

# Preparation of isotropic spinnable pitch and carbon fiber from biomass tar through the co-carbonization with ethylene bottom oil

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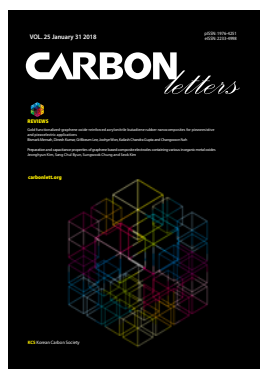
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## Abstract

In this study, we tried to prepare an isotropic spinnable pitch which can be useful to prepare the general purpose carbon fiber through the co-carbonization of biomass tar with ethylene bottom oil under two different preparation methods (atmospheric distillation, pressurized distillation). The results showed that the ethylene bottom oil added co-carbonization was very effective to decrease of the oxygen contents for obtaining a stable spinnable pitch. The pressurized distillation was more effective to reduce the oxygen functional groups of pitches than atmospheric distillation. The obtained spinnable pitch by the pressurized distillation showed higher pitch yield of 42% and lower oxygen content of 9.12% than the spinnable pitch by the atmospheric distillation. The carbon fiber derived from the pressurized distillation spinnable pitch by carbonization at 800°C for 5 min showed that the higher tensile strength of carbon fiber was increased up to 800 MPa.

**Key words:** biomass tar, ethylene bottom oil, isotropic pitch, pitch-based carbon fiber

## 1. Introduction

Carbon fibers are important reinforcement materials for high performance composites which provide a way to reduce the weight of structural components and to reduce carbon footprint. However, the high cost of carbon fiber limits its applications and widespread use [1]. The basic difficulty is the combined result of precursor cost, yield, processing cost and so forth. To solve the problem, the extensive work has been carried out to be interest in identifying alternative fiber precursors, for which biomass pitch shows great potential as precursors for carbon fiber production [2-5]. Differently from coal tar pitches, biomass tar pitches have been very little studied so far as precursors of advanced carbonaceous materials. However, the development of applications for biomass tar pitch is important to increase the value of the charcoal manufacturing industry and to stimulate the use of biomass, thereby answering the appeals of environment preservation [4-6]. As we know, biomass tar (BT) consists of aromatic compounds with many oxygen functional groups. Under the heat treatment, the phenolic (-OH) and methylol (-OCH<sub>3</sub>) groups undergo cross-linking at low temperature, forming non-meltable solid. Therefore, it is difficult to obtain the spinnable pitch for carbon fiber directly. In order to obtain the high thermally stable and spinnable pitch, Prauchner et al. [5,6] reported the addition of CH<sub>2</sub>O or AlCl<sub>3</sub> to the Biotar precursor to increase the softening point (SP) and thermal stability of pitches, the modification improved its SP from 76 to 112°C, but the obtained carbon fiber prepared by carbonization at 1000°C showed much inferior mechanical properties (a tensile strength of 130 MPa). Qiao et al. [7] have prepared biomass resin-based carbon fibers of tensile strength up to 632 MPa by using oxalic acid and HCl as catalysts. However, the above processes were ineffective to increase the tensile strength and costly. A simple and cheap process is necessary to be considered to develop

carbon fiber with high pitch yield and high performances from BT. In our work, ethylene bottom oil (EO) is relatively cheap and abundant, which composes of 1–2 six-membered rings and is almost 90% of aromaticity. Especially, it is expected to react with BT at less than 300°C and is effective to remove the oxygen functional groups and inhibit self-hardening of BT. Therefore, we tried to prepare a spinnable isotropic pitch which can be useful to prepare the general purpose isotropic pitch based carbon fiber through the co-carbonization of BT with EO under atmospheric distillation (AD) or pressurized distillation (PD) method. The present paper reports on pitch processing and the characterization of the obtained carbon fibers.

