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Empirical study of petroleum-based pitch production via pressure- and temperature-controlled thermal reactions

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ABSTRACT

Three-stage thermal reactions were conducted to investigate empirical trends of petroleum-based pitch production and the chemical characteristics of pitch produced by controlling the temperature and pressure operating parameters. The softening point of pitch increased with increasing reaction temperature under atmospheric pressure, whereas the pitch yield increased with decreasing reaction temperature under a pressurized condition. Elemental analysis supported the result of decreased hydrogen content. In addition, thermogravimetric analysis revealed that higher reaction temperatures could induce the polymerization and condensation of polyaromatic hydrocarbons (PAHs) with carbon yield at 900 °C. The molecular weight distribution (MWD) of pitch was analyzed by MALDI-TOF analysis according to the operating parameters during the thermal reaction. The MALDI-TOF spectrum was normalized to observe the variation in the MWD by Anthracene (178 Da) as a pseudo-component. Range 2–3 and range 6–8 in the MWD coincided with the trends of the pitch yield and the softening point, respectively. The results suggested that pitch yield is related to the PAHs with 2–6 aromatic rings and that the softening point is related to highly condensed PAHs with more than 6 aromatic rings. The anisotropy/isotropy of the pitch was analyzed by polarized light microscopy. The pitch produced under the pressurized condition was isotropic. However, the pitch produced under atmospheric pressure exhibited a well-oriented domain texture. We concluded that volatile contents disturb the polymerization and condensation of PAHs because of side reactions involving the aliphatic contents.

Introduction

Pitch is an intermediate material for producing useful carbon materials, such as graphite electrodes for arc furnaces, artificial graphite, and carbon fibers and anodes for lithium-ion batteries. The International Union of Pure and Applied Chemistry (IUPAC) defines pitch as a residue from the pyrolysis of organic material or tar distillation that is solid at room temperature, consisting of a complex mixture of numerous, essentially aromatic hydrocarbons and heterocyclic compounds [1].

Petroleum- and coal-derived residues have been used as representative feedstocks for pitch production. Petroleum-based sources, including fluid catalytic cracking decant oil (FCC-DO) of the FCC process, pyrolyzed fuel oil (PFO) of the ethylene cracking process, and vacuum residue (VR) of the vacuum distillation process, are by-products of the refining process. The coal-based source is coal tar from the coking process of iron ore in a coking oven. Because these residues are composed of chemically complicated polyaromatic hydrocarbons (PAHs) with impurities, such as ash and metals, researchers have attempted to optimize the operating conditions for controlling the properties of pitch during pitch production [2–4].

Petroleum based pitch is generally produced by thermal reaction, during which volatilization, cracking, polymerization, aromatization, and condensation are well known to occur [5–7]. The vacuum distillation is used to produce coal tar pitch for anode production in aluminum industry in many western countries. In

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addition, the chemical and physical properties of pitch can be controlled by modulating the operating parameters of the thermal reaction.

The primary operational parameters of thermal reactions are temperature, pressure, and soaking time. Among the operating parameters related to the thermal reaction, temperature is the most important. For example, the production of mesophase pitch requires a temperature greater than 380 °C [8–10]. The pressure can control the distillation of volatile contents, which consist of low-boiling aliphatic compounds generated during the thermal reaction; thus, pressure can affect the product yield and the optical structure of the pitch [11]. The soaking time is a minor factor in the thermal reaction, although an insufficient or excessive soaking time can negatively affect the desired pitch properties [3]. An additional parameter is the introduction of a catalyst [10,12]. A Brønsted or Lewis acid and a halogen source are introduced to enhance the condensation or polymerization of PAHs that contain petroleum residues.

