtained from condensing the extracts.

Table 1 indicates the characterization of the as-received NCB oil. Elemental analysis (Flash EA 1112, Thermo Fisher Scientific) was carried out to confirm C, H, N and O contents of the as-received NCB oil and extracts. FT/IR (IR Prestige-21, Shimadzu) was used to analyze the chemical structure of components in extract. MALDI/MS (VoagerTM DE-STR, PerSeptive Biosystems) was used to verify molecular weight distributions, and 2,5-Dihydroxybenzoic acid was used by matrix. GC/MS (Clarus500, Perkinelmer) was used to identify the components of the as-received NCB oil

Table 1. Characterization of the As-received NCB Oil

Density at 15°C (g/cm ³)	1.0836
Flash point (°C)	90
Pour point (°C)	-10
Kin viscosity at 40°C (mm ² /s)	150
Atomic mole ratio (C/H)	1.07
Aromaticity (F _a)	0.85
Carbon residue 10%	14.85
Ash (%)	0.006
Content of water or sediment (%)	< 0.05

Table 2. Elemental Analysis of As-received NCB Oil and Extracts Reformed at 1 hr

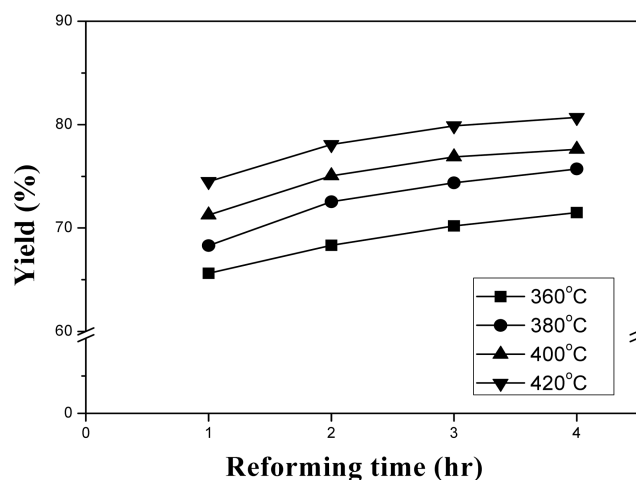
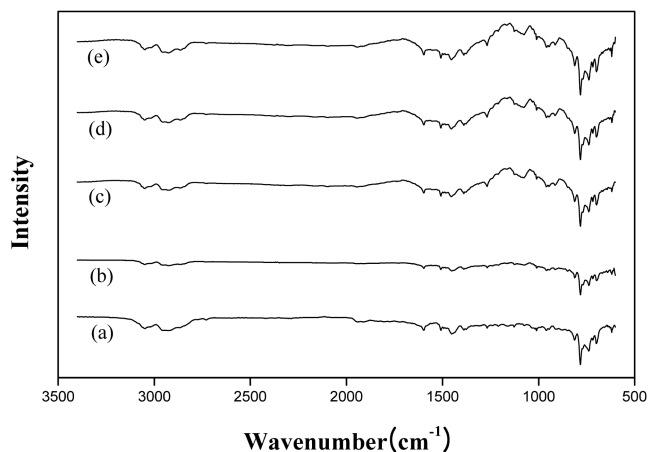
Conditions	C	H	N	O	C/H
NCB oil	89.49	6.95	0.00	4.56	1.07
360	88.92	7.74	2.76	0.58	0.96
380	89.94	7.66	1.86	0.54	0.98
400	91.57	7.08	0.88	0.47	1.08
420	92.56	6.54	0.77	0.47	1.18

and extracts. Gas chromatograph was analyzed by using HP 5 amin column and Helium carrier gas of 0.5 ml min⁻¹ flow rate; the column temperature was as follows: initial temperature was maintained at 60°C for 2 minutes, increased to 300°C by increasing temperature rate 5 min⁻¹, and maintained 20 minutes for 20 minutes. Injector was analyzed at 290°C, and transfer line temperature was 270°C and. The ionic source temperature and ionization mode for mass spectroscopy were 270°C EI (electronic ionization), respectively.

3. Results and discussion

Fig. 1 shows yields of extract as functions of reforming temperature and time. The yields logarithmically increased as increasing the reforming time and linearly increased as the increase of reforming temperature. It was reached up to 80 wt% when the NCB oil was reformed at 400°C for 4 hr. Yamada [7] reported similar results in reforming petroleum tar pitch. The yields of high temperature and short time reforming were larger than the yields of low temperature and long time reforming, which means degradation in severe than polymerization at higher temperature. From Fig. 1, yield of extract could be adjusted by controlling the reforming temperature and time.

