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*Brief Report*

# Study of Quinoline Insoluble (QI) Removal for Needle Coke-Grade Coal Tar Pitch by Extraction with Fractionalized Aliphatic Solvents and Coke Formation Thereof

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**Abstract:** Various fractionalized solvents with different paraffinicities were adopted to maximize the efficiency of the quinoline insoluble (QI) extraction process for coal tar pitch. In addition, highly pressurized conditions combined with raised temperature (4 bar at 300 °C) were used to accelerate the reaction kinetics of the extraction process. The QI content of purified coal tar pitch was analyzed to be 0.1% at a process yield of up to 72% as a solvent with a *K*-factor of 10 and above was used. Purified coal tar pitch was then processed to form anisotropic coke using a lab-scale tube bombe reactor. The texture observed under a polarized light microscope showed an anisotropic flow domain, a unique morphological feature of needle coke. The additives and reaction conditions used in this study for QI extraction for coal tar pitch were found to be effective and feasible as preliminary processing in needle coke production.

**Keywords:** coal tar pitch; quinoline insolubles; needle coke; extraction; paraffinicity



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## 1. Introduction

Carbon/graphite materials exhibit excellent physical and chemical properties such as high electrical/thermal conductivity, mechanical strength, and thermal/chemical resistance due to their unique molecular and orbital structures. With these beneficial engineering properties, works on various applications have been reported [1–3]. Coal tar pitch has a high degree of aromaticity of constituent atoms and is able to develop layered graphene structures through intermolecular stacking upon heat treatment. Due to its unique molecular structure and composition, superior properties (e.g., high carbonization yield, high degree of graphitization) in the final carbonaceous/graphitic products thereof can be obtained. Like petroleum-based raw materials (i.e., residues, heavy oils from oil refineries), coal tar pitch is also regarded as an important resource for the production of needle coke and artificial graphite and is widely used in the carbon/graphite materials industry. It is generally known that quinoline insolubles (QI) and aromatic properties existing in raw coal tar pitch are critical components determining micro-texture development in the delayed coking process. [4–6]. QI can be defined as a variety of solid carbonaceous particles and highly aromatic hydrocarbons with a high molecular weight that are the by-products of the metallurgical coke production process. The solid carbonaceous particles in QI are generally ashes, cenospheres, char, and pyrolytic carbon [7]. The concentration of QI should be minimized to promote the coalescence of burgeoning mesophase spheres upon heat treatment of coal tar pitch, yielding the needle-shaped (uniaxially oriented) coke texture [8–12]. However, the QI removal (or extraction) process is known to be strenuous and complicated due to the complexity of the coal tar pitch composition and the requirement of delicate process controls [13].

In this work, aliphatic-rich solvents fractionally distilled at different boiling point ranges were used as additives in the extraction process to separate the QI component present in coal tar pitch. For an efficient extraction process, mixing between coal tar and the added solvent was conducted under pressurized and heated conditions. The aliphatic components in the extraction solvent are believed to facilitate the precipitation of QI in coal tar pitch by undermining the stabilized dissolution state of QI [14]. The paraffinicity of the aliphatic solvent can be estimated with a *K*-factor, as defined in the following formula [15]:

$$K = \frac{\sqrt[3]{1.8\,T_b}}{S.G.} \tag{1}$$

where $T_b$ is the molar average boiling point (Kelvin) and *S.G.* is the specific gravity.

As shown in Equation (1), paraffinicity is relevant to the boiling point and specific gravity of the solvent. The stronger paraffinic property of a solvent is expected to reduce its dissolution performance toward larger molecules with high aromaticity (i.e., QI components in coal tar pitch), yielding easier precipitation of QI. To alter solvent paraffinicity, fractional vacuum distillation with a multi-columned apparatus was conducted on a petroleum-derived aliphatic-rich solvent. Each recovered distillate fraction possessing a different *K*-factor (calculated from Equation (1)) was used as an additive in the consecutive QI extraction process. For efficient mixing between coal tar and the added solvent, a pressurized heating reactor was used, as shown in Figure 1. Through the extraction process, QI-rich fractions in coal tar are precipitated and concentrated at the bottom of the reactor; thus, QI-removed fractions can be separated easily. For the evaluation of rheological properties, dynamic viscosity measurement over coal tar pitch was performed at various shear rates and temperatures. The coke-forming behavior was evaluated with a lab-scale coking apparatus. Polarized microscopy was used to obtain micro-texture images from the produced coke specimens. Finally, the influence of the added solvent's *K*-factor in the subsequent extraction process on the coke-forming characteristics was investigated.

