

CHARACTERIZATION OF HIGH SOFTENING POINT PITCHES BY CATALYTIC OXIDATION WITH RuO₄

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Introduction

Many studies have been devoted to elucidate the structures of the individual components of pitches. However, it is not an easy task due to the complexity of the mixtures and the large molecular weight of many compounds. This becomes even more difficult when pitches are treated in order to improve their properties as carbon precursors. Depending on the treatment, the polymerization of pitch components yields different molecular structures. It is generally accepted that pitch thermal treatment results in the development of planar structures, while pitch air-blowing generates cross-linked ones. However, conventional analytical techniques do not show a clearly defined picture of the molecular arrangement in each case.

Oxidation catalyzed by RuO₄ has been widely used to study the molecular structure of different carbonaceous materials, such as coal, asphaltenes and kerogenes [1]. In this reaction, aromatic carbons are selectively oxidized to carbon dioxide, generating benzene polycarboxylic acids when polynuclear aromatic rings are present [2]. In this work, catalytic oxidation with RuO₄ is used to study the differences in the molecular structure of an air-blown pitch and a thermally treated pitch, both obtained from the same parent pitch and with similar properties (softening point, carbon yield and solubility in toluene and N-methyl-2-pyrrolidone).

Experimental

A commercial impregnating coal-tar pitch was thermally treated at 430°C for 4 h to obtain pitch C3 [3] and the same parent pitch was air-blown at 275°C for 18 h to obtain pitch AB18 [4].

100 mg of pitch was mixed with 2.15 g of potassium metaperiodate and 0.025 g of RuCl₃ in a solution of 4 mL of CCl₄, 6 mL water and 4 mL acetonitrile. The reaction was carried out in an ultrasonic bath at 40°C. The reaction was monitored by analyzing the organic and the aqueous phases at different reaction times. The organic phase was analyzed by GC whereas the aqueous phase was analyzed by HPLC. Finally, the aqueous phase was extracted with CH₂Cl₂/ether and mixed with the organic phase. The acids present were esterified with chlorotrimethylsilane and methanol and then analyzed by GC-MS.

The oxidation rate was determined by measuring CO₂ formation. During the reaction, the resultant CO₂ was purged through NaSO₄/CaCl₂ and ascarite containing tubes. The CO₂ formed was determined from the weight increase of the ascarite. The results are given as a percentage of carbon oxidized during the reaction, considering the carbon content of the pitches determined by elemental analysis [3, 4].

In addition, the reactions were also carried out using pure aromatic compounds and their reaction products were then characterized by the above described techniques. The results obtained were compared to those obtained from the pitches.

Results and discussion

The GC analyses of the organic phases showed that the concentration of the main PAHs initially present in each pitch decreased with increasing reaction time. A higher reaction rate was observed for the more condensed aromatic compounds. No new compounds were detected.

The analysis of the aqueous phase by HPLC only showed three compounds, these being the same for the thermally treated pitch and the air-blown pitch. The compounds were identified as 1,2-dibenzocarboxylic acid, 1,2,3,4-tetrabenzocarboxylic acid and *o,o'*-diphenic acid. Their relative concentration was different depending on the pitch. In the case of pitch C3, the concentration of 1,2,3,4-tetrabenzocarboxylic acid, originated by the oxidation of highly aromatic condensed molecules, was significantly higher than the concentration of *o,o'*-diphenic acid, which was the oxidation product of less aromatic condensed structures. On the other hand, the relative concentration of both acids was similar for pitch AB18, the *o,o'*-diphenic acid being slightly higher.

GC-MS results showed that the samples obtained from the reaction of both pitches contained the methylic ester corresponding to the 1,2-dibenzocarboxylic acid, while the methylic ester corresponding to the *o,o'*-diphenic acid was only present in the sample obtained from pitch AB18.

The extent of the oxidative reaction was also different for the two types of pitches. In the thermally treated pitch (C3) 85 wt. % of carbon was oxidized to CO₂ after 36 h of reaction. Meanwhile, in the air-blown pitch (AB18) only 65 wt. % of carbon was converted into CO₂ after 48 h. Similar behavior was also observed for pure aromatic compounds, confirming the differences in the molecular structure of the components of each type of pitch.

Conclusions

The thermally treated pitches showed a higher rate and extent of reaction than the air-blown pitch. This is a consequence of the greater condensation degree of the molecules present in the thermally treated pitch.

References

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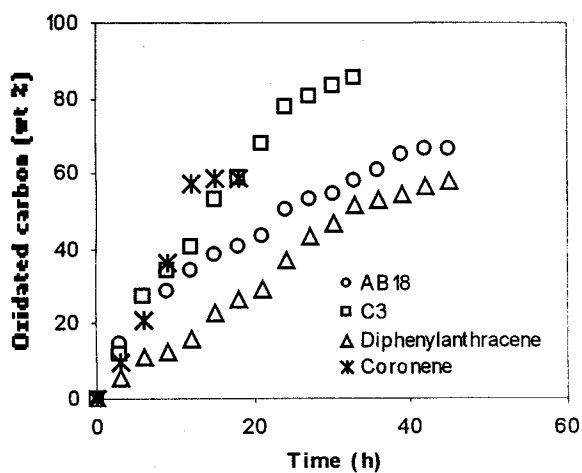


Figure 1.- CO₂ evolution throughout the reaction.