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Blending effect of pyrolyzed fuel oil and coal tar in pitch production for artificial graphite

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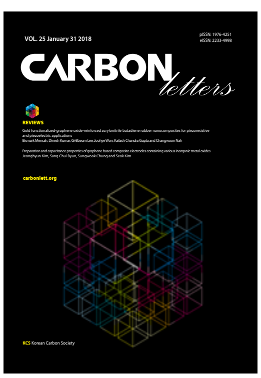

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Abstract

Pyrolyzed fuel oil (PFO) and coal tar was blended in the feedstock to produce pitch via thermal reaction. The blended feedstock and produced pitch were characterized to investigate the effect of the blending ratio. In the feedstock analysis, coal tar exhibited a distinct distribution in its boiling point related to the number of aromatic rings and showed higher Conradson carbon residue and aromaticity values of 26.6% and 0.67%, respectively, compared with PFO. The pitch yield changed with the blending ratio, while the softening point of the produced pitch was determined by the PFO ratio in the blends. On the other hand, the carbon yield increased with increasing coal tar ratio in the blends. This phenomenon indicated that the formation of aliphatic bridges in PFO may occur during the thermal reaction, resulting in an increased softening point. In addition, it was confirmed that the molecular weight distribution of the produced pitch was associated with the predominant feedstock in the blend.

Key words: pyrolyzed fuel oil, coal tar, pitch, thermal reaction, blending effect

1. Introduction

In particular, artificial graphite has been manufactured in various forms such as sheet, film, and powder matrix. Artificial graphite is used for various metal smelting and electrodes for electrolytic furnaces. Recently, it has been used in various fields such as silicon semiconductor and optical fiber manufacturing and also use as anode materials in lithium ion battery.

In general, artificial graphite is produced by mixing the filler materials such as coke and binder pitch to produce a graphite block. These kinds of materials are manufactured from pitches which are based by petroleum and coal tar [1-3]. So, it is necessary to understand precisely the pitch. Pitch can be classified as pitch coke, binder pitch, and impregnating pitch according to its chemical properties, such as softening point, carbon yield, solubility in solvents, and anisotropic/isotropic texture [4-6]. These properties of pitch originate from the chemical characteristics of the feedstock [7-9].

Coal tar has been commonly used as a feedstock for producing pitch. It has the positive advantage of being able to produce high-density carbon materials due to its high carbon yield and high aromatic content [10]. Petroleum residue is another feedstock for producing carbon precursors because of its high carbon content. However, petroleum residue has less aromatic content than coal tar due to petroleum residue containing an aliphatic content of approximately 10%–30%, depending on the petroleum refining process [11,12]. This difference leads to low yields of the produced carbon due to unexpected chemical reactions, such as the cracking of methyl and ethyl chains branched to aromatic rings. Because of the above reason, petroleum-based pitch has remained at the level of lab-scale research, with few commercial applications.

Nowadays, many studies have been conducted to improve the various properties of petroleum-based pitch such as liquid crystal, pitch yield, and so forth [13-15]. One attractive approach to improving these properties of pitch is blending with coal tar pitch. Researchers have observed synergetic effects of blended coal tar- and petroleum-based pitch. Pérez et al. [13] reported an interaction between coal tar and petroleum pitch during pyrolysis. In addition, they found that blended pitch exhibited intermediate characteristics between that of coal tar and petroleum. Marsh et al. [14] showed that the co-carbonization of coal with petroleum pitch could lead to the growth of a mesophase and anisotropic coke. Until now, a blending of different types of pitches has been studied, but almost not studied in which petroleum and coal tar are blended in the feedstock despite the chemical characteristics of the feedstock being an important parameter in the production of pitch.

In this study, the effects of blending and experimental trend according to the petroleum residue and coal tar blending ratio in the feedstock were studied and produced pitch to improve their characteristic properties for making artificial graphite. The petroleum residue and coal tar were blended in the feedstock without any preparation steps. The blended feedstock was thermally reacted to produce pitch. The blended feedstock and produced pitch were characterized to investigate the effect of the blending ratio.

2. Experimental

2.1. Materials

Coal tar (Posco Chemtech Co. Ltd., Korea) and pyrolyzed fuel oil (PFO) (Yeochun NCC Co. Ltd., Korea) were used as the feedstock for producing pitch. 7,7,8,8-Tetracyanoquinodimethane (TCNQ, 98%, CAS number 1518-16-7; Sigma-Aldrich, USA) was used as the matrix in matrix-assisted laser desorption/ionization–time of flight (MALDI-TOF) analysis.