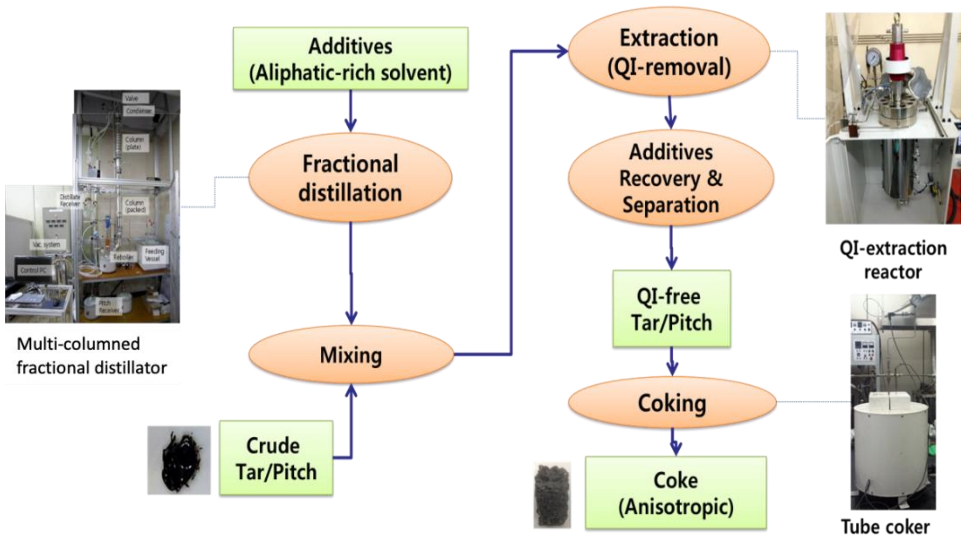



**Figure 1.** Experimental process flow.

## 2. Experimental

### *2.1. Materials*

Coal tar and a petroleum-derived aliphatic-rich solvent used in the present work were obtained from Dong-Suh Chemical Industry Co. Ltd. (Pohang, Korea). Coal tar was further treated with a continuous screw-decanting machine (Z2LL-V, Fine Inc., Busan, Korea) to remove intrinsic ashes. The QI content of decanted coal tar was analyzed to be 1.5% (by weight).

## 2.2. Sample Preparation

### 2.2.1. Preparation of Fractionalized Solvents

The aliphatic-rich solvent was distilled by a multi-columned continuous distillation apparatus (KF50, McCoy Corp., Korea). The reactor pressure was varied to separate distillate products based on the boiling point range. Two distillate products (distillate #1 and #2) and the remaining residue were collected after distillation. The production yield and properties thereof are presented in Table 1.

**Table 1.** Properties of fractionally distilled solvents.

| Property \ Product | Distillate #1 | Distillate #2 | Residue |
|---|---|---|---|
| Fraction (%) | 46.7 | 25.7 | 12.8 |
| Pressure (mbar) | 500 | 200 | - |
| Reboiler temp. (°C) | 160–200 | 176–199 | - |
| Gas temp. (°C) | 110–174 | 149–178 | - |
| AET * (°C) | 134.5–207.7 | 224.8–265.6 | >265.6 |
| S.G. (g/mL) | 0.759 | 0.790 | 0.802 |
| *K*-factor ** | 9.8–10.0 | 10.0–10.3 | >10.3 |

* AET: Atmospheric Equilibrium Temperature, Heat of evaporation ($\Delta H_{vap}$) ~37.4 kJ/mol (decane). ** *K*-factor: Representative calculated value to represnt paraffinicity of substances. $T_b$: Molar Average Boiling Point (Kelvin), *S.G.*: Specific Gravity. $\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$.

### 2.2.2. Preparation of Soft Pitch from Coal Tar

Decanted coal tar was distilled by a continuous thin-film evaporating reactor (KD6, UIC, Germany) to prepare soft pitch with a softening point of 30 to 60 °C. The reactor pressure varied from 20 to 200 mbar to change the softening point of the pitch product, while the temperature of the evaporating section was maintained at 250 °C.