## 2. Experimental

### 2.1. Materials

The BT was used as a precursor for the preparation of the spinnable pitch for carbon fiber, which was collected from the gasification of crop stalks at 500–600°C from Akita Industrial Technology Center, Japan. And the EO was a byproduct of ethylene production, which was supplied from SK Company, Korea. The BT and EO were pretreated to remove the insoluble particles with tetrahydrofuran and dichloromethane by filtration and rotary evaporation, respectively.

### 2.2. Preparation of spinnable isotropic pitches and carbon fibers

A suitable pitch precursor must satisfy several requirements, including higher SP, as well as maintaining its good spinnability. Unfortunately, both the properties change in opposite trends. Therefore, a compromise between both parameters is necessary for satisfactory performance of the final spinnable pitches [8]. In our experiment, two-steps method to produce spinnable pitch from BT was developed. Firstly, the basic pitches were prepared through co-carbonization of BT with EO, then the obtained basic pitches were vacuum heat treated by thin layer evaporation to prepare the spinnable pitch. The thin layer evaporation method could only remove volatiles matters from the basic pitches without further polycondensation reaction in the low temperature, which is necessary to obtain the enough high SP and good spinnability. Thus, the preparation process of pitches and carbon fibers were as follows: (1) BT and EO with different weight ratios were heat treated by the AD or PD conditions at 350°C for 1 h to obtain basic pitches. (2) The obtained basic pitches were continuously heated treater under vacuum of 5 hPa at different temperatures range of 250–350°C for varying durations heat to remove their volatile components and adjust their SP for obtaining spinnable pitches. (3) The obtained reasonable spinnable pitches were spun into pitch fibers at temperature of the SP+50°C by melt spinning method through a stainless steel die (diameter, 0.2 mm; length/diameter, 2) using a laboratory-scale spinning apparatus under a nitrogen pressure of 0.1 MPa with winder speed of about 800 m min<sup>-1</sup>. (4) The obtained pitch fibers were stabilized at 230°C with heating rate of 0.5°C/min in the 200 mL min<sup>-1</sup> air mood and carbonized at 800°C for 5 min in the 100 mL min<sup>-1</sup> nitrogen mood. The basic pitch was denoted

as BT/EO=X/Y T AD (PD) t, where X/Y is the weight ratio of BT and EO, T and t are the distillation temperature and distillation periods, respectively, and AD and PD represent atmospheric distillation and pressurized distillation, respectively.

### 2.3. Characterization of pitches and carbon fibers

The SP of pitches were determined by thermal mechanical analyzer (EXSTAR SII, TMA/SS6300, Japan). The physical properties and chemical composition of raw materials and pitches were measured by TG analyzer (EXSTAR SII, TG/DTA6300), TOF-MS analyzer (JMS-S3000; JEOL, Japan), elemental analyzer (MT-5 CHN Corder; Yanaco, Japan) and <sup>13</sup>C-NMR analyzer (JEOL ECA400). The diameter of obtained carbon fibers was measured by laser analyzer (M550A; Anritsu, Japan). And the tensile strength of obtained carbon fibers were measured according to the JIS7601 standards (single-fiber method with gauge length of 25 mm and 20 tests) with strength tester apparatus (Tensilon UTM-II-20; Orientec Corp., Japan). The morphology of obtained carbon fibers were observed by SEM (JEOL-6700F, 3 kV).