In this study, PFO was selected as a feedstock. PFO, which is a by-product of the naphtha cracking process, is produced at a rate of over 100 MTA in South Korean refineries and is used as a low-cost plant fuel because of the difficulty of the re-treatment process and its low utilization. Nevertheless, the abundant aromatic contents and low impurity concentrations in PFO make it an attractive pitch feedstock. However, the content of volatile components in PFO is greater than 20%; these components comprise aliphatic contents with hydrogen. Petroleum-based residue is known to have aliphatic contents that are much higher than those of coal-tar [13]. Aliphatic contents result in various side reactions, such as cracking and volatilization of PAHs [14], thereby hindering the coalescence of mesogen during the thermal reaction. In addition, predicting the yield and properties of pitch during the thermal reaction is difficult because of side reactions involving the aliphatic components.

Finally, we conducted an empirical study of petroleum-based pitch to investigate the relationship between the operating conditions and the properties of pitch produced by a 3-stage thermal reaction. The 3-stage thermal reaction was designed to confirm the effects of different temperatures and pressures during pitch production. The temperature and pressure conditions were established as operating parameters. The experimental tendency of pitch production was characterized on the basis of the softening point, pitch yield and elemental analysis (EA) results. Thermogravimetric (TG) analysis supported the production trends related to the temperature and pressure conditions. Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) analysis was performed to investigate the influence of the operating parameters on the molecular weight distribution (MWD) of the produced pitch. The anisotropy/isotropy of the pitch was analyzed using polarized optical microscopy.

Experimental methods

Materials

PFO (Yeochun NCC Co. Ltd., Korea) was chosen as the feedstock for the petroleum residue and was used without further purification. The compound 7,7,8,8-tetracyanoquinodimethane (TCNQ) was used as the matrix for MALDI-TOF measurements.

Design of the 3-stage thermal reaction for pitch production

A 3-stage thermal reaction for pitch production was designed. The temperature and pressure were established as operating parameters. Detailed operating conditions for the 3-stage thermal reaction are listed in Table 1. The pressure parameter was set to either the pressurized or the atmospheric condition, as shown in Fig. 1. The pressurized condition suppresses the emission of volatile contents and induces their chemical reaction, whereas the atmospheric pressure condition removes volatile compounds generated during the thermal reaction. To investigate the influence of volatile contents on the chemical reaction during the thermal reaction in terms of the pressure parameter, stage-1/stage-2 settings were established as the four conditions of atmospheric/atmospheric (A/A), atmospheric/pressurized (A/P), pressurized/atmospheric (P/A), and pressurized/pressurized (P/P). Temperature, which is the most influential parameter in pitch production, affects the chemical kinetics of condensation and polymerization [15,16]. Reaction temperatures were determined by simulated distillation (SIMDIS) analysis of the PFO. The temperature parameter was established as either 220 °C or 420 °C in stage-1 according to the SIMDIS results, as shown in Fig. 2. We confirmed that the volatile contents were distilled 10% and 60% at 220 °C and 420 °C, respectively. The temperature condition of stage-2 was fixed at 420 °C to introduce condensation and polymerization during the thermal reaction. In stage-3, 420 °C and the atmospheric condition were established to promote the emission of volatile matter and the final condensation of pitch. In addition, the 3-stage reaction has a small difference of retention time because of limitation of operating apparatus.

Thermal reaction

The thermal reaction was conducted using a 5-L batch autoclave reactor. The reaction temperature was carefully controlled to prevent overheating. The experimental error range of the controlled temperature was maintained within ±2 °C using a proportional–integral–derivative controller system. The pressure valve connected to the 5-L vessel was opened and closed in accordance with the atmospheric and pressurized condition, respectively. When the pressure increased by 10 bar, the relief

Table 1
Experimental conditions of the 3-stage thermal reaction.

Series	Sample name	Stage-1		Stage-2		Stage-3	
		Pressure (bar)	Temp. (°C)	Pressure (bar)	Temp. (°C)	Pressure (bar)	Temp. (°C)
22 series	2242-A/A	1	220	1	420	1	420
	2242-A/P	1		10			
	2242-P/A	10		1			
	2242-P/P	10		10			
42 series	4242-A/A	1	420	1			
	4242-A/P	1		10			
	4242-P/A	10		1			
	4242-P/P	10		10			

N_2 flow rate: 200 mL/min.