Preparation of QI-removed soft pitch

Soft pitch with a softening point of 44 °C was mixed for 3 h with each fractionalized solvent in an extracting reactor (2G-AL stirred autoclave, Suflux, Korea). The temperature and pressure used in the extraction reaction were 300 °C and 4 bar, respectively. After extraction, the QI-removed product was retrieved by a decanting apparatus.

Preparation of coke specimen from soft pitch

To prepare a coke specimen, the QI-removed soft pitch was processed through pressurized heating for 5 h in a custom-made tube reactor. The temperature and pressure used in the coking reaction were 500 °C and 8 bar, respectively. For micro-texture observation, the prepared coke specimen was further carbonized at 1200 °C in an atmosphere-controlled furnace (CM-1200, CM Furnaces Inc., USA).

## 2.3. Characterization

Qualitative component analysis of the fractionalized aliphatic solvents was carried out using GC-MS. Tetrahydrofuran (THF) was used as an organic solvent; it was mixed with fractionalized aliphatic solvents at a mass ratio of 1:1 and injected into the GC column (Agilent Technologies 7890A). HP-1 (Material: Dimethlypolysiloxane) was used as a GC column, and irradiation was performed up to a range of 300 °C at a temperature increase rate of 10 °C/min. FTIR spectra were recorded using an infrared spectrometer (Bruker Vertex 70) between 4000 and 400 cm$^{-1}$. The QI content of coal tar pitch was determined by a standardized method (ASTM D2318). For rheological investigations of the QI-removed coal tar pitch, dynamic viscosity at various shear rates was measured by a programmable viscometer (Brookfield DV-II+). A reflected polarized light microscope (Leica, DM4500P) was used to analyze the optical textures and anisotropic characteristics of the prepared coke specimens. Each sample was mounted in an epoxy resin block and polished up to an optical quality using diamond paste. Observations were made using polarized illumination and an analyzer at 90° (cross-polar) with the insertion of a half-wave retarder.

## 3. Results and Discussions

The aliphatic-rich solvent was fractionalized by distillation to alter its paraffinicity. As distillation pressure drops, the *K*-factor (i.e., a theoretically calculated parameter representing paraffinicity) increases due to the rising atmospheric equilibrium temperature of evaporating substances (Table 1). The individual chemical component was identified by GC-MS, and major substances were analyzed as decane ($C_{10}H_{22}$) for distillate #1, dodecane ($C_{12}H_{26}$) for distillate #2, and tridecane ($C_{13}H_{28}$) for the residue, as shown in Figure 2a. The strong absorbance peak found at ca. 2925 $cm^{-1}$ is attributed to paraffinic characteristics (i.e., vibration of axial deformation of C-H of the $CH_2$ group) [16] and was found to increase in the order of distillate #1, distillate #2, and the residue. The paraffinicity was confirmed to be proportional to the boiling temperatures of aliphatic substances in the solvent, well corresponding to the calculated *K*-factors in this work (Table 1).