Table 2 shows elemental analysis of the as-received NCB oil and extracts obtained from different heat-reformed temperature for 1 hr. Carbon content linearly increased as increasing the temperature over 360°C, and atomic mole ratio(C/H) also increased from 1.07 to 1.18 at 420°C. Hwang et al. [2] reported that C/H of pitch based precursor reformed at 300°C, 2 hr under N₂ blowing was 1.08. The other

**Fig. 1.** Yields of NCB oil extracts as functions of reforming temperature and time in 0.5 vvm N₂.**Fig. 2.** FT-IR spectra of (a) NCB oil and extracts reformed at (b) 360, (c) 380, (d) 400 and (e) 420°C for 1 hr in N₂.

elements decreased showing the degradation of hydrogen and oxygen functional groups as increasing the time.

Fig. 2 shows FT-IR spectra of the as-received NCB oil and reformed extracts. There was no difference in spectra between NCB oil and extracts. Aromatic C-H bond was appeared at 3030 cm⁻¹, aliphatic C-H bond was appeared at 2920 cm⁻¹, aromatic C=C bond was appeared at 1600 cm⁻¹, aromatic C-H-H bond was appeared hydrogen and oxygen functional groups between 700 and 900 cm⁻¹, and C=O bond was appeared at 1900 cm⁻¹. There results were corresponding well with Kim's [6] report.

Fig. 3 shows spectra of the precursor pitch and extract reformed at 380°C for 1 hr. Because the properties of precursor pitch reformed at 380°C were better than others [6]. Extract has a C-H stretching bond and ethyl/n-propyl bond. On the other hand, reformed precursor pitch didn't show such bonds which means that both components were

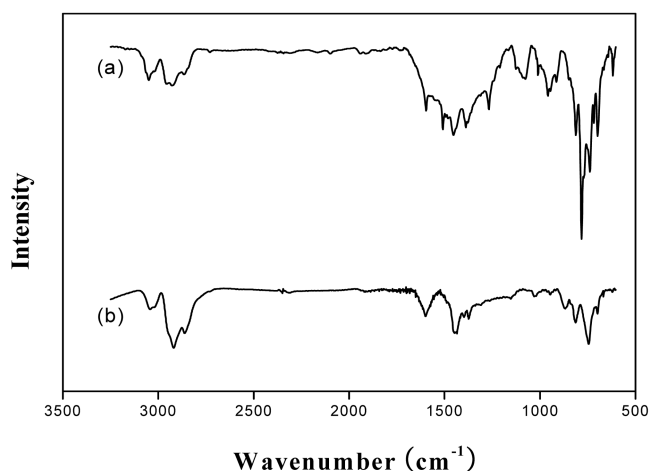


Fig. 3. FT-IR spectra of (a) precursor pitch and (b) extract reformed at 380°C for 1 hr in N₂.

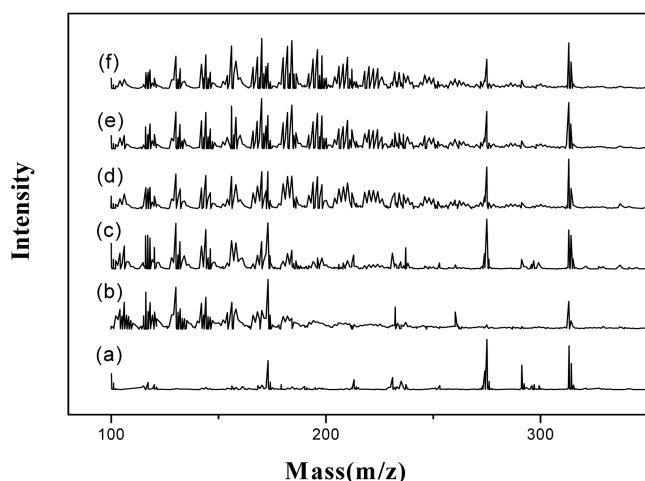


Fig. 4. Molecular weight distributions of (a) matrix, (b) as-received NCB oil and extracts reformed at (c) 360, (d) 380, (e) 400 and (f) 420°C for 1 hr in N₂.

completely different.

Fig. 4 shows molecular weight distribution of the as-received NCB oil and extracts reformed at different temperature for 1 hr. The peaks appearing over 250 mass are molecular weight distribution of matrix. Molecular weight of the as-received NCB oil was under 200 mass, and those of extracts were distributed in the range of 100-250 mass. Larger molecular weight compounds were formed as increasing the reforming temperature. The molecular weight distributions of precursor pitch were 300-800, which was reported about 1190 mass by Edie et al [8]. This difference was derived from different raw materials.

