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Preparation of pitch-based general purpose carbon fibers from catalytic slurry oil

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ABSTRACT

Preparation of high-value pitch-based carbon fiber from catalytic slurry oil is of great importance, but is very difficult with traditional routes. In this work, a new route studied on the development of suitable pitch precursor from catalytic slurry oil was carried out using the techniques of thermal polymerization to increase the content of heavy components, centrifugal separation to remove the quinoline insolubles (QI), solvent extraction to remove light components and vacuum distillation to remove extractant. The effects of the above treatment processes on the QI particles size distribution, thermo-gravimetry, other properties of asphalt, micro-structure of pitch fibers and mechanical properties of carbon fibers were investigated. The result showed that thermal polymerization could significantly improve the contents of heavy components, accelerate the conversion of active components (alkenes, heterocycles, etc) into QI, and greatly increase QI particles size. The process of solvent extraction could effectively remove the light components and increase the softening points of asphalt. With increasing the time of thermal polymerization, QI particles became bigger and more easily removable, the micro-structures of pitch fibers were much smoother, and the mechanical properties of carbon fibers were more uniform.

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1. Introduction

As a high-performance carbon material, carbon fiber provides a number of excellent properties, such as high strength and good resistance to high temperature, corrosion and fatigue. It is widely used in the fields of aerospace, automobile, medical devices and athletic equipments [1,2]. As by-product of catalytic cracking, slurry oil is generally used as fuel oil or supplementary feed for delayed coking, which features low value and poor benefit. As the slurry oil is rich in aromatic components, it is an excellent raw material for preparing high-value products such as pitch-based carbon fiber [3]. Pitch-based carbon fiber can be produced from coal tar pitch, petroleum pitch, or other heavy oils by modification, spinning, pre-oxidation and carbonization. The main difficulties of producing pitch-based carbon fiber lie in the modification of spinnable pitch. Spinnable pitch is mainly obtained by means of air oxidation [4–6] and thermal treatment [7–9]. The air oxidation method features high carbon yield, low reaction temperature, and effective increase of the softening points of raw materials [10]. However, a large amount of exhaust gas will be generated during oxidation, which contains strong carcinogenic substances such as 3,4-benzopyrene and nitrogen oxides, resulting in high cost of exhaust treatment. As the carbon materials are increasingly used, their effects on the public health and the environment during their production and life cycle, including end-of-life are drawing more and more attentions [11]. Besides, the uneven distribution of oxygen and the generation of mesophase are very difficult to overcome. When thermal treatment is adopted to modify asphalt, high temperature treatment, nitrogen purging, or molecular distillation processes are required, which are inevitably accompanied by the generation of secondary quinoline insolubles (QI) or mesophase and has effects on spinning performance of asphalt [12,13]. Thus, the treatment temperature is restricted by the generation of QI. The softening point of spinnable pitch obtained by thermal treament is limited and diffcult to reach above 250 °C. Though the secondary QI generated can be separated by high temperature centrifugation or filtration [14], the operation is very difficult due to the high viscosity of treated pitch [15]. In general, the process of producing pitch-based carbon fiber is complex and the conditions are rigorous, so the difficulty and the high cost are problems remaining to be solved.

Pitch-based carbon fiber precursor typically consists of aromatic hydrocarbons with 7–8 cycles and with the ideal softening point at 250–280 °C. Catalytic slurry oil mainly consists of aromatic hydrocarbons with 2–4 cycles and short side chains [16]. On one hand, the small molecular weight and low softening point of catalytic slurry make it impossible to meet the basic requirements of spinnable pitch. On the other hand, QI (mostly catalytic powders) contained in catalytic slurry oil will directly have effects on the spinning performance of asphalt and properties of carbon fibers, so they have to be removed thoroughly in advance. However, it is very diffcult to separate QI since they are very fine. Thorough removal of catalytic powder has been a challenge in industry [16]. Besides, slurry oil tends to generate secondary QI during subsequent processing.

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Therefore, suppression of the generation of secondary QI is also one of the major difficulties during the modification of spinnable pitch [17]. Due to the above reasons, so far as we know, no detailed literature or patent reports have been published about the preparation of carbon fibers from catalytic slurry oil.

To solve the above problems, in this study, catalytic slurry oil firstly underwent thermal polymerization at high temperature. In this process, dehydro-condensation of large molecules occurred, resulting in the increase of the content of heavy components, and also, active components in the raw material were converted into QI preferably, avoiding conversion into secondary QI during the subsequent treatment. Besides, during thermal polymerization, the generated QI would collide, merge and grow, changing QI with small sizes into those with big sizes [18–20]. The QI would be more easily removed off in subsequent processes since their particle sizes increased dramatically. Moreover, to suppress the generation of secondary QI during thermal treatment, an extraction method under mild conditions would be adopted to remove light components and avoid exhaust pollution caused in the oxidation.

To this end, the effects of the thermal polymerization and extraction on their thermo-gravimetry and other basic properties, QI particle size distribution, fiber micro-structure, and carbon fiber mechanical performance were studied to provide technical supports for production of pitch-based carbon fiber from catalytic slurry oil.

2. Materials and experiment

2.1. Materials

The raw materials including catalytic slurry oil and kerosene (boiling point 180–220 °C) were suppilied by Sinopec Beijing Yanshan Branch Refinery. As summaried in Table 1, the toluene-insolubles (TI) content of catalytic slurry oil is very low, but can be increased by thermal polymerization. The washing oil was industrial grade coking solvent, which was suppilied by Tangshan Branch of Koppers (China) Carbon & Chemical Company Limited.