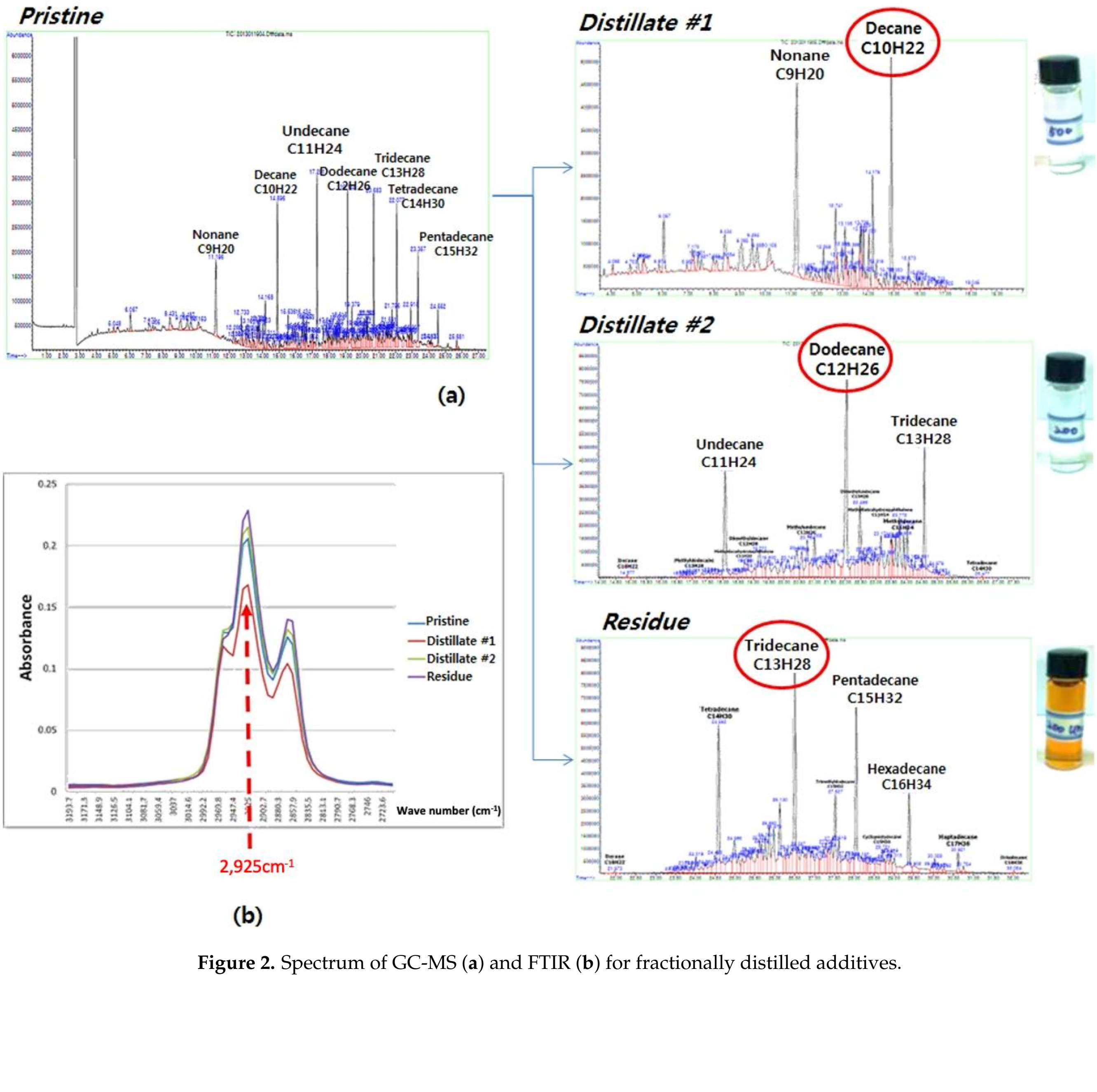



**Figure 2.** Spectrum of GC-MS (**a**) and FTIR (**b**) for fractionally distilled additives.

The high-temperature- and pressure-assisted extraction condition adopted in this work is believed to enhance the QI-extraction efficiency because it is governed by solubility and mass transfer effects dominantly. A high reaction temperature promotes faster diffusive transport between components of the system, while pressurized conditions are beneficial to maintain the liquid state of volatile substances, yielding enhanced solubility. When this process is combined with high-*K*-factor additives, a drastic reduction in the QI content of the treated coal tar pitch results, as shown in Table 2. The QI content of purified coal tar pitch was analyzed to be 0.1% at a process production yield of up to 72%. However, the extraction condition with a lower-*K*-factor additive (i.e., distillate #1) was not found to be effective to remove QI from the coal tar pitch. This result confirms that the paraffinic nature of the extracting solvent is strongly relevant to the QI removal performance for coal tar pitch, as discussed in a previous study [14].

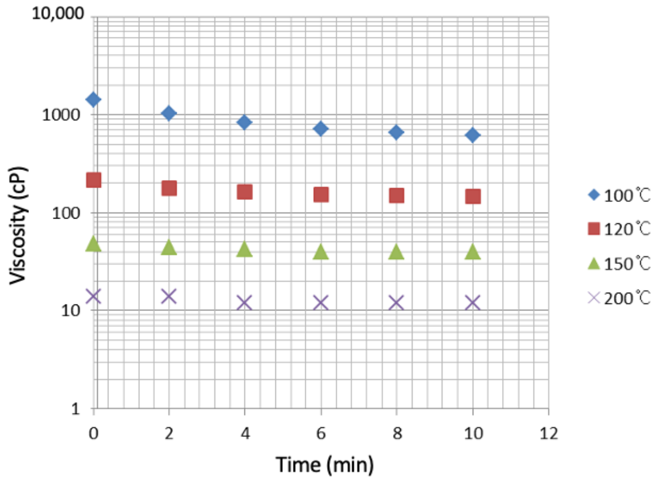
**Table 2.** Quinoline insoluble (QI) content of treated coal tar pitch by extraction combined with various additives.

