

Pitch-based carbon fibers from coal tar or petroleum residue under the same processing condition

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Abstract

Spinnable pitches and carbon fibers were successfully prepared from petroleum or coal pyrolysis residues. After pyrolysis fuel oil (PFO), slurry oil, and coal tar were simply filtered to eliminate the solid impurities, the characteristics of the raw materials were evaluated by elemental analysis, ¹³C nuclear magnetic resonance spectrometer, matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOF-MS), and so on. Spinnable pitches were prepared for melt-spinning carbon fiber through a simple distillation under strong nitrogen flow, and further vacuum distillation to obtain a high softening point. Carbon fibers were produced from the above pitches by single-hole melt spinning and additional heat treatment, for oxidation and carbonization. Even though spinnable pitches and carbon fibers were processed under the same conditions, the melt-spinning and properties of the carbon fiber were different depending on the raw materials. A fine carbon fiber could not be prepared from slurry oil, and the different diameter carbon fibers were produced from the PFO and coal tar pitch. These results seem to be closely correlated with the initial characteristics of the raw materials, under this simple processing condition.

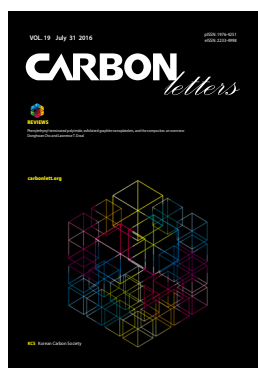
Key words: pitch, carbon fibers, pyrolysis fuel oil, slurry oil, coal tar

1. Introduction

Carbon fibers provide a lot of advantages including high strength, low density, good thermal and electrical conductivity along the fiber axis, chemical resistance, and so on [1-4]. Recently, carbon fibers have been used as key industrial materials in various fields including aerospace, automobile, military, sports, and medical [5-7]. To ensure the growth of potential applications and create new markets for carbon fibers, stable mass production and low cost are critically essential. It is therefore necessary to develop selective carbon fibers which have competitive costs and properties that are appropriate for their intended use [8,9].

The typical precursors used to produce carbon fibers are polyacrylonitrile (PAN) and pitch. Because PAN-based carbon fibers have high tensile strength and productivity, the current commercial market is mostly dominated by fibers from that source [10]. However, the relatively low carbon content in the PAN precursor also results in cost limitations that have to be overcome. Another precursor of carbon fibers, pitch, is obtained by the distillation process of natural resources such as petroleum and coal [11,12]. The typical raw materials for producing pitch are pyrolysis fuel oil (PFO), catalytic slurry oil, and coal tar. The production of carbon fiber from pitch can result in cost reductions or very high properties with an additional processing step. Therefore, efforts to produce carbon fiber using pitch have flourished in recent years [13-16].

The properties and cost of carbon fiber are determined by their precursors and manufacturing process. This study investigates the effect of the raw materials of the pitch



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precursor on the final carbon fiber under the same processing conditions. Spinnable isotropic pitches with similar softening points were prepared by two-step distillation from various raw materials such as PFO, catalytic slurry oil, and coal tar. Subsequently, carbon fibers were produced through melt-spinning, oxidization, and carbonization processes under the same conditions. We report the relations between the raw material and the properties of the produced carbon fiber.

2. Experimental

2.1. Raw materials

PFO, catalytic slurry oil, and coal tar were used as the raw materials to produce pitch. PFO was obtained from GS Caltex Co. (Seoul, Korea). Slurry oil was provided from Hyundai Oilbank Co. (Seoul, Korea). These raw materials from petroleum resources were placed in a 70°C oven for a week and were shaken occasionally to make it homogeneous before use. Coal tar was supplied by POSCO Chemtech Co. (Seoul, Korea). The coal tar was also kept in the oven for a week, then mixed with tetrahydrofuran (THF) at a volume ratio of 1:1 and stirred for 24 h. THF-insolubles were removed by filtration of the coal tar mixture and refined coal tar was collected by separating the THF at 80°C in vacuum. All raw materials were used in a THF-insoluble free state.

2.2. Preparation of pitches

Spinnable pitches were prepared via a two-step distillation. The first distillation was conducted under vigorous nitrogen bubbling, to handle a large amount of raw material at once. Afterward, heat treatment under vacuum was carried out to elevate the softening point for the melt-spinning of pitch fibers.

Two-hundred grams of the PFO or the coal tar was heated up to 370°C under nitrogen bubbling at 1 L/min. After 1 h of the above simple distillation, the reactor was cooled down to room temperature and the intermediate pitches were collected. The slurry oil was treated at 430°C. Yield softening point curves (Yield-SP curves) were obtained from further heat treatments under vacuum to find the final manufacturing conditions for producing spinnable pitches.