## 3. Results and Discussion

### 3.1. Analysis of raw materials

The BT and EO were characterized by elemental analysis, <sup>13</sup>C-NMR and TOF-MS in detail. The main characteristics of the raw materials are summarized in Table 1. The elemental analysis results show that the BT are much higher oxygen content of 22.53 wt% than coal tar, which will cause cross-linking reaction even at low temperature, forming non-meltable solid due to their high reactivity. On the other hand, the EO almost had not the oxygen, which can be expected to reduce the oxygen content of pitches and prepare the spinnable pitches by the co-carbonization of BT with EO. Fig. 1 shows <sup>13</sup>C-NMR spectra of BT and EO. The BT had high aliphatic carbon contents (peak at 10–50 ppm) and high oxygenated aromatic carbon contents (peak at 150–170 ppm), which agrees with its higher levels of oxygen contents. While the EO had high non-oxygenated aromatic carbon contents (peak at 110–145 ppm) and high naphthenic carbon atoms (peak at 30–50 ppm). Fig. 2 shows TOF-MS spectra of BT and EO. Both BT and EO had a broad molecular weight distribution of 100–400 *m/z*. Therefore, the calculated data from <sup>13</sup>C-NMR and TOF-MS results indicate that BT consisted of an aromaticity fraction (*f<sub>a</sub>*) of 0.52 and an average molecular

**Table 1.** Characteristics of the raw materials

Sample	Elemental analysis (wt%)				<i>f<sub>a</sub></i>	<i>M<sub>w</sub></i>
	C	H	N	O		
EO	92.44	7.47	0.02	0.07	0.88	186
BT	70.01	7.28	0.18	22.53	0.52	247

*f<sub>a</sub>*, carbon aromaticity degree was calculated from <sup>13</sup>C-NMR result; *M<sub>w</sub>*, average molecular weight was calculated from TOF-MS result.

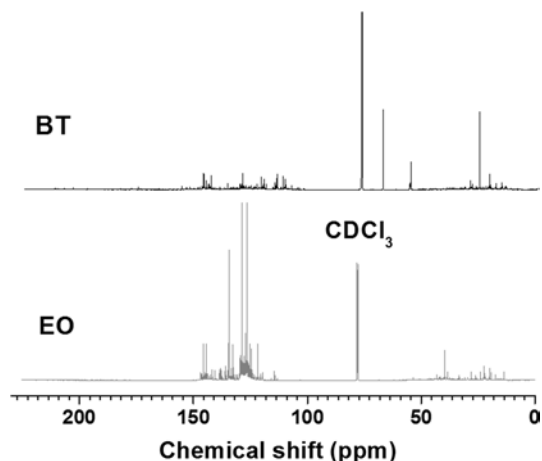


Fig. 1.  $^{13}\text{C}$ -NMR spectra of BT and EO.

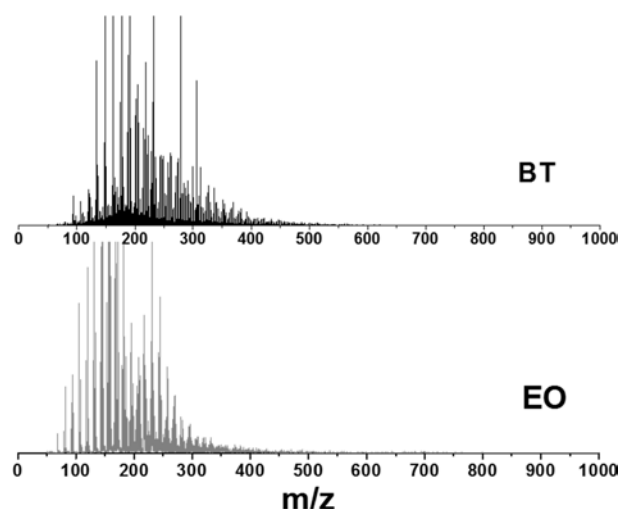


Fig. 2. Molecular weight distributions of BT and EO.

weight ( $M_w$ ) of 247  $m/z$ , while EO had an  $f_a$  of 0.88 and an average  $M_w$  of 186  $m/z$  (Table 1). All such differences influence the co-carbonization of BT and EO for their development into BT-derived spinnable pitches.

