**Synthesis and characterization of pitch from pyrolysed fuel oil (PFO)**

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**Highlights**

* Pitch was synthesized as a function of temperature in the range of 390-410oC.
* Pitch was identified by XRD, TGA, MALDI-TOF, EA, softening point analysis.
* Pitch showed enhanced stacking height (Lc), and C/H indicating graphitic structure.
* To control the softening point of pitch, a modified thermal treatment was studied.

**1. Introduction**

Petroleum residues can be used as a feedstock to prepare pitch which is one of a main precursors for the production of carbon materials [1]. The pitch characteristic is an important factor because the properties of carbon materials can be determined by the chemical and physical characteristics of pitch, which are classified as mesophase contents, solubility by organic solvents, softening point, chemical compositions, and molecular weight distribution (MWD) [2] etc. Previously, air-blowing is a simple and effective way to increase the softening point [3]. In this work, PFO based pitch was prepared by thermal reaction in the range of 390-410oC as a function of time, and the basic chemical/physical properties were characterized. Based on the results of MWD, a chemical reaction was suggested the changes of each molecular weight fraction during the thermal reaction. And also oxidative thermal treatment of pitch with O2/N2 mixture gas was investigated as an efficient way to increase softening point of pitch without loss of pitch yield. It is expected that using gas with a higher O2 concentration than air would be a better effective way to increase softening point because a higher O2 concentration could enable the condensation reaction to progress at lower gas flow rate, suppressing the volatilization of light components that can minimize the pitch yield.

**2. Methods**

PFO (Yeochun NCC Co., Korea) was used as a feedstock. 7,7,8,8-tetracyanoquinodimethane (TCNQ) was used as a matrix for MALDI-TOF analysis. The pitch synthesis reaction was conducted with a 1L scale batch type autoclave with the following procedure (1) 500g PFO was placed in the reactor, (2) 200cc/min of N2 was injected for 30min, (3) the reactor was heated and the detailed reaction conditions and summarized in Table 1 In order to modify pitch properties, O2 and/or N2 containing gas was blown into the reactor with a flow rate of 0.5L/min at 360oC for 5hours. Treated pitch was identified by EA (Thermo Scientific FLASH EA-2000), XRD (Rigaku Ultima IV), softening point (DP-70, Mettler Toledo), MALDI-TOF (with Autoflex MALDITOF mass spectrometer).

**3. Results and discussion**

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| Table 1. Experimental conditions for synthesizing pitch from PFO | | | | | | |
| Sample | Reaction conditions | | | | | |
| T (oC) | t (h) | P (P) | N2 flow  (cc/min) | Pitch yield  (%) | Volatile mass  (%) |
| P-390 | 390 | 1 | 1 | 100 | 28.9 | 67.5 |
| P-400 | 400 | 1 | 1 | 100 | 26.5 | 68.3 |
| P-410 | 410 | 1 | 1 | 100 | 25.4 | 69.2 |

The pitch synthesis reaction was considered with MWD variation relative to the area fractions as shown in Figure 1 [4]. Low boiling point components were emitted due to the volatilization during the thermal reaction or converted to the high molecular weight area fraction by means of condensation and polymerization reaction. The softening point increased linearly with vac. distillation time, as shown in Figure 2, the softening point was further increased with increasing flow rate reaching at

282oC. Heat treatment of PFO under inter condition at 360oC for 5h produced a pitch with a softening point of 130oC and a yield of 34.0%. In order to suppress the loss of pitch yield, O2 concentration was increased rather than rather than increasing the flow rate of reaction mixture gas. When the O2 concentration was increased to 35%, the softening point increased to 249oC [5].

Figure 1. Diagram of the molecular weight

fraction divided by the pseudo-component.



Figure 2. Softening point and yield variation of pitches prepared by thermal treatment as a function of (a) vacuum distillation time, (b) flow rate of reaction gas and (c) O2 concentration of reaction gas.

**4. Conclusions**

(1) The empirical pitch synthesis reaction from PFO was carried out to reveal the physical and chemical properties of the feedstock and produced pitch. (2) The treatment was highly effective at increasing the softening point while maintaining high pitch yield by oxidative thermal condensation and suppressing volatilization of light components.

**References**

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