2.2. Blending of feedstocks

Two feedstocks were blended in various ratio as follows: 75:25, 50:50, and 25:75. Blending was conducted in a 5-L vessel at 100 rpm for 3 h. Precipitation or phase separation of the blended feedstock was not found during the blending stage.

2.3. Thermal reaction for producing pitch

The thermal reaction was conducted in a 5-L batch autoclave reactor. The reaction temperature was carefully controlled to prevent coke formation. The experimental error range of the controlled temperature was maintained within ±2°C using a proportional-integral-derivative controller system. The reaction procedure was as follows: (1) 1500 g of the blended mixture was added in the 5-L vessel of the reactor; (2) 200 cc min^{-1} of N_2 gas was injected into the vessel to create an inert gas atmosphere over 30 min; and (3) after the N_2 purging step, the furnace was heated according to the programmed temperature. The detailed operation conditions are listed in Table 1. These optimal chemical treatment conditions were determined based on our previous work [16]. The produced pitches were labeled corresponding to the feedstock ratio as follows: P100, P75-C25, P50-C50, P25-C75, and C100.

Table 1. Experimental conditions of the thermal reaction

Sample name	Blending ratio of feedstock		Reaction condition	
	PFO	Coal tar	Temperature (°C)	Time (min)
P100	100	0	420	180
P75-C25	75	25		
P50-C50	50	50		
P25-C75	25	75		
C100	0	100		

2.4. Analysis of the pitch and feedstock

To observe the surface characteristics and microstructure of the manufactured samples, an analysis was carried out using a mini-scanning electron microscope (Mini-SEM, COXEM Co., EM-30AX, in Korea Basic Science Institute (KBSI) Jeonju Center). The carbon, hydrogen, sulfur and nitrogen contents were analyzed using a Thermo Fisher Scientific Flash 2000 organic elemental analyzer (in Korea Research Institute of Chemical Technology [KRICT]). The Conradson carbon residue (CCR) was analyzed by micro carbon residue tester (MCRT160, Alcors, ASTM D189, in KRICT). The boiling point fraction of the feedstock was analyzed by a gas chromatography–simulated distillation system (GC-SimDis, AC HT750 system, ASTM D7169, in KRICT). The blended feedstocks were characterized using a Bruker ALPHA-T infrared spectral analyzer (USA). The samples were measured from 4000 cm^{-1} to 500 cm^{-1} at a resolution of 2 cm^{-1} using dried KBr pellets. The aromaticity was calculated from the ratio of the C-H aromatic vibration (3150–2990 cm^{-1}) region to the C-H aliphatic vibration (2990–2800 cm^{-1}) region ($C\text{-}H_{ar}/C\text{-}H_{al}$) [17]. The softening point of the produced pitch was measured using a softening point analyzer (DP-70, Mettler Toledo, in KRICT) according to ASTM D3416. Thermogravimetric analysis (TGA; Shimadzu TGA-50H thermo analyser, in KRICT) was conducted at a heating rate of 10°C/min and at temperatures of up to 900°C in N_2 atmosphere. MALDI-TOF (Bruker Daltonics Autoflex MALDI-TOF mass spectrometer, in KRICT) analysis was conducted over a range of 0–1500 *m/z* [18].

3. Results and Discussion

3.1. Chemical characteristics of the feedstocks

Elemental analysis (EA) was conducted to analyze the chemical contents in the feedstock, as listed in Table 2. PFO exhibited a lower carbon content (91.7%) and higher hydrogen content (7.7%) than coal tar, which could be explained by the higher hydrogen content of PFO being related to the original characteristics of the petroleum residue, which contains aliphatic contents [12]. As a result of CCR analysis (listed in Table 2), coal tar and PFO exhibited values of 26.6% and 11.4%, respectively. It was

Table 2. Elemental analysis and CCR results of the feedstocks

Feedstock	EA (%)				CCR (%)
	C	H	N	S	
PFO	91.7	7.7	0.0	0.1	11.4
Coal tar	94.1	5.0	0.4	0.1	26.6

