

RADICALS PRODUCED BY 2,3-DIMETHYL-2,3-DIPHENYLBUTANE FOR HOMOGENEOUSLY RAPID STABILIZATION OF COAL TAR PITCH

Guoli zhang^{1,2}, Taotao Guan^{1,2}, Jianlong Wang¹, and Kaixi Li^{1,2*}

¹ *Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, P. R. China*

² *Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, P. R. China*

*Presenting author's e-mail: likx@sxicc.ac.cn

Introduction

Oxidation stabilization is an essential important step for pitch-based carbon products in maintaining structure and increasing carbon yield. However, low reactivity of pitch molecules with oxygen in oxidation process makes its stabilization extremely difficult. Many efforts have been performed have been put to accelerate oxidation stabilization¹⁻³. Hence, an effective method for accelerating oxidation stabilization of coal tar pitch is particularly needed without sacrificing the operational environment and product performance. If the monomer contained the thermolabile covalent bonds are mixed into CTP prior to oxidation stabilization, considerable additional radicals may generated by the cleavage of the bonds in CTP matrix interior. The radicals generated could facilitate the cross-linking reaction between pitch molecules, achieving oxidation stabilization of pitch rapidly and homogeneously, and no longer solely depending on oxygen diffusion and self-reactivity of the polycyclic aromatic molecules of pitch. In present work, 2,3-dimethyl-2,3-diphenylbutane (bicumene, DMDPB) was first used to promote CTP oxidation stabilization through an environmentally friendly and mild modification process. The specific mechanisms (radical generation, transfer, and cross-linking between modified pitch molecules) also investigated in detail. The concentration of free radicals could be easily controlled by adjusting the weight ratio of pitch and DMDPB, and the oxidation time is shortened to one-third under the optimum DMDPB dosage is 8% of the raw material mass.

Materials and Methods

The coal tar pitch (100 g) without DMDPB heat treated at 170°C for 1 h under stirring. The product was tagged as Raw pitch. The CTP (100 g) was blended with varied amount of DMDPB (2~10 g) and then heated at 170°C for 1 h under stirring. The modified CTPs were labelled to as M-x, where x represented for the amount of DMDPB. 2 g sample was laid on a disk equipped with a nickel mesh. The disk was then placed in a vertical furnace and heated at a rate of 1°C min⁻¹ under a continuous dry air flow up to 200-300°C and held for 1 h. The oxidized Raw pitch and M-x were named R-O-Y and M-xO-Y, respectively, and Y represented the oxidation temperature.

Results and Discussion

Figure 1 illustrates the air oxidation mechanism of coal tar pitch accelerated by the cumyl cracked from DMDBP. A cumyl peroxy radical captures a hydrogen atom on a PAHs molecule of pitch to produce a PAHs molecule radical. Then, the captures of carbon-based radicals in PAHs molecules by O₂ in air facilitate an automatically accelerated reaction sequence from a

PAHs free radical into some oxygen-centred radicals. The combination of PAHs alkyl radicals with oxygen is expected to continue the auto-initiation process beyond the point of cumyl radical involvement⁴. The disproportionation of secondary oxygen-centred PAHs molecules radicals produces the ketone and ether byproduct. Then the cumyl hydroperoxide derived from hydrogen abstraction from PAHs molecules could decompose to produce cumyl oxygen free radicals, which establish an equilibrium with the ketone product and methyl radical or ethers and alcohols. Methyl radicals attack adjacent pitch PAHs molecules and are expected to enlarge the aromatic nucleus or increase the side chain length of PAHs molecules. This will repeat the above reaction mechanism to produce a larger ketone, ether product. These generated oxygen-containing functional groups may decompose during high-temperature carbonization, promote the further

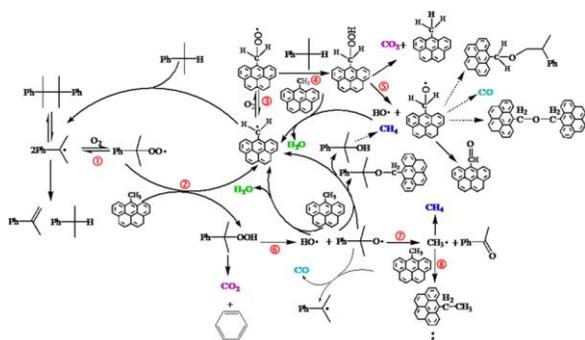


Figure 1. The promoting oxidation mechanism of coal tar pitch with DMDPB

cross-linking reaction of pitch molecules, and improve carbonization yield. At the same oxidation condition, the oxygen content of M-8 is significantly increased compared with the Raw pitch, which is five times that of the raw material, and the carbonization yield thereof is also increased from 75% of the Raw pitch to 85% of M-8. The carbonization yields of M-8 after stabilization under a nitrogen atmosphere and an air atmosphere are 74% and 85%, respectively, and the corresponding Raw pitch are 69% and 75%, respectively.

Conclusions

Based on the free radical mechanism of pitch stabilization, the pitch is quickly and homogeneously stabilized by increasing the free radical concentration of the pitch matrix. The free radical concentration of DMDBP modified CTP reach almost 1.5 times than that of the raw CTP at the same treatment temperature under nitrogen atmosphere. After stabilization, the oxygen content of the pitch modified by DMDBP and the yield of the corresponding carbon product are significantly increased, and its morphology is well maintained. The effective approach for rapid and homogeneous stabilization of CTP offers the possibility of producing pitch-based carbon products at low cost.

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