### 3.2. Preparation and characterization of pitches

Firstly, as to the thermal stability of prepared pitch, which was estimated by annealing treatment of basic pitch at 300°C from 1 to 10 h under 200 mL  $\text{min}^{-1}$  nitrogen flow. Fig. 3 shows the changes of SP of basic pitches prepared with different weight ratios of BT and EO as increasing annealing times. The SP of obtained basic pitch was rapidly increased as increasing annealing times up to 5 h, but the SP of basic pitches prepared by adding EO were changed slightly after 5 h, indicating the thermal stability of them was improved. So, we can see that the pitch prepared through the co-carbonization of BT with EO had better thermal stability property and their SP of about 180°C. Secondly,

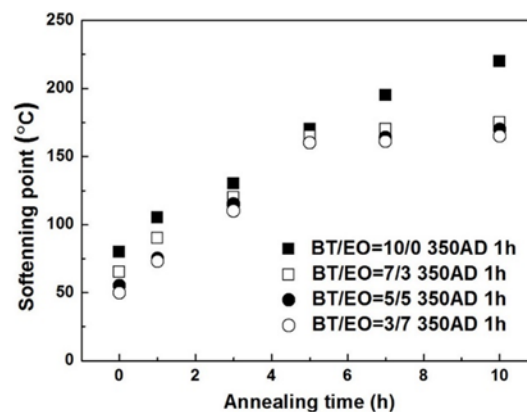


Fig. 3. Changes of SP of basic pitches with annealing times at 300°C under 200 mL/min nitrogen flow.

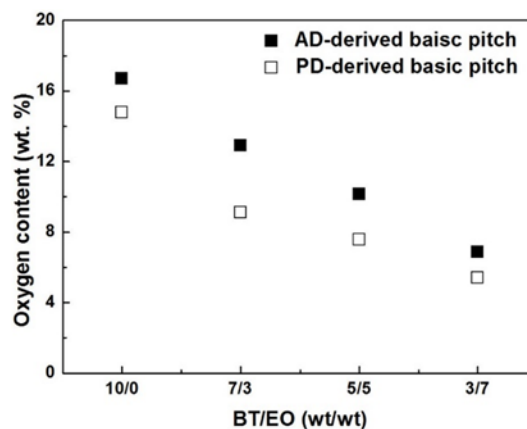


Fig. 4. Oxygen contents of basic pitches prepared at 350°C for 1 h under AD and PD method with different weight ratio of BT and EO.

compared to the differences between AD and PD methods, Fig. 4 shows the oxygen contents of basic pitches prepared at 350°C for 1 h under AD and PD methods with different weight ratios of BT and EO. We found that the oxygen content of basic pitch was decreased as increasing the added amount of EO, which indicated that EO can react with BT and be effective to remove the oxygen functional groups of BT. On the other hand, the PD method was more effective to reduce the oxygen contents of pitches than AD method. The reasons can be explained from these: during the PD process, the low weight matter of EO can repeatedly polymerized with BT to remove the side chain with oxygen functional groups of BT. In addition, the produced hydrogen rich small volatile species which did not get away from the reactor can make further efforts to react with BT as a hydrogenation in the closed system in accordance with higher yield of PD-derived basic pitch.

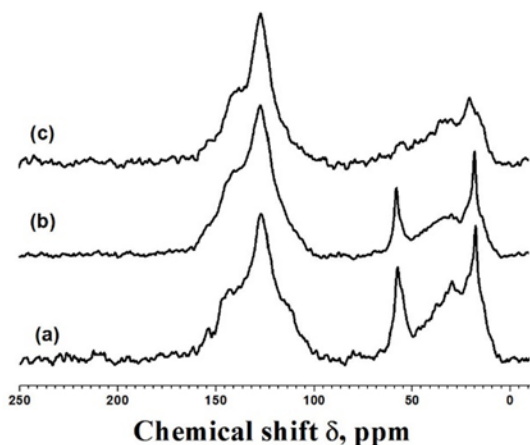
Next, suitable spinnable pitch must have a high SP and excellent spinnability at spinning temperature. High SP temperature allows the spun pitch fiber to be oxidation stabilized in a short time and increases tensile strength of the resulting carbon fiber [9,10]. In order to obtain spinnable pitches with the desirable