Fig. 5 shows chromatographic mass pattern of the as-received NCB oil. Peaks corresponding to 1H-indene, naphthalene, naphthalene, 1-methyl, 1,1'-biphenyl and phenan-

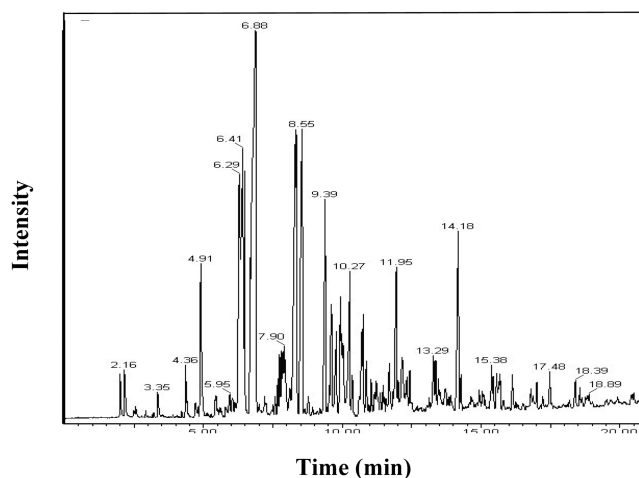


Fig. 5. Chromatographic pattern of as-received NCB oil.

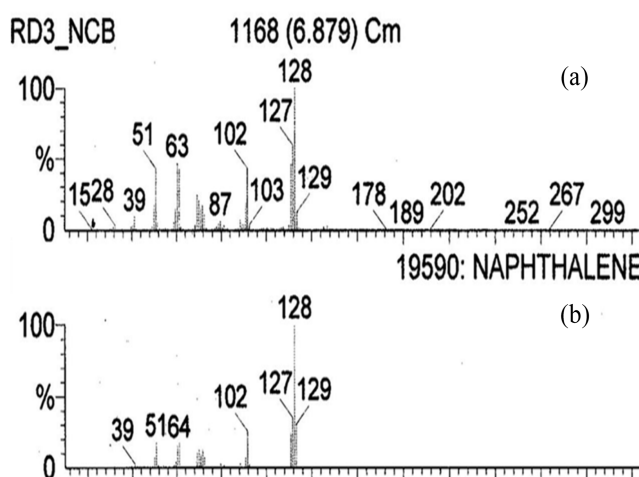


Fig. 6. Mass spectra of (a) specific component detected at 6.879 min in the as-received NCB oil, and (b) naphthalene of NIST.

threne et al. indicated at 4.91, 6.88, 8.33, 9.39 and 14.17 min of retention times.

Fig. 6 shows mass spectra of specific component detected at 6.879 min in the as-received NCB oil and naphthalene of NIST (National Institute of Standards and Technology). Specific ions of this component appeared at 39, 51, 64, 87, 102, 127, 128 and 129 m/z in first mass spectrum, but weak peaks such as 15 and 28 m/z were ignored. Therefore, the component was identified as naphthalene by comparison of the spectrum with a computerized mass spectra database from NIST.

Table 3 shows volatile components in the as-received NCB oil. The amount of each component in the as-received NCB oil was quantitatively analyzed by using the areas underneath peak in the chromatograph, and listed in Table 3.

Table 3. Volatile Components in the As-received NCB Oil

RT	Area (%)	Chemicals	Formula
2.00	0.96	1,3-Cyclopentadiene	C ₅ H ₆
2.16	1.38	1,3-Cyclopentadiene, 5-methyl-	C ₆ H ₈
3.35	0.84	Styrene	C ₈ H ₈
4.36	0.91	Benzene, 1-ethenyl-2-methyl-	C ₉ H ₁₀
4.91	5.74	1H-Indene	C ₉ H ₈
6.49	5.07	1,4-Dihydronaphthalene	C ₁₀ H ₁₀
6.88	36.26	Naphthalene	C ₁₀ H ₈
8.33	20.91	Naphthalene, 1-methyl-	C ₁₁ H ₁₀
9.39	6.84	1,1'-Biphenyl	C ₁₂ H ₁₀
9.61	3.13	Naphthalene, 2-ethyl-	C ₁₂ H ₁₂
10.70	2.17	Acenaphthylene	C ₁₂ H ₈
10.75	2.50	1,1'-Biphenyl, 3-methyl-	C ₁₃ H ₁₂
11.93	5.04	9H-Fluorene	C ₁₃ H ₁₀
13.28	1.82	9H-Fluorene, 4-methyl-	C ₁₄ H ₁₂
14.17	6.44	Phenanthrene	C ₁₄ H ₁₀

