



Full Length Article

Study on effect of cross-linked structures induced by oxidative treatment of aromatic hydrocarbon oil on subsequent carbonized behaviors



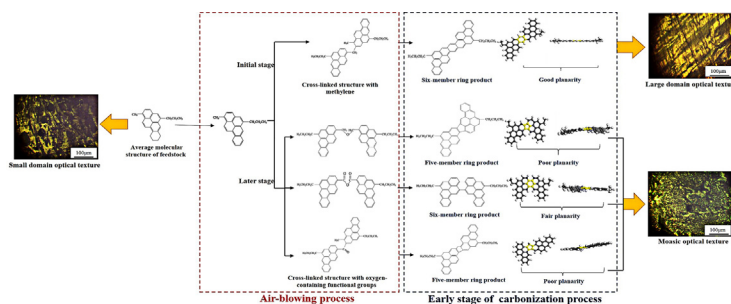
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GRAPHICAL ABSTRACT



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ABSTRACT

The variations in softening points, sub-fraction contents and carbon residue of air-blown pitches prepared from air blowing treatment of refined hydrocracking tail oil at the different conditions were monitored to select the suitable oxidative condition to prepare the feedstock of mesophase pitch. Furthermore, molecular structures of as-prepared pitches with different oxidative degree were investigated and the influence of cross-linked structural types on the carbonized performance of air-blown pitches was also discussed in terms of carbonized reactivity and planarity of fused-ring aromatic compounds formed at the initial stage of carbonization. During the early stage of oxidative treatment, the dealkylation, dehydro-aromatization of naphthenic ring and the following formation of methylene-bridged polycyclic aromatic compounds are mainly responsible for promoting the softening point of feedstock to 55 °C of PP23 pitch and 91 °C of PP38 pitch; those structural changes contribute to smoothly generating fused-ring aromatic compounds with good planarity configuration, which significantly improves the mesophase development during subsequent carbonization process: i) mesophase content of the carbonized parent pitch (MP-H) is 46% while for the carbonized oxidized pitches MP-PP23 and MP-PP38 it is 84% and 80% respectively; ii) lamellar orientation degree O_g increases from 0.957 (MP-H) to 0.970 (MP-PP23 or MP-PP38) and iii) stacking height L_c increase from 2.07 nm (MP-H) to 2.94 nm for MP-PP23 and 2.98 nm for MP-PP38. With the oxidative degree deepening, the competitive cross-linked reaction featured with the formation of the polycyclic aromatics bridged by oxygen-containing functional groups such as CdbndO and OsbndCsbndO becomes dominant, whose cross-linked structure not only accelerates the carbonized reactivity but also kinetically contributes to converting into five-member-ring bridged fused-ring aromatic compounds with poor molecular planarity, thereby leading to reducing mesophase content of MP-PP48 (prepared from PP48 pitch) and

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MP-PP52 (derived from PP52 pitch) to 75% and 54%, accompanying by increasing interlayer space d_{002} to 0.344 nm and 0.350 nm as well as decreasing the stacking height L_c to 2.56 nm and 1.53 nm, respectively.

1. Introduction

Owing to its excellent properties such as high thermal and electrical conductivities induced by high degree of orientation of its aromatic lamellae, carbonaceous mesophase has been extensively regarded as a precursor for a wide range of materials, such as carbons of high density and strength [1], carbon fiber [2], C/C composites [3], catalyst carriers [4] or high specific surface-active carbons for batteries [5], and so on. Nevertheless, the properties of carbonaceous mesophase delicately and strongly depend on the chemical structures of constituent molecules and, to a considerable level, on the nature of the feedstock used. Among the diverse raw materials, the coal tar pitch and petroleum pitch, which are featured with aromatic hydrocarbons with various functionalities and molecular configuration, are both excellent feedstock and widely studied. However, coal tar pitch possesses abundant aromatic molecules attached to very little aliphatic side chain while petroleum pitch contains polycyclic aromatic hydrocarbons with more aliphatic chains [6]. Besides, the existence of primary quinoline insolubles in coal tar pitch is another important difference. These differences in the molecular composition obviously affect their carbonized behavior, thereby determining the morphology evolution of mesophase that is an intermediate stage in the formation of the pregraphitic structure of graphitizable carbons [7,8].