**Table 2.** Properties of the spinnable pitches

Spinnable pitch	Yield (%)	SP (°C)	O (wt%)	$f_a$
BT/EO=7/3 350AD 1h	37	180	11.27	0.55
BT/EO=7/3 350PD 1h	42	180	9.12	0.67
BT/EO=5/5 350PD 1h	45	182	6.13	0.70

properties, effective treatment of basic pitch are needed. Therefore, the basic pitches were vacuum heat treated by thin layer evaporation with variation temperatures and times to prepare the spinnable pitches. During the thin layer evaporation process, it can be said that the thin layer evaporation is effective to increase the SP of pitch due to the removal of relatively lower molecular weight component from the basic pitch, as well as to the polymerization and condensation reactions taking place between the various planar aromatic molecules present in the basic pitch. However, if basic pitch was heat treated by thin layer evaporation for a long time or at a relatively high temperature, a higher SP was achieved, but this is usually accompanied by the generation of spinnable pitch which leads to heterogeneous of the pitch and destroys its spinnability. Therefore, through many evaluations of experimental conditions, we noticed that the SP of BT-derived spinnable pitch should be adjusted at about 180°C. Table 2 shows some properties of three obtained spinnable pitches. It was noticed that the yield of PD-derived spinnable pitch was 42%, which higher than that of AD-derived spinnable pitch of 37%. While the oxygen content of PD-derived spinnable pitch was 9.12 wt%, which was lower than that of AD-derived spinnable pitch of 11.27%. As increasing the added amount of EO, the yield of pitch was increased and the oxygen content of pitch was further reduced (yield, 45%; oxygen content, 6.13% of BT/EO=5/5 350PD 1h-derived spinnable pitch).

The  $^{13}\text{C}$ -NMR spectra of the obtained spinnable pitches are presented in Fig. 5. The spectra was divided into five signal



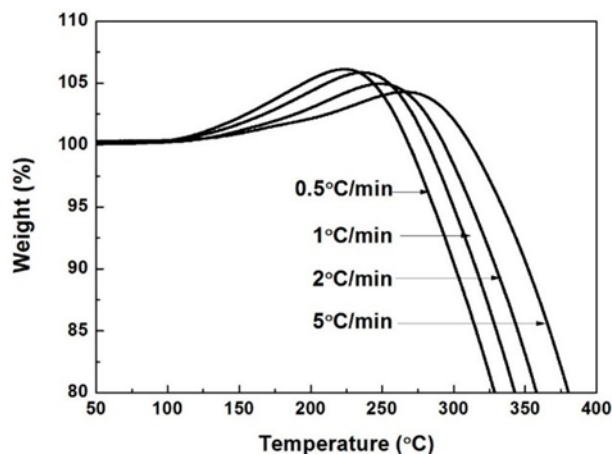
**Fig. 5.**  $^{13}\text{C}$ -NMR spectra of obtained spinnable pitches from (a) BT/EO=7/3 350AD 1h, (b) BT/EO=7/3 350PD 1h, (c) BT/EO=5/5 350PD 1h basic pitches.

groups based on our experimental data and reference of Prauchner et al. [11] summarized method, which was around 0–50, 50–90, 90–140, 140–170 and 170–190 ppm relative to alkyl, methoxyl, non-oxygenated aromatic carbon, oxygenated aromatic carbons, and carboxylic groups, respectively. It was noticed that the signal at 170–190 ppm (carboxylic groups) of BT-derived spinnable pitches was significantly disappeared through the co-carbonization of BT with EO, and the  $f_a$  of spinnable pitch was increased as increasing the added amount of EO (Table 2). Furthermore, the signal around 50–70 ppm (remnants of methoxyl carbon) was significantly disappeared as increasing the added amount of EO to 5/5. As well as comparing to the AD, the PD was more effective to remove the alkyl and methoxyl groups of BT, which was in accordance with previously investigation of their oxygen content.