Table 4. Representative Components in Extracts Reformed at 360, 380, 400, and 420°C, 1 hr

No	360°C	%	380°C	%	400°C	%	420°C	%
1	1,2-Butadien, 3-phenyl-	24.57	Naphthalene	28.00	Naphthalene	28.48	Naphthalene	23.55
2	Naphthalene, 2-methyl-	9.96	Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene	12.86	Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene	13.27	1H-Indene, 1-methyl-	12.64
3	Benzene, 1-propynyl-	8.56	Benzene, 1-methyl-1,2-propadienyl-	11.99	1H-Indene, 2-methyl	8.38	Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene	11.24
4	Benzene, 1-methyl-1,2-propadienyl-	7.14	Acenaphthene	6.31	Acenaphthene	4.91	Naphthalene, 1-(2-propenyl)-	6.02
5	Naphthalene, 2-ethyl-	6.55	Naphthalene, 2-ethenyl	5.13	1,1'-Biphenyl	4.71	Naphthalene, 1-[1-(bromomethyl)vinyl]-	5.35
6	1H-Indene	4.33	Phenanthrene	4.12	Benz[a]anthracene	4.49	1,1'-Biphenyl	4.99
7	1-Isopropenyl-naphthalene	2.88	Naphthalene, 2-ethyl	3.96	1H-Indene	4.43	Phenanthrene	4.27
8	Naphthalene, 1-[1-(bromomethyl)vinyl]-	2.60	1H-Indene, 2,3-dihydro-1-methyl-	2.91	Naphthalene, 2-ethyl-	3.79	Naphthalene, 1-ethyl-	4.02
9	Azulene	2.52	9H-Fluorene-9-carboxylic acid	2.80	9H-Fluorene	3.04	1H-Indene	3.96
10	Naphthalene, 2-ethenyl-	2.26	(E,E,E)-1,3,5,11-Tridecatetraene-7,9-Diyne	2.80	Naphthalene, 1-[1-(bromomethyl)vinyl]-	3.01	Benzene, (2-methyl-1-propenyl)-	2.92
11	Benzene, 1-ethyl-3-methyl-	2.20	Naphthalene, 1,4,5-trimethyl-	2.11	1H-Indene, 2,3-dihydro-1-methyl-	2.58	9H-Fluorene	2.62
12	9H-Fluorene	2.12	Benzene, 1-ethenyl-2-methyl-	1.82	Naphthalene, 1-(2-methylethenyl)	2.09	Naphthalene, 2-(1-methylethenyl)-	2.35

Form quantification of each peak area, representative components in the as-received NCB oil were analyzed as naphthalene (36.26%), naphthalene, 1-methyl- (20.91%), 1,1'-biphenyl (6.84%), phenanthrene (6.44%), 1H-indene

(5.74%), and so on.

Table 4 shows representative components in the volatile extracts reformed at 360, 380, 400, and 420°C, 1 hr. Most of compounds were isomers of compounds bonding functional

groups, such as methyl (CH₃-) and ethyl (C₂H₅-). When the NCB oil was reformed at 360°C, 1 hr, the representative compound was 1,2-butadien, 3-phenyl- (24.57%), while naphthalene became representative component again as increasing the reforming temperature.

4. Conclusions

Volatile extracts can be obtained from reforming the as-received NCB oil as by-products and characterized during the preparation of precursor pitch for pitch-based carbon fibers.

The yields of high temperature and short time reforming were larger than the yields of low temperature and long time reforming, which means that degradation is severe than polymerization at higher temperature. The yield of extracts increased as increasing the time and temperature.

The main components of extracts were mixtures of C₈-C₁₈ aromatic compounds such as naphthalene, benzene, and indene, and those having functional groups of methyl-, ethyl-, and so on. The molecular weight of the as-received NCB oil was about 150, while the volatile extracts were in the range of 100-250.

The volatile extracts can be used a new petroleum chemicals by reforming and differentiation.

Acknowledgements

This research was financially supported by the Ministry of Education, Science Technology (MEST) and Korea Industrial Technology Foundation (KOTEF) through the Haman Resource Training Project for Regional Innovation, also supported by Joint Technology Development Consortium Business among Industry, Academy and Research Institute.

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