After the reactor was filled with 10 g of each intermediate pitch, it was heated to the designed temperatures (200°C–360°C) for 10 min under vacuum using an oil pump, and the weight of the whole reactor was checked to calculate the yield. Softening points were also measured. The spinnable precursor pitches were prepared with high softening points for the melt-spun carbon fibers by the further distillations, on the basis of the above Yield-SP curves. The intermediate pitches with low softening points were heat-treated under vacuum to increase the softening point. The heating temperature of 330°C was applied for the PFO and the coal tar based pitch, and the slurry oil pitch was heated at 350°C. The final softening point of every pitch was 260°C.

2.3. Preparation of melt-spinning carbon fibers

Precursor pitches were spun into a fiber shape and passed oxidization and carbonization steps to obtain carbon fibers. Melt-spinning was conducted using a single hole spinning nozzle system at 310°C. A spinneret with a diameter and a length of 0.2 and 0.4 mm ($L/D=2$) was used. The diameter of the winding rotor was 100 mm and a wide range of winding speeds (200–1500 rpm, 6-steps; with the unit converted to $m/min=63$ to 471 m/min) were adopted to obtain the spun-pitch. The oxidization temperature in air flow was 280°C for 1 h at a heating rate of 1°C. The oxidized fibers were carbonized at 800°C for 10 min with a heating rate of 5°C in nitrogen atmosphere. The weights of each of the fibers were measured to calculate the processing yield.

2.4. Characterization

The elemental compositions of the raw materials and the pitches were examined by elemental analyzer (TruSpec Elemental Analyzer and SC-432DR Sulfur Analyzer; LECO, Saint Joseph, MI, USA). Aliphatic and aromatic structures of the raw materials were determined by ^{13}C nuclear magnetic resonance spectrometer (Avance-500 FT-NMR; Bruker, Karlsruhe, Germany) [17]. The molecular weights of the raw materials and pitches were measured via matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOF-MS; Autoflex Speed TOF/TOF Mass Spectrometer; Bruker). α -Cyano-4-hydroxycinnamic acid was used as a matrix and all samples were dissolved in THF at the ratio of 10 wt%. Thermal degradation of the raw materials and pitches was carried out on a thermogravimetric analysis (TGA) system (STA 409 PC; Netzsch, Germany) in a nitrogen flow. The heating rate of 5°C/min was adopted in the temperature range of 25°C to 600°C. The status of pitch oxidization was detected using the same TGA system, except air atmosphere. The characteristics of the mesophase development were observed with a polarized light microscope (BX51M; Olympus, Japan, Japan). The mean diameter of the carbon fibers was observed using scanning electron microscopy (Mini-SEM and SNE-3000M; SEC, Suwon, Korea) at 25 kV.

3. Results and Discussion

Table 1 shows the results of the elemental analysis of the PFO, slurry oil, and coal tar. The PFO and the slurry oil from petroleum have an abundant carbon content, close to 90%, and at the same time have a high amount of hydrogen, up to 8%. The H/C atomic ratio of the PFO was 1.10, and that of the slurry oil was 1.04. These were relatively higher values compared to the 0.74 of the coal tar. Even though the PFO and the slurry oil were both refined from petroleum, there were differences in nitrogen and sulfur contents. The PFO contained 1.59% of nitrogen, but it had only few sulfur components. However, a considerable sulfur content was observed in the slurry oil, up to 2.66%, and it had the lowest nitrogen. The coal tar had higher carbon and nitrogen contents than the petroleum-based raw materials, with a small

Table 1. Elemental analysis of raw materials for pitch-based carbon fibers

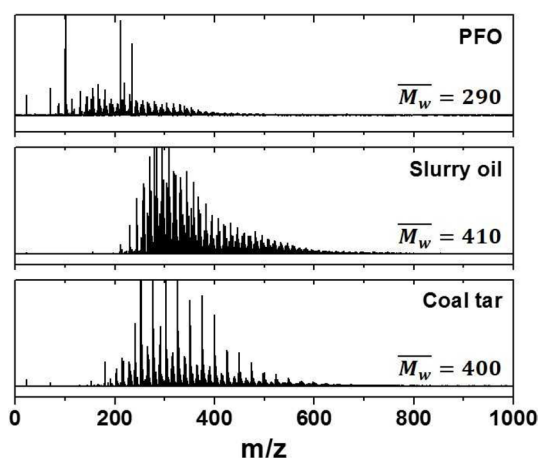
	C (%)	H (%)	N (%)	S (%)	H/C (atomic)
PFO	90.12	8.25	1.59	0.04	1.10
Slurry oil	89.39	7.72	0.24	2.66	1.04
Coal tar	91.77	5.74	1.75	0.64	0.74

PFO, pyrolysis fuel oil.