### 3.3. Preparation and characterization of carbon fibers

As mentioned above spinnable pitches were successfully spun into pitch fibers by the melt spinning method at the spinning temperature of  $\text{SP}+50^\circ\text{C}$ . The results showed the prepared spinnable pitch with SP of about  $180^\circ\text{C}$  could be spun into pitch fibers without fiber breakage over 10 min spinning times, and its SP was not altered after spinning, which indicated that the spinnability and thermal stability of the obtained spinnable pitch were excellent and stable.

During the manufacture of pitch based carbon fibers, the reactions that occur during the stabilization process are oxidation, dehydration, condensation, crosslinking, and elimination [12]. The chemical and physical changes of stabilization of pitch fiber are complex and poorly defined because of the complexity of the pitch materials. However, Yoon et al. [13] have successfully developed a simple mean to monitor and optimize the stabilization process by thermal analyses at several heating rates. Therefore, the stabilization behavior of spun pitch fiber was studied by TG with different heating rates under  $50\text{ mL min}^{-1}$  air atmosphere as shown in Fig. 6. The results revealed that slower heating rate of  $0.5^\circ\text{C/min}$  allowed larger weight gain as high as 106.2% and



**Fig. 6.** TG curves of spun pitch fibers from BT/EO=7/3 350PD 1h-derived pitch with different heating rates in the 100 mL/min air flow.

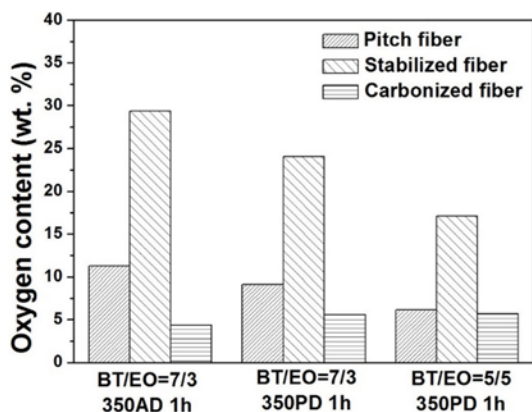


Fig. 7. Oxygen contents of prepared pitch fiber, stabilized fiber and carbonized fiber.

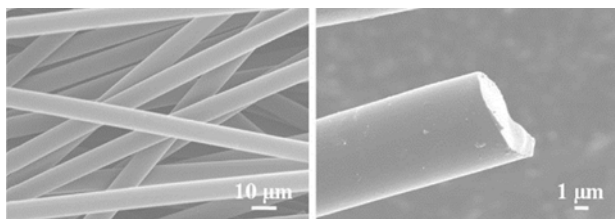


Fig. 8. SEM images of obtained carbon fibers from BT/EO=5/5 350PD 1h-derived pitch.

lower decomposed temperature of 225°C, which indicated that the BT-derived pitch fiber would accomplish its stabilization process at low temperature of below 250°C. Thus, in the present work, the obtained pitch fibers were determined to stabilize at 230°C for 1 h with heating rate of 0.5°C/min under the 200 mL min<sup>-1</sup> air flow in the heating furnace in order to sufficient oxidation of it. Then in order to reduce the production cost of carbon fiber, the stabilized fiber was carbonized at low temperature of 800°C for short holding time of 5 min under the 100 mL min<sup>-1</sup> nitrogen flow.