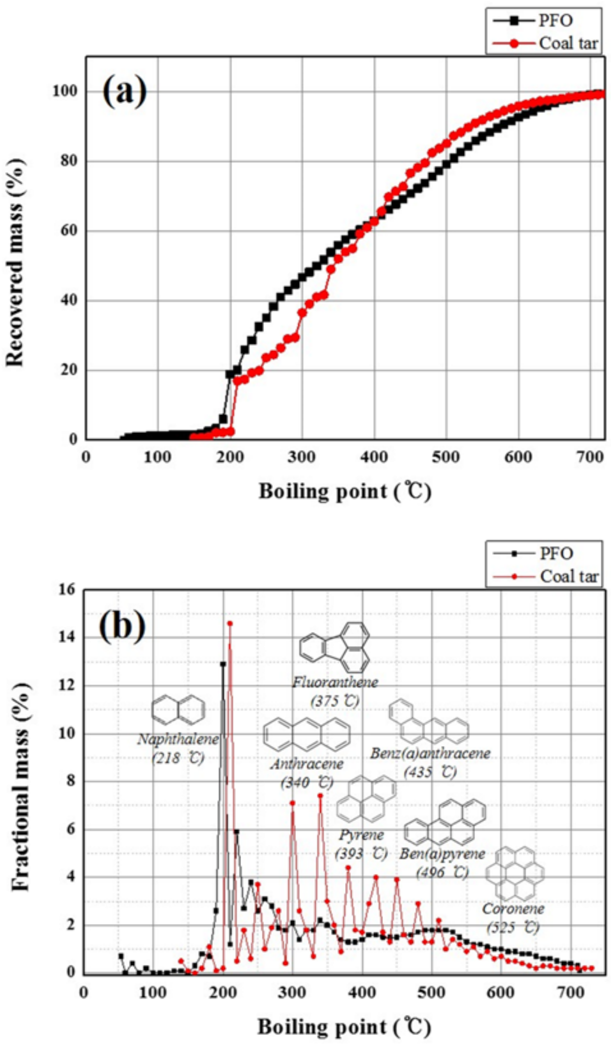

Fig. 1. Boiling point distribution plot from GC-SimDis analysis. (a) Recovered mass and (b) fractional mass.

assumed that the lower CCR value of PFO is also attributed to its higher aliphatic content. It is well known that aliphatic compounds undergo cracking and decomposition during pyrolysis [19]. On the other hand, coal tar mostly consists of aromatic compounds, which facilitates the conversion of graphitizable carbons by condensation or polymerization.

GC-SimDis analysis was carried out to investigate the boiling point distribution of the feedstocks, as shown in Fig. 1. The recovered mass with respect to the boiling point is shown in Fig. 1a. The initial boiling point of PFO and coal tar was measured to be 53.8°C and 140.2°C, respectively. The recovered mass plot of the two feedstocks shows the difference in the feedstocks. PFO showed a higher recovered mass than coal tar until 400°C. However, the recovered mass of coal tar turned around after 400°C. The faction mass according to the boiling point is displayed in Fig. 1b. PFO showed a significant fractional mass of approximately 12.9% in the range of 200°C, and then the fractional mass decreased steadily. On the other hand, coal tar exhibited a distinct distribution of boiling points related to the number of aromatic rings. This result may be correlated with the chemical characteristics of coal tar, which has a simple structure of aromatic rings with a few alkyl chains, as displayed in Fig. 1b. The even distribution of PFO is assumed to be due to the chemical structure of the aromatic compounds with various alkyl chains. In addition, these results coincide with previous research [5,12]. Kershaw and Black [12] found through NMR analysis that coal tar and petroleum-based pitch exhibit different degrees of aromatic substitution.