Table 2. Aliphatic and aromatic fractions of raw materials for pitch-based carbon fibers [17]

	Aliphatic (%)			Aromatic (%)		f_a
	CH ₃	CH ₂	C _{a2}	C _{ar1,3}	C _{ar1,2}	
PFO	4.7	5.0	12.6	55.7	22.0	0.78
Slurry oil	9.8	9.0	4.7	47.3	29.2	0.76
Coal tar	1.4	1.4	1.4	74.0	21.8	0.96

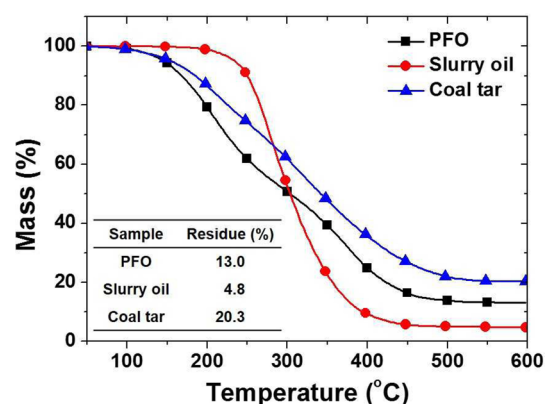
CH₃, methyl carbons; CH₂, methylene carbons (different from C_{a2}); C_{a2}, bridge/hydroaromatic structure; C_{ar1,3}, protonated or pericondensed aromatic carbons; C_{ar1,2}, aromatic carbons bonded to aliphatic chains or catacondensed aromatic carbons; f_a , aromaticity; PFO, pyrolysis fuel oil.

**Fig. 1.** Matrix-assisted laser desorption/ionization time-of-flight mass spectrometer spectra of the raw materials and their average molecular weights. PFO, pyrolysis fuel oil.

quantity of sulfur. There were no ash or impurities in any of the raw materials.

The chemical structure and aromaticity of the raw materials are summarized in Table 2. Though the PFO and the slurry oil had a very similar value of aromaticity, about 0.78 and 0.76, respectively, there was a significant difference in their chemical structures. The substantial aliphatic component in the PFO was comprised of bridge structures between two aromatic rings. On the other hand, a lot of aliphatic carbon in the slurry oil was an end or exposed position of the hydrocarbon chain of methyl or methylene carbon. Accordingly, the aromatic component C_{ar1,2} of the slurry oil was slightly higher than that of the PFO. It has been generally known that the coal tar is mainly composed of aromatic carbons.

Fig. 1 shows the molecular weight distributions obtained by MALDI-TOF-MS for each raw material. PFO, slurry oil, and

**Fig. 2.** Thermogravimetric profiles of the raw materials. The residue values in the inner table were obtained at 600°C. PFO, pyrolysis fuel oil.

coal tar exhibited a molecular weight distribution in the range of 100–500, 200–800, and 150–700, respectively. As shown in Fig. 1, the average value of molecular weight calculated from above distribution range was 290, 410, and 400 in the order of PFO, slurry oil, and coal tar. The PFO was mainly made up of relatively low molecular weight substances with two major peaks at 100 and 220 m/z. In contrast, the slurry oil and the coal tar had a broad molecular distribution in the center of the main fragment, at around 300 m/z. The PFO and the slurry oil possessed comparable H/C ratios and aromaticity, but the average molecular weight of the slurry oil was about 40% higher, suggesting that the slurry oil would have bigger or bulkier structures than the PFO.

The thermal degradations of raw materials in nitrogen flow are represented in Fig. 2. The PFO and the coal tar showed a similar profile over the entire range, except for the amount of the final residue. Low-molecular weight substances such as volatiles began to be removed at about 100°C, and a gradual re-

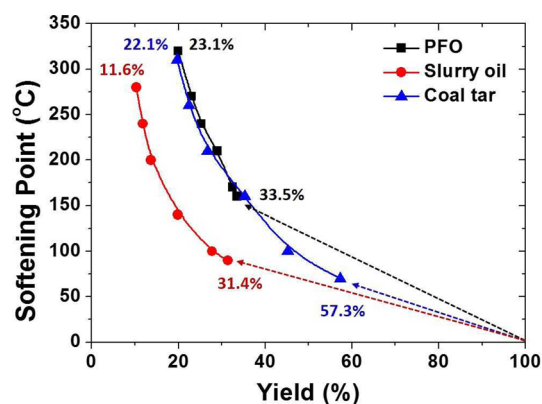


Fig. 3. Yield and softening point curves of the raw materials using the two-stage distillation processes (dash-line, simple distillation with nitrogen flow; solid-line, vacuum distillation). PFO, pyrolysis fuel oil.

duction in weight occurred until the temperature reached 500°C. The slurry oil started weight loss at about 250°C. After decreasing very rapidly, only 5% residues remained.