The yield of stabilized fiber was increased after successful stabilization, which was due to a mix of a small loss of volatile matter, the uptake of oxygen, and possibly some loss of carbon as CO<sub>2</sub> during stabilization process [14]. Fig. 7 showed the oxygen content of obtained pitch fiber, stabilized fiber and carbonized fiber. It was noticed that the oxygen uptake of stabilized fiber from BT-derived pitch was over 10 wt%, which was higher than those from coal tar based pitches (less than 3%) [15], because the BT-derived pitch contains many aliphatic groups. Furthermore, the oxygen content of BT/EO=7/3 350AD 1h resultant stabilized fiber was increased to about 30 wt%, which was higher than those from BT/EO=7/3 350PD 1h-derived pitch due to the lower aromaticity and higher oxygen content of pristine AD-derived pitch fiber. Then the oxygen content of carbon fiber was still about 5 wt% after 800°C carbonization.

The carbon fibers obtained from the BT-derived pitches were observed by scanning electron microscope (SEM). Fig. 8 gives an example of the obtained carbon fibers prepared from BT/EO=5/5 350PD 1h-derived pitch. From the images, it is dis-

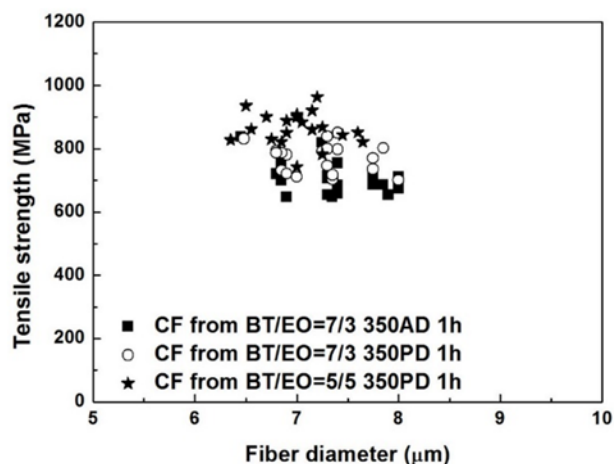


Fig. 9. Tensile strength of obtained carbon fibers.

played that the surface morphology of fibers is smooth and homogeneous carbon fibers (diameter of fibers were about 7 μm). Moreover, it is observed that the fibers exhibited no fusing, indicating that the stabilization process has been adequate and appropriate. The cross section of carbon fiber is random structure, which indicates that the prepared pitch is isotropic pitch.

Fig. 9 showed that the tensile strength of obtained carbon fiber was reached to 800 MPa with a diameter of 6–8 μm only by heat treatment at 800°C for 5 min. This value was high if compared to the other biomass tar pitch based carbon fiber which was reported by Prauchner et al. (130 MPa) [6] and Qiao et al. (632 MPa) [7]. The important reason is due to the BT-derived pitch prepared through the co-carbonization of BT and EO in our experiment had lower oxygen contents, which helps the biomass tar pitch to achieve high SP and excellent spinnability. Therefore, the diameter of resultant carbon fibers in our experiment was decreased to 6–8 μm, which was hugely thinner than that of carbon fibers prepared from others. On the other hand, it was noticed that the tensile strength of PD-derived pitch based carbon fiber was higher than that of AD-derived pitch based carbon fiber and the tensile strength of resultant carbon fiber was increased as increasing the added amount of EO due to the higher aromaticity and lower oxygen content of pristine spinnable pitch. Hence, in any case, the results showed that BT was a potential precursor of spinnable pitch by the co-carbonization with EO for carbon fiber production.

#### 4. Conclusions

The present work showed that the isotropic spinnable pitch and carbon fibers have been achieved through the co-carbonization of BT with EO, which revealed that BT had great potential as precursor for carbon fiber production, and EO was very effective to decrease of the oxygen contents of BT for obtaining a stable spinnable pitch. Furthermore, the PD was more effective to reduce the oxygen content of pitches than AD. The SP of prepared BT-derived spinnable pitch with good spinnability was increased up to 180°C through the co-carbonization with EO.

The tensile strength of resultant carbon fiber was increased up to 800 MPa with fiber diameter of 6-8  $\mu\text{m}$  only by heat treatment at 800°C for 5 min.

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### Conflict of Interest

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

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