| *K*-Factor of Additives | QI Content of Treated Coal Tar Pitch (wt%) | Extraction Process Yield (wt%) |
|---|---|---|
| 9.8–10 | 1.1 | N/A |
| 10–10.3 | 0.1 | 62 |
| 10.3 and above | 0.1 | 72 |

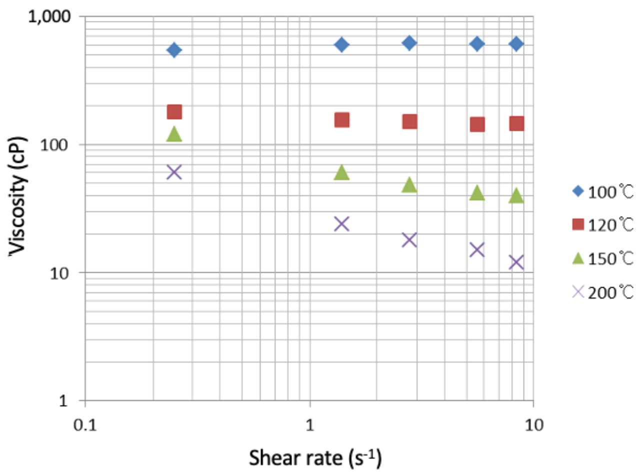
To evaluate the rheological behavior of QI-removed coal tar pitch, dynamic viscosities were measured at various temperatures, times, and shear rates. Figure 3 represents the non-Newtonian thixotropic (i.e., time-dependent) and shear-thinning characteristics of the QI-removed coal tar pitch. The shear-thinning phenomenon was found to be more prominent at higher temperatures (above 150 °C).

Figure 4 shows Arrehenius-type plots ln (μ) versus 1/T for QI-removed coal tar pitch and linear regression fits to experimental data. When fitted to an Arrhenius-type equation, the shear activation energy was calculated as 56.6 kJ/mol. As stated in previous work [17], the shear activation energy can be used as a crucial index for molecular susceptibility to environmental temperature variation, the degree of intermolecular entanglement, interaction, and steric hindrance. The shear activation energy of the commercial pitch product with a higher softening point (A240, Marathon Petroleum Corp., softening point of 115 °C) was reported to be 136 kJ/mol, indicating higher molecular stiffness or restricted inter-molecular motions [17].

The coke texture images attained by the polarized light microscope are shown in Figure 5. The microscopic texture found in all the prepared coke specimens can be categorized into the general anisotropic flow domain. However, coke derived from the QI-removed coal tar soft pitch with an additive solvent having a *K*-factor of 10 or above (Figure 5b,c) presented better texture orientation: needle-like uniaxial orientation as the *K*-factor fell between 10 and 10.3. This result is believed to be derived from the increased freedom of molecular motion in the QI-removed soft pitch during the coking process [18]. Further studies of the effect of different micro-texture development on various process parameters should be performed, but the influence of the QI-removing solvent's *K*-factor on the coke-forming behavior is thought to be subsistent in this experimental work.




(**a**)




(**b**)

**Figure 3.** Rheological behaviors of purified (QI-removed) coal tar pitch: viscosity vs. time (**a**) and viscosity vs. shear rate (**b**) at different temperatures (100 to 200 °C).