Spinnable pitches were prepared by simple distillation in nitrogen bubbling, prior to elevating the softening point using vacuum distillation. Based on the thermogravimetric (TG) results, the temperature of the simple distillation was set to 370°C. However, in the case of the slurry oil, with its high molecular weight structure, effective distillation did not occur. Therefore, the simple distillation temperature was raised up to 430°C for the slurry oil.

Fig. 3 indicates the Yield-SP curves used to determine the final synthetic condition of the spinnable pitches, with high softening points, for carbon fiber production. Even though the PFO and the coal tar were simply distilled in the same condition, they resulted in different yields, with the PFO at 33.5% and the coal tar at 57.3%. The reason seems to be due to the difference in the average molecular weight. It was not enough to remove the low molecular weight components with the nitrogen flow alone, due to the larger size of the coal tar as compared to the PFO.

However, similar curve shapes and final yield appeared after the vacuum distillation process to raise the softening point. The simple distillation of the slurry oil was conducted at a higher temperature, and had a comparable level of yield to the PFO. The pitch from the slurry oil had a relatively low softening point, so endured a significant weight loss in order to get a high softening point. From the above Yield-SP curves, the final stage temperature of the vacuum distillations to make spinnable pitches was set at 330°C. The slurry oil was processed at 350°C. As a result of the two-stage distillation, spinnable pitches with a softening point of about 260°C were successfully prepared from the three kinds of raw materials.

Fig. 4 shows the molecular distributions of the prepared pitches. The low molecular weight components of less than 300 m/z remained in the pitch from the PFO. In contrast, in the slurry oil pitch, a shoulder shape in the high molecular region, of more than 700 m/z, was observed. While the raw materials had significantly different forms of profiles (Fig. 1), all of the pitches showed an almost identical distribution of molecules, in the range of 300 to 800 m/z. The average molecular weights were also nearly the same values, of 540, 560, and 520, in the

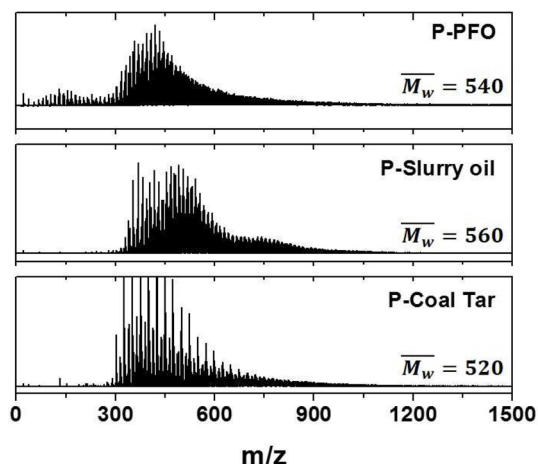


Fig. 4. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometer spectra of the pitches and their average molecular weights. P, pitch; PFO, pyrolysis fuel oil.

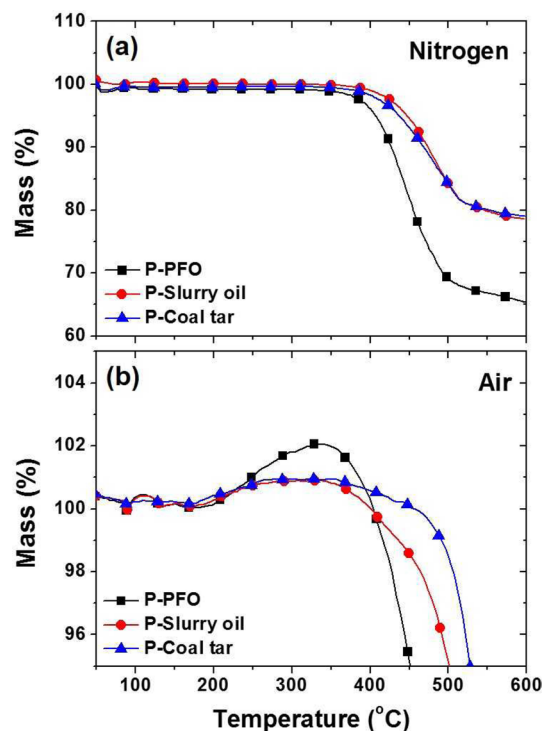


Fig. 5. Thermogravimetric profiles of the pitch powders in (a) nitrogen and (b) air atmosphere. P, pitch; PFO, pyrolysis fuel oil.

order of PFO-, slurry oil-, and coal tar pitch.