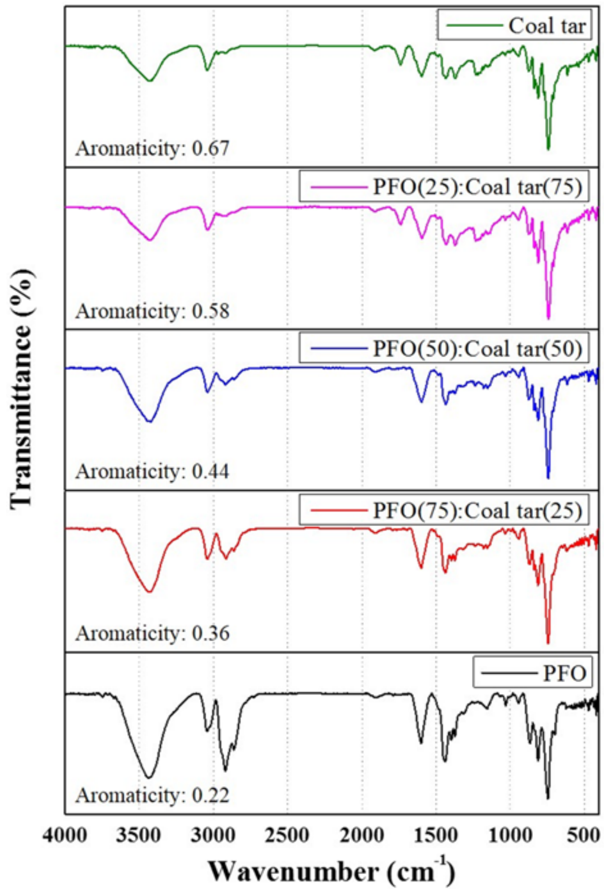

Fig. 2. FT-IR analysis of the blended feedstocks and their aromaticity.

FT-IR analysis was carried out to investigate the aromaticity of the blended feedstocks, as shown in Fig. 2. Increasing the coal tar ratio in the blend contributed to increased aromaticity. Coal tar presented the highest aromaticity value of 0.67, whereas PFO presented the lowest value of 0.22. This result supports that coal tar has more aromatic compounds than PFO, corresponding to the EA and CCR analysis.

3.2. Experimental characteristics of pitch production derived from PFO-coal tar blends

Thermal reaction was carried out to understand the effect of the PFO-coal tar blending ratio on pitch production. The pitch yield and softening point were used as indices for the experimental characteristics, as shown in Fig. 3. The pitch yield increased upon blending the feedstocks. The P50-C50 sample exhibited a maximum yield of 32.5%. The unblended samples (P100 and C100) showed lower yields of 19.8% and 21.9%, respectively. It was assumed that synergetic effects the blended feedstock increased the pitch yield. Although the pitch yield changed with the blending ratio, the softening point of the produced pitch depended on the PFO ratio in the blends. The softening point increased with an increasing ratio of PFO. P100 exhibited the highest softening point of 179.1°C.

Fig. 4 shows the surface images of the PFO and coal tar based pitch sample. The surface roughness of the Fig. 4a PFO-pitch was smooth. The particles were attached on pitch surface and shows clear shape. The sizes of the particles fell within the range of 2–10 µm. In Fig. 4b coal tar-pitch, it has an irregular surface as a whole. It seems like the pitch particles were aggregated and influenced the morphologies of the coal tar-pitch significantly. Through this result, the coal tar-pitch particles were easily to aggregate each other more than PFO-pitch because it has a low softening point. The PFO-coal tar blend sample (P50-C-50) shows the irregular flow structure with particles. So, we assumed that some of coal tar-pitch particles were aggregated and blended with PFO-pitch particles. It is considered that the softening point is improved due to these phenomena.

TGA was conducted to investigate the thermal properties of the produced pitch according to the blending ratio, as shown in Fig. 5. The carbon yield at 900°C increased in the order of P100 < P75-C25 < P50-C50 < P25-C75 < C100, increasing the coal tar ratio in the blends. C100 exhibited the highest value of 52.3%. As shown in the above results, the ratio of coal tar is related to the carbon yield, and the ratio of PFO is related to the softening point. However, it is generally reported that the softening point and carbon yield have a proportional relationship because the two indices are related to the thermal properties [20]. For example, pitch with a higher softening point should exhibit a higher carbon yield because the softening point is an index for the degree of polymerization [21]. Finally, this result was presumed to be related to the alkyl chains in the petroleum feedstock. Following the above assumption, it has been suggested that aliphatic compounds in PFO undergo chemical reactions, not only cracking and decomposition but also bonding reactions, during thermal reaction. It was assumed that bonding reactions of lower binding energies, for example, the formation of aliphatic bridges in PFO may occur during the thermal reaction, leading to the increased softening point. This expected phenomenon may negatively affect pitch properties such as carbon yield and thermal stability due to the disordered chemical structure of bridge formation. The TGA results coincided with the above

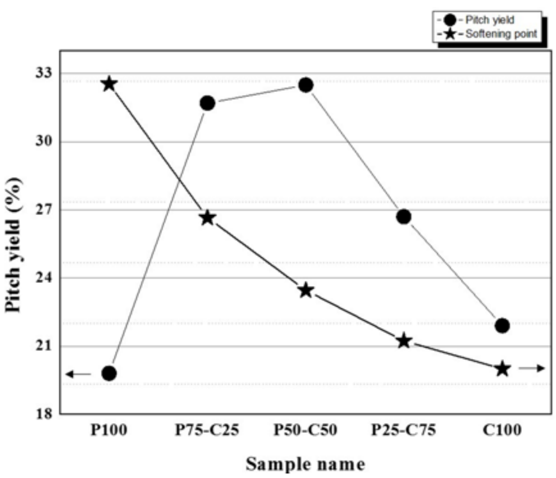

Fig. 3. Experiment results of the pitch produced by the thermal reaction.