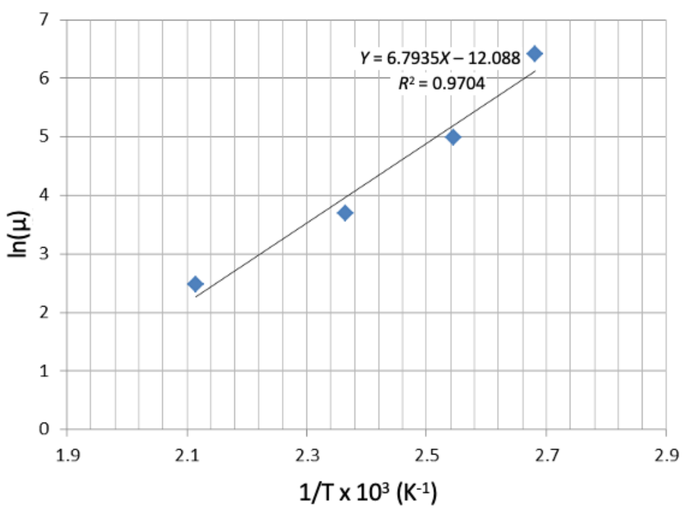



**Figure 4.** Arrhenius-type plots of ln (μ) versus 1/T and regression fit to calculate shear activation energy (at a shear rate of 8.4 $s^{-1}$) for the QI-removed coal tar pitch.

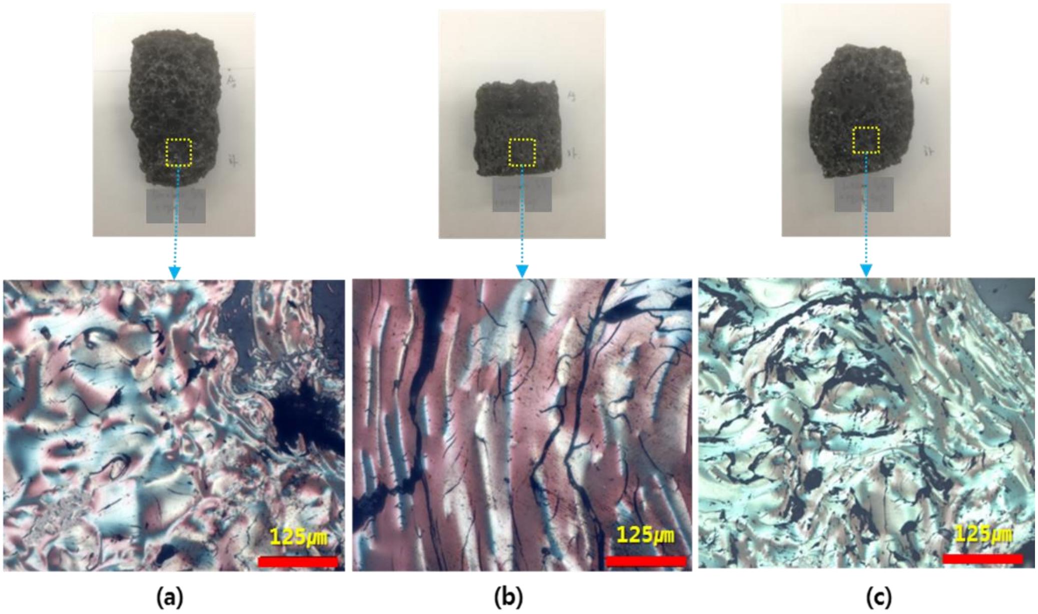



**Figure 5.** Morphological textures of coke specimens prepared with treated coal tar pitch. The *K*-factor of additives varied as 9.8–10 (**a**), 10–10.3 (**b**), and 10.3 and above (**c**).

## 4. Conclusions

The controlled paraffinicity of the additive solvent and the pressurized QI-extraction reaction condition presented in this study were found to be effective as raw material (i.e., coal tar pitch) treatment for needle coke production. Fractionalized distillation was confirmed as an effective method to manipulate the paraffinicity of an aliphatic-rich solvent, enhancing QI-removing performance. QI-removed coal tar pitch indicated non-Newtonian characteristics (i.e., thixotropic and shear thinning), and its shear activation energy was measured as 56.6 kJ/mol. The developed micro-texture in anisotropic coke was found to be strongly relevant to the paraffinicity of the solvent added in the QI-removing process.

**Author Contributions:** J.-C.A., S.-Y.L., and I.H. designed the paper and wrote the Introduction and Experimental sections. J.-I.P., and J.S. conducted formal analysis. M.H. conducted raw material preparation. J.-C.A., S.-Y.L., and I.H. wrote the Results and Discussion section and prepared figures and tables. Discussions and conclusions were the collective work of all authors. Writing—review and editing was performed by J.-C.A. All authors have read and agreed to the published version of the manuscript.

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