Fig. 5 is the TG profile of the spinnable pitches in nitrogen or air atmosphere. Thermal stability at high temperature is essential for the stable spinning of pitch with a high softening point, because melt spinning is typically conducted at a temperature 50°C above the softening point. In Fig. 5a, with nitrogen, the weight loss caused by thermal decomposition did not occur until 400°C. In case of the pitch from the PFO, a larger amount of the pitch had decomposed. This may be due to the elimination of low molecular components below 300 m/z, shown in the

Table 3. Summary of average yield at each stage for carbon fiber production

Yield (%)	Raw material to pitch	Spun pitch to oxidized fiber	Spun pitch to carbon fiber	Raw material to carbon fiber
PFO	23.1	112.3	78.1	18.0
Slurry oil	11.6	-	-	-
Coal tar	22.1	104.3	82.3	18.2

PFO, pyrolysis fuel oil.

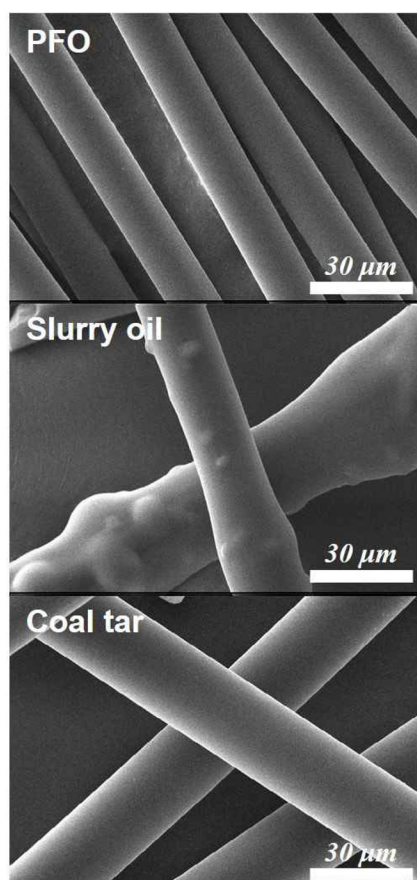
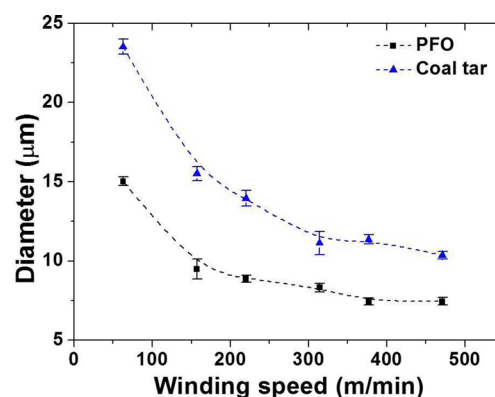
**Fig. 6.** Scanning electron microscopy images of the carbon fibers spun at 63 m/min (200 rpm). PFO, pyrolysis fuel oil.**MALDI-TOF-MS result.**

Fig. 5b shows the mass increase produced by the heat treatment in air flow used to determine the oxidization condition of the spun pitch fibers. When the temperature exceeded 200°C, it started the mass increase, and the oxygen adhered to the surface of the pitch and passed throughout its core. At a temperature above 350°C, pitch combustion took place in order of PFO-, slurry oil-, and coal tar pitch. It was determined based on the TG analysis that spun pitch fibers were oxidized at 280°C.

Carbon fibers from these spinnable pitches were prepared via melt spinning using a mono-hole spinneret and further heat treatment. Prior to the heat treatment for carbonization, the pitch

**Fig. 7.** Average diameters and standard deviation of the carbon fibers at various winding speeds (63–471 m/min). PFO, pyrolysis fuel oil.

fibers need to go through an oxidization process to avoid filament adhesion and to maintain the fiber form. The average yield of each step from raw materials to final carbon fibers are summarized in Table 3. The pitch from the slurry oil was excluded from the table because it failed to be spun. The yields of over 100% in the process from spun pitch fibers to oxidized fibers indicates that the intended oxidization occurred successfully. The weight increases produced by oxidization of the PFO and the coal tar pitch fiber were 12.3% and 4.3%, respectively. As could be predicted from the results of Fig. 5b, the pitch fiber from the PFO was more efficiently oxidized than that of the coal tar. After the carbonization process, a significant reduction in weight was observed. The final yields of carbon fiber from raw materials were almost equal, at about 18%.