In general, commercial pitch has the disadvantage of relatively low carbon yield and the formation of a significant porosity during the carbonization process [9] that adversely affects resultant carbon properties when it is used for the preparation of high performance materials, specially prepared for anode production. In order to increase carbon yield but maintaining other excellent properties of commercial pitch, several modified treatments including distillation [10], solvent extraction [11], air/oxygen oxidation [12], thermal condensation [13] and addition of iodine [14] have been explored. Air oxidation treatment is widely applied due to significant transformations of composition and structure [15,16]. Barr [17] and Fernández [18] propose that the principal mechanism during the air blowing treatment is the formation of both oxygen groups induced by oxidation of alkyl side chains and Ar-Ar structure (namely, biphenyl-type structure) generating by decomposition of naphthenic structures. Moreover, Metzinger et al. [19] conclude that during the controlled oxidative treatment the oxygen-containing functional groups (hydroxyl, carbonyl, carboxyl) firstly form and are decomposed into biphenyl-type bonds and CO_2 or CO during the subsequent carbonized treatment. However, Maeda and Zeng et al. [20,21] select three kind of feedstock including petroleum pitch, coal pitch and its hydrogenated derivate to study comparatively the oxidative reactivity and find that after elimination of alkyl side chains and aromatization of naphthenic structures, highly aromatic constituents in coal tar are prone to further condense into larger aromatic ring by the creation and decomposition of peroxide radicals while the aromatic molecules in petroleum pitch undergo the intermolecular linking by methylene instead of enlargement of aromatic rings to raise the softening point. Also, Yamaguchi et al. [22] choose aromatic hydrocarbons having 2–3 rings as pitch models and report that alkyl-substituted aromatic compounds can polymerize with methylene, biphenyl-type or ether bonding, changing partial methylene into carbonyl during the air-blowing process. Besides, Siddiquee et al. [23] consider that during low-temperature autoxidation of aromatic class, the disproportionation of hydrogen radical locating in the naphthenic structures produces olefins and the addition reactions between other free radicals and those olefins contribute to the observed increase in viscosity of oxidized bitumen. But this addition reaction pathway cannot explain the viscosity

growth of aromatic oil with little naphthenic structure, such as coal tar. To sum up, it is commonly believed that the air-blowing reaction proceeds via the radical reaction mechanism and three kinds of intermolecular cross-linking form are proposed: one is biphenyl form, always appearing in oxidative treatment for feedstock with high aromaticity such as coal tar; the second one is methylene or oxygen-containing functional groups as bridged bond that can be found in derived pitch from feed with relatively abundant aliphatic side chains like petroleum pitch; the third one is the formation of C–C bonds by addition reactions between olefins induced by hydrogen disproportionation and the free-radicals. Hence, we can conclude that the oxidative mechanism is strongly dependent on the feedstock properties and also on oxidative conditions. Few study focuses on further understanding of the relationship between the reactions taking place during oxidation and the subsequent mesophase development during carbonization, although this investigation would facilitate the preparation of excellent carbon precursor with high carbon residue and superior graphitizable ability.

Hydrocracking is one of the most important conversion processes used in petroleum refineries to manufacture gasoline, olefinic gases, and other products. Hydrocracking tail oil (HCTO) as the by-product of hydrocracking process is always subjected to furfural refining to remove the aromatics in order to further produce the lubricating oil. The furfural extract oil, i.e., refined hydrocracking tail oil (RHCTO) called in this study, is rich in aromatic hydrocarbon and contains slight heteroatoms (S, N and O), which can serve as precursor to prepare premium pitch. But as far, little investigation on effect of the cross-linked structure induced by oxidative treatment of hydrocracking tail oil on its mesophase development has been reported. In addition, preparation of mesophase pitch can achieve high value-added utilization of hydrocracking tail oil as by-products of hydrocracking process and greatly promote the economic efficiency of hydrocracking unit.

In this work, refined hydrocracking tail oil was subjected to air blowing modification, and the relationship between oxidation mechanisms induced at different stages of air blowing and subsequent carbonized properties of air-blown pitch was also investigated to illustrate structural peculiarities of oxidized pitches and then control their carbonization behavior.

2. Experimental

2.1. Materials

The refined hydrocracking tail oil as the parent pitch was obtained from Sinopec Qilu petrochemical company. Some properties of this feedstock are listed in Table 1. In this study, the used solvents including the petroleum ether (boiling range 60–90 °C), n-heptane, toluene, ethanol are AR graded and purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Oxidative treatment

About 300 g feedstock was subjected to four-neck flask connected with mechanical stirring device (seen in Fig. 1(a)). The air inlet and thermocouple are immersed into the reactants whereas the outlet is connected with a water condenser to obtain the liquid products. When the feedstock is heated to 30 °C, the stirring runs at a speed of 200 r/min and the air pump is also started up to provide the air flow whose rate is adjusted by rotor flow meter. When the temperature reach the preset one with the heating rate is 3–5 °C/min controlled by an electric

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