The polymerization process was carried out with a 0.5 L KCF-10 high-pressure reactor. A LDJ-5C centrifuge was used for QI separation. A Rise-2002 laser granularity statistical analyzer was used for QI granularity analysis. Melt spinning was adopted with single-hole pressure spinning machine developed by Beijing University of Chemical Technology. The fiber micro-structure was observed with a Quanta 400 F scanning electron microscope (SEM). The thermo gravimetric curves of asphalt were measured with a HTG-1 microcomputer differential thermal balance.

2.2. Experimental procedures

The flow diagram of experiment processes is shown in Fig. 1.

Firstly, the raw material was polymerized to increase the heavy components. Three-hundred fifty grams of the slurry oil was polymerized in the 500 ml high-pressure reactor at 410 °C, 0.5 MPa for 7 h or 12 h, producing polymerized asphalt A or F. After that, 300 g of asphalt A or F was distilled in 1000 ml flasks at 350 °C and 10 kPa until no light components came out, and about 200 g of asphalt was gained. The purpose of this step was to prevent the light components lower than 350 °C from mixing with the subsequent wash oil when it was recovered.

Table 1
Properties of catalytic slurry oil.

Saturates (wt.%)	Aromatics (wt.%)	Asphaltenes + resins (wt.%)	QI (%)	TI (%)	C/H[a]	Ash (%)	Iar[b]
42.85	51.43	5.72	0.12	6.1	0.83	0.04	0.47

[a] Atomic ratio of C to H.
[b] Aromaticity index, Iar = the absorbance at 3050 cm^{-1} / (the absorbance at 3050 cm^{-1} + the absorbance at 2920 cm^{-1}).

Then, centrifugal separation was adopted to remove the QI impurity. After 200 g of asphalt was mixed with 400 g of the washing oil at 180 °C, the asphalt-washing oil solution was separated by tube centrifuge at 4000 rpm for 5 min, and the lower residues which were insoluble impure matters (including QI impurities) were abandoned. Then, the upper asphalt-washing oil solution experienced vacuum distillation in a 1000 ml flask at 230 °C and 10 kPa for about 10 min to remove the solvent, and purified asphalts B and G were obtained.

Furthermore, extraction was employed to remove the light components. Two-hundred grams of kerosene was added into 100 g of asphalts B and G in a 500 ml tank, then mixed at 180 °C, and naturally settled for 1.0 h. Then the reactor was inclined to pour out the upper liquid, and the lower heavy phase asphalts C and H were obtained. After that, 60 g of washing oil was added to 100 g of asphalts C and H in flasks. After mixing at 180 °C for 2.0 h, the mixture was distillated at 350 °C and 250 Pa for 3 min to obtain spinnable pitches D and I. Both mixing and distillation were carried out in 500 ml flasks, and the flasks were placed in the salt bath to keep uniform temperature, and the temperatures were controlled by the salt bath. The purpose of this step was to completely remove the kerosene and wash oil.

Finally, spinning, pre-oxidation and carbonization were used to obtain carbon fibers. The spinnable pitches D and I were spun in the melt spinning machine, and after pre-oxidation and carbonization in the tubular furnace, the general-purpose carbon fibers E and J were obtained. The spinning temperatures for pitches D and I were 345 °C and 355 °C respectively, with the pressure of 0.016 MPa and speed of 450 m/min. The pre-oxidation temperatures for pitch fibers from D and I were 300 °C and 310 °C, respectively, with the heating rate of 1 °C/min. Both asphalt fibers were subjected to carbonization at temperatures of 1000 °C for 10 min under a nitrogen flow with heating rate of 4 °C/min. Since the softening point of pitch I was higher than that of pitch D, the spinning and pre-oxidation temperatures were higher accordingly.

2.3. Asphalt characterization and QI particle size distribution

The asphalt softening point was measured with cup-and-ball method according to ASTM D3461-1997. QI content was measured according to ASTM D2318-1998 (2008).

QI in polymerized asphalts A, F and catalytic slurry oil were separated and washed with toluene and alcohol [16], and then the QI particle size distribution was analyzed by laser granularity statistical analyzer.

3. Results and discussion

3.1. Effect of the thermal polymerization time on QI particle size distribution

As shown in Fig. 2, the minimum and peak values of QI particle sizes of the catalytic slurry oil appear approximately at 0.5 μm and 2.0 μm respectively. After thermal polymerization for 7 h, these values were changed to 1.3 μm and 3.4 μm, respectively. After thermal polymerization for 12 h, these values were further increased to 3.1 μm and 10.1 μm. This indicated that thermal polymerization could obviously enlarge the QI particle size.

3.2. Effects of the treatment processes on thermo-gravimetry of asphalt

As Fig. 3 shows, the weight loss of the raw material (catalytic slurry oil) was fast. The weight loss reached over 70% at 400 °C. After the slurry oil was polymerized for 7 h, the weight loss at 400 °C was about 45%. After polymerization for 12 h, the weight loss at 400 °C was only about 30%. This can be explained by the fact that during thermal treatment, the slurry oil experienced polycondensation reactions, accompanied with dehydro-condensation reaction, chain hydrocarbons and lateral groups were broken into small hydrocarbons and emitted, and the molecular weights of polymerization products increased. This

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