The morphology of the carbon fibers spun at 63 m/min (200 rpm) was examined by SEM (Fig. 6). Carbon fibers with uniform and clear surfaces were successfully manufactured from the PFO and the coal tar pitch. On the other hand, the pitch of the slurry oil did not properly form a uniform fiber shape. In the case of the PFO and the coal tar pitch, an appropriate tension between the spinneret and winding rotor in the spinning process ensured the formation of fiber. The slurry oil pitch, however, seemed like melted pitch and streamed down from the spinneret hole. The slurry oil pitch could only be spun a few minutes at 63 m/min, and no spinning occurred at a higher winding speed.

Both of the PFO and the coal tar pitch were successfully spun into fibers at winding speeds from 63 to 471 m/min (200 to 1500 rpm) without filament breakage during extrusions of 3 to 10 min. Typically, it was known that coal tar pitch had a poorer spinnability than PFO due to its high aromaticity and solid contents. In this study, however, the pitch produced by the heat treatment removal of the THF-insoluble component from the coal tar also converted well into carbon fiber.

Fig. 7 indicates the average diameter of the carbon fibers obtained at various winding speeds from 63 to 471 m/min. The diameters of the carbon fibers produced at 63 m/min, shown in Fig. 6, were 15.0 and 23.5 μm for the PFO and the coal tar pitch, respectively. The diameters of the carbon fibers became thinner with increases in the winding speed, and converged at about 7.5 μm for the PFO and 10.0 μm for the coal tar pitch. In all spinning conditions, the diameter of the carbon fiber from the PFO was always thinner than that of the coal tar.

Table 4. Elemental analysis of the pitches from the raw materials

	C (%)	H (%)	N (%)	S (%)
P-PFO	94.12	5.65	0.02	0.06
P-slurry oil	92.52	4.43	0.11	1.96
P-coal tar	94.03	3.48	0.89	0.64

P, pitch; PFO, pyrolysis fuel oil.

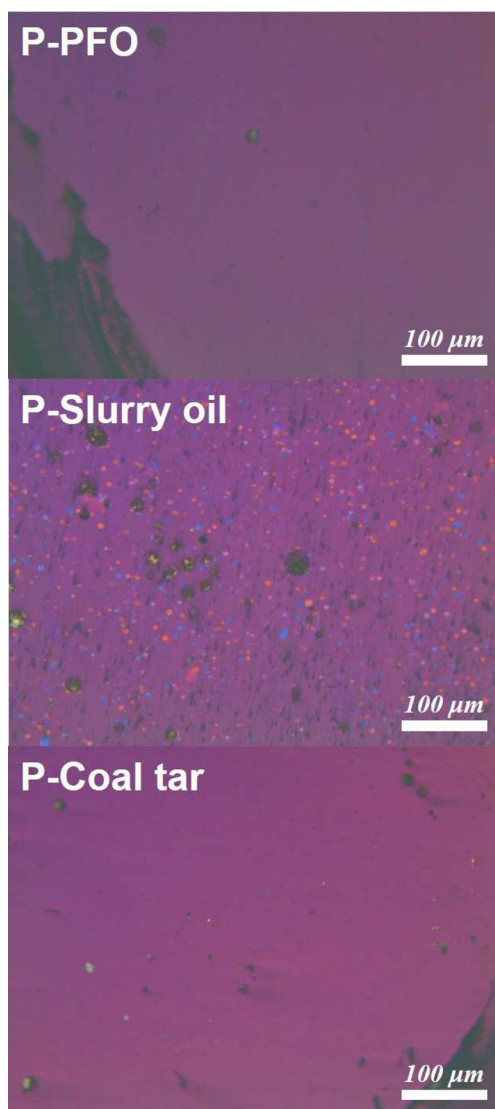


Fig. 8. Polarized light microscope images of the pitches. P, pitch; PFO, pyrolysis fuel oil.

Spinnable pitches with same softening point, and carbon fibers using them, were successfully prepared from the raw materials of PFO and coal tar. Proper carbon fiber could not be prepared from the slurry oil via the short time simple distillation, and further vacuum heat treatment to raise the softening point. From SEM images in Fig. 6, the rugged appearance and some impurities in the shape of a lump were observed in the carbon from the slurry oil. The slurry oil had a relatively high sulfur

content of 2.66% in the elemental analysis of Table 1.