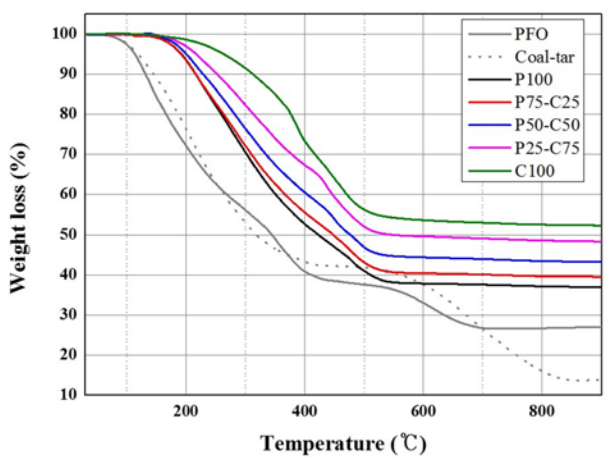

Fig. 5. TGA data of the feedstock and produced pitch.

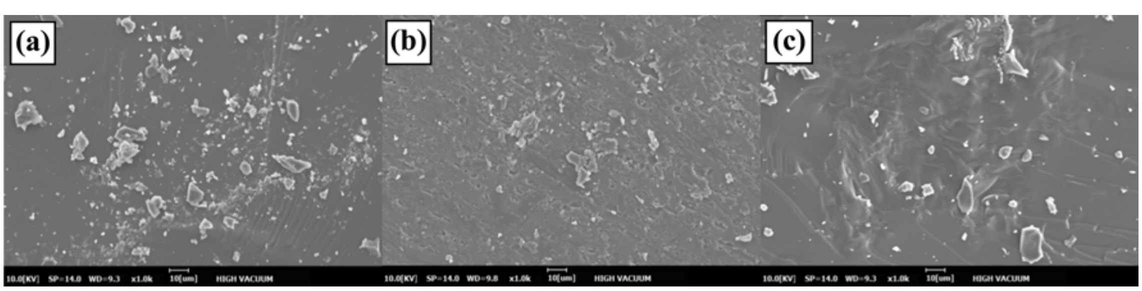

Fig. 4. SEM image of pitch. (a) PFO, (b) Coal tar, and (c) PFO-coal tar blend (P50-C50).

expected phenomenon. PFO-based pitch exhibited a lower carbon yield and higher softening point due to bridge formation of the alkyl chains. On the other hand, coal tar, which consists of aromatic compounds, showed a higher carbon yield due to the resonance and hybridization of the aromatic chemical structure [22]. In addition, it was assumed that the increased pitch yield may be related to synergetic effects of the blended feedstock. The aromatic and aliphatic ratio can be optimized to increase the pitch yield by blending the feedstock.

3.3. Molecular weight distribution of produced pitch derived from PFO-coal tar blends

MALDI-TOF analysis was conducted to investigate the MWD of the pitch produced via thermal reaction. The MALDI-TOF spectrum is displayed in Fig. 6. Molecular weight range of the produced pitch increased to over 1000 *m/z*. In addition, it was found that the MWD of the produced pitch was associated with the predominant feedstock in the blend. Pitch produced from coal tar-based blends (P25-C75 and C100) showed a broader range than that from PFO-based blends (P75-C25 and P100).

The MALDI-TOF spectrum was normalized to observe variations in the MWD. Anthracene (178 Da) was selected as a pseudo-component for the MALDI-TOF spectrum because a standard material is required to separate the molecular weight region. Each range was calculated from the integrated area and is displayed in the diagram in Fig. 7. Range 1 increased with increasing PFO ratio in the blend. When associated with the GC-SimDis results, it can be considered that this result originated from the volatile matter with a lower boiling point in PFO. Ranges 2 and 3 were attributed to the ratio of each component in the feedstock. The PFO-based samples (P100 and P75-C25) showed the highest value in range 2, while the coal tar-based samples (C100 and P25-C75) showed the highest value in range 3. P50-C50 showed similar values in ranges 2 and 3. Ranges 4–7 increased with increasing coal tar ratio. In our previous research, we discussed the relation between the MWD range and the pitch properties [23]. However, a relation between the MWD and pitch properties when using two different feedstocks was not confirmed due to insufficient data.