Table 4 presents the elemental composition of the pitches prepared from the raw materials. A substantial portion of the hydrogen and nitrogen components were removed with the volatile or low molecular weight substances, through the two-stage simple distillation. However, the sulfur component remained in the pitches at values almost similar to those of the raw materials in Table 1. The sulfur content of the slurry oil pitch reached 1.96%. Sulfur is typically used as a cross-linking agent in the process of producing a mesophase pitch [18].

In addition, a shoulder pattern in the MALDI-TOF-MS profile was found in the region above 700 m/z in the slurry oil pitch (Fig. 4). From these results, it appears that the weak development of a partial mesophase seems to have started during the heat treatment. The polarized microscope images of the prepared pitches are shown in Fig. 8. No liquid crystalline texture was observed in the spinnable isotropic pitches from the PFO and the coal tar. However, the slurry oil-derived pitch possessed a number of small ball-shaped aggregates. This could be seen as the early stages of the mesophase development. Usually, slurry oil is used to produce a mesophase pitch for a high quality carbon fiber through expensive processes [19]. In the above referenced research, partial development of a mesophase makes the spinning difficult, due to the differences in the viscosity and density of the anisotropic and isotropic regions.

The PFO and the coal tar pitch could be made into carbon fiber, but had different fiber diameters. Even though the PFO and the coal tar were converted into carbon fiber using the same processing condition, the carbon fiber using the PFO pitch had thinner diameters. As a raw material for making pitch, the PFO has a higher linearity than coal tar. As shown in Table 2, the PFO contained up to 12.6% of the aliphatic carbon of C_{a2} , which connects two aromatic rings like a bridge, as compared to 1.4% of the coal tar.

Also, from the Fig. 2 TG results, although the PFO and the coal tar started thermal decomposition at a similar temperature, the slope of the PFO appeared sharply at a temperature below 300°C. The coal tar left more residues after the pyrolysis, which may indicate that the coal tar has a more bulky structure compared to the PFO.

Comparing the MALDI-TOD-MS results, the different profiles of the raw materials changed into a similar pattern of spinnable pitches after heat treatment. In spite of the two-stage distillation, a considerable amount of low molecular weight components under 300 m/z was observed in the PFO pitch. Thus, the physical and structural properties of the raw materials seem to have remained in the final spinnable pitches following this simple distillation.

A rapid rate of thermal decomposition and oxygen introduction appeared in the PFO pitch in Fig. 5. This fact also supports that the carbon structure of the PFO pitch is more linear compared to the one prepared from the coal tar. Therefore, the thinner diameters of the carbon fibers from the PFO seem to have been caused by the high linearity of the raw material, and the spinnable pitch [20]. Not only the manufacturing process of the pitch and the spinning of the carbon fiber, but also the selection of raw materials and its treatment, are very important for producing carbon fibers with desired properties.

4. Conclusions

Spinnable pitches were prepared from cheap petroleum and coal-based resources, PFO, slurry oil, and coal tar, via two-stage distillation without any additives. Carbon fibers with various diameters were successfully produced by the melt-spinning of spinnable pitches produced from the PFO and the coal tar. Although the spinnable pitches and carbon fibers were prepared from each precursor under the same processing conditions, their properties and morphologies were obviously different, depending on the raw materials. A fine carbon fiber could not be obtained from the slurry oil due to the development of a partial mesophase form. Even though excellent carbon fibers were stably produced from the PFO and the coal tar, the average diameters of the carbon fibers produced at various winding speeds were different, being about 7.5 μm for the PFO and 10.0 μm for the coal tar. The inherent properties of the raw materials seemed to be reflected in the carbon fibers produced through the simple distillation, and they should be fully considered when producing a carbon fiber with target properties.