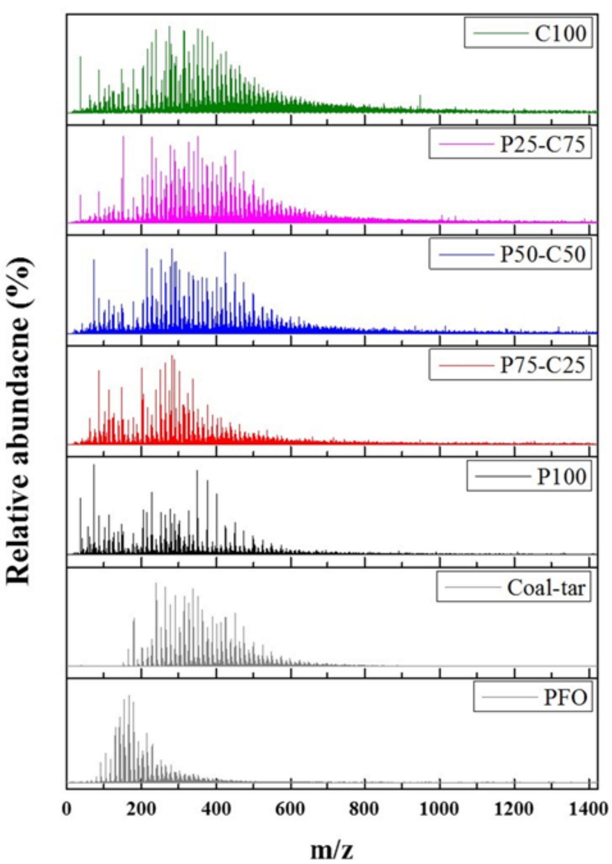

Fig. 6. MALDI-TOF spectrum of the feedstock and produced pitch.

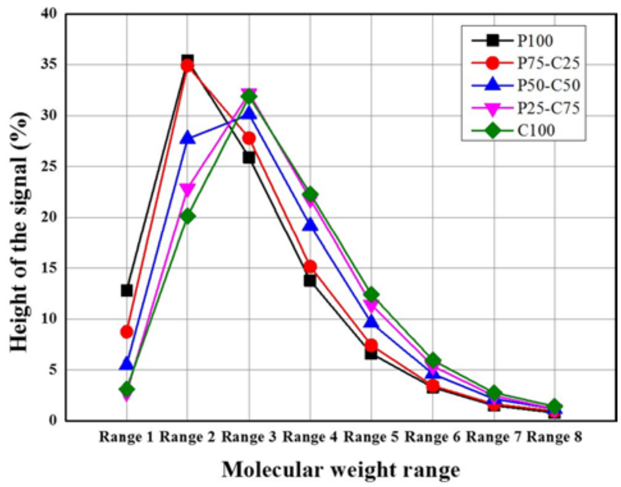

Fig. 7. Diagram of the molecular weight range divided by the pseudo-component.

4. Conclusions

A thermal reaction was conducted to produce pitch from a feedstock with different blending ratios of PFO and coal tar. The blended feedstock and produced pitch were characterized to investigate the effects of blending and experimental trend according to the blending ratio in the feedstock. Coal tar exhibited more aromatic structures than PFO. The blended feedstock showed an increased pitch yield, indicating the optimization of the aromatic and aliphatic ratio. In addition, it was found that the softening point and carbon yield were dominated by the PFO and coal tar content, respectively. This result indicates that the aliphatic contents in PFO underwent a bonding reaction, which increased the softening point. It was suggested that bridge formation can occur among the aliphatic contents in the petroleum feedstock during the thermal reaction. It was found that a lower MWD (ranges 1 and 2) is related to the PFO ratio, and a higher MWD (ranges 3 and 4–7) is related to the coal tar ratio. In conclusion, the blending of different feedstocks presented diverse experimental characteristics based on the blending ratio. Further research on blending feedstocks is required to optimize the characteristics of the produced pitch and the trends in pitch production.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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