Conflict of Interest

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

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References

- [1] Hong SH, Korai Y, Mochida I. Development of mesoscopic textures in transverse cross-section of mesophase pitch-based carbon fibers. *Carbon*, **37**, 917 (1999). [http://dx.doi.org/10.1016/S0008-6223\(98\)00236-X](http://dx.doi.org/10.1016/S0008-6223(98)00236-X).
- [2] Chung DDL. *Carbon Fiber Composites*, Butterworth-Heinemann, Boston, MA, 3 (1994).
- [3] Frank E, Steudle LM, Ingildeev D, Spörl JM, Buchmeiser MR. Carbon fibers: precursor systems, processing, structure, and properties. *Angew Chem Int Ed*, **53**, 5262 (2014). <http://dx.doi.org/10.1002/anie.201306129>.
- [4] Yang KS, Kim BH, Yoon SH. Pitch based carbon fibers for automotive body and electrodes. *Carbon Lett*, **15**, 162 (2014). <http://dx.doi.org/10.5714/CL.2014.15.3.162>.
- [5] Otani S, Oya A. *Carbon Fiber Nyumon*, Ohmusha, Tokyo, 127 (1983).
- [6] deVries J. *Carbon Fiber in the Automotive Industry... the Holy Grail or Reality?* Technologies Workshop on Low Cost Carbon Fiber Composites for Energy Applications, Oak Ridge, TN (2009).
- [7] Huang X. Fabrication and properties of carbon fibers. *Materials*, **2**, 2369 (2009). <http://dx.doi.org/10.3390/ma2042369>.
- [8] Mochida I, Toshima H, Korai Y, Matsumoto T. Blending mesophase pitch to improve its properties as a precursor for carbon fibre. Part I: blending of pvc pitch into coal tar and petroleum-derived mesophase pitches. *J Mater Sci*, **23**, 670 (1988). <http://dx.doi.org/10.1007/BF01174704>.
- [9] Baker DA, Rials TG. Recent advances in low-cost carbon fiber manufacture from lignin. *J Appl Polym Sci*, **130**, 713 (2013). <http://dx.doi.org/10.1002/app.39273>.
- [10] Roberts T. *The Carbon Fibre Industry: Global Strategic Market Evaluation 2006-2010*, Materials Technology Publications, Watford (2006).
- [11] Berruero C, Álvarez P, Díez N, Granda M, Menéndez R, Blanco C, Santamaría R, Millan M. Characterisation and feasibility as carbon fibre precursors of isotropic pitches derived from anthracene oil. *Fuel*, **101**, 9 (2012). <http://dx.doi.org/10.1016/j.fuel.2011.10.005>.
- [12] Yoo MJ, Ko HJ, Lim YS, Kim MS. Modification of isotropic coal-tar pitch by acid treatments for carbon fiber melt-spinning. *Carbon Lett*, **15**, 247 (2014). <http://dx.doi.org/10.5714/CL.2014.15.4.247>.
- [13] Derbyshire F, Andrews R, Jacques D, Jagtoyen M, Kimber G, Rantell T. Synthesis of isotropic carbon fibers and activated carbon fibers from pitch precursors. *Fuel*, **80**, 345 (2001). [http://dx.doi.org/10.1016/S0016-2361\(00\)00099-5](http://dx.doi.org/10.1016/S0016-2361(00)00099-5).
- [14] Kim BJ, Kil H, Watanabe N, Seo MH, Kim BH, Yang KS, Kato O, Miyawaki J, Mochida I, Yoon SH. Preparation of novel isotropic pitch with high softening point and solvent solubility for pitch-based electrospun carbon nanofiber. *Curr Org Chem*, **17**, 1463 (2013). <http://dx.doi.org/10.2174/1385272811317130013>.
- [15] Zhu J, Park SW, Joh HI, Kim HC, Lee S. Preparation and characterization of isotropic pitch-based carbon fiber. *Carbon Lett*, **14**, 94 (2013). <http://dx.doi.org/10.5714/CL.2013.14.2.094>.
- [16] Díez N, Álvarez P, Santamaría R, Blanco C, Menéndez R, Granda M. Optimisation of the melt-spinning of anthracene oil-based pitch for isotropic carbon fibre preparation. *Fuel Process Technol*, **93**, 99 (2012). <http://dx.doi.org/10.1016/j.fuproc.2011.09.016>.
- [17] Diaz C, Blanco CG. NMR: a powerful tool in the characterization of coal tar pitch. *Energy Fuels*, **17**, 907 (2003). <http://dx.doi.org/10.1021/ef020114r>.
- [18] Mochida I, Korai Y, Ku CH, Watanabe F, Sakai Y. Chemistry of synthesis, structure, preparation and application of aromatic-derived mesophase pitch. *Carbon*, **38**, 305 (2000). [http://dx.doi.org/10.1016/S0008-6223\(99\)00176-1](http://dx.doi.org/10.1016/S0008-6223(99)00176-1).
- [19] Park YD, Mochida I. A two-stage preparation of mesophase pitch from the vacuum residue of FCC decant oil. *Carbon*, **27**, 925 (1989). [http://dx.doi.org/10.1016/0008-6223\(89\)90043-2](http://dx.doi.org/10.1016/0008-6223(89)90043-2).
- [20] Kim BJ, Eom Y, Kato O, Miyawaki J, Kim BC, Mochida I, Yoon SH. Preparation of carbon fibers with excellent mechanical properties from isotropic pitches. *Carbon*, **77**, 747 (2014). <http://dx.doi.org/10.1016/j.carbon.2014.05.079>.