

KINETICS OF MESOPHASE FORMATION FROM PETROLEUM AND COAL-DERIVED PITCHES

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INTRODUCTION

Pitch materials, when heat treated in an inert atmosphere, produce discotic, nematic liquid crystals called mesophase. The formation of mesophase has been studied extensively due to its varied application in the manufacture of value-added carbon products. The kinetics of mesophase formation from petroleum pitch (A240) has been studied by a number of researchers (1,2,3). Herein, the kinetics of mesophase formation from petroleum pitch (A240) and coal-derived pitch has been studied and compared. The coal-derived pitch (HEXT450) was produced by hydrogenating high-volatile bituminous coal (WV13423) and extracting it with N-methyl pyrrolidone (NMP). The manufacturing technique to produce the hydrogenated coal extract is given elsewhere (4). The mesophase pitches of varying mesophase contents were produced at different time and temperature of the heat treatment. The resultant mesophase pitches were characterized and compared. Finally, a kinetic model for the kinetics of mesophase formation is developed and discussed.

EXPERIMENTAL

The kinetics of mesophase formation was carried out by heat treating the pitches in a special test tube using a cylindrical ceramic radiant heater. A typical run consisted of weighing approximately 20 gm of A240 pitch (20 mesh) into the test tube and placing it in the ceramic heater. The stirrer and thermocouple probe were dipped into the test tube. The heater-test tube assembly was covered with a purge cell and a gas (Argon) purge was started. The gas flow was set at 50 ml/min and was allowed to purge the cell for approximately 15 mins. The temperature indicator controller was switched on to commence heating. The reaction temperature was reached in 3-4 minutes. The stirrer was engaged with the motor shaft after the softening temperature of the pitch was reached. The heat

treatment was continued for the desired time duration at the end of which the heater power was switched off. The stirrer motor was turned off and the stirrer disengaged. The test tube was removed from the heater and submerged into a water bath to arrest the reaction by quenching the reaction mixture. The resultant heat-treated pitch was separated from the shattered glass of the test tube and allowed to dry. The dried mesophase pitch was ground to 20 mesh and stored for characterization. Similarly, other heat-treated pitches of varying mesophase contents were obtained by varying the time and temperature of the heat treatment. This procedure was repeated with HEXT450 pitch at the same time and temperature. Mesophase contents of the heat treated pitches were determined using optical microscopy (5) and computer-assisted area calculation (6).

RESULTS AND DISCUSSION

Figures 1 and 2 show the time and temperature dependence of mesophase formation from the petroleum (A240) and coal-derived precursors, respectively. As expected, the mesophase content of the pitch increased with time and temperature. It was observed that the mesophase formation from coal-derived pitch was rapid as compared with that from petroleum pitch. This may be due to the high aromatic content of the coal-derived pitch. The kinetics of mesophase formation was modeled using an empirical equation for the n th order reaction. This type of rate equation is generally used when the reaction mechanism is not known (7). The value for n is obtained by a trial-and-error procedure. The value of n which minimizes the variation in k is taken as the desired value of n . The empirical equation is,

$$[I]^{1-n} - [I]_0^{1-n} = (n-1)kt$$

where $[I]$ is isotropic volume fraction, n is the order of reaction, k is the reaction rate constant and t is time. Using a computer program the

trial-and-error procedure was performed on the data from the kinetic runs for A240 and HEXT450 pitches. The order of reaction for A240 and HEXT450 was found to be more than unity. In fact, the order of reaction for A240 is 2.7 and for HEXT450 is 2.9. Figures 1 and 2 show the model fit to the experimental data points. The model fit is found to be good. The activation energy for pitch pyrolysis using this model was found to be 336 kJ/mol and 288 kJ/mol for A240 and HEXT450, respectively. The values of the activation energy indicate that the coal-derived precursor pitch is more reactive than the petroleum pitch. This is consistent with that observed by Azami et al. (8) using high temperature ^{13}C -NMR. In that study (8), the time required from mesophase appearance till complete mesophase transformation were determined for petroleum, coal-tar and hydrogenated-petroleum pitch samples. The study concludes that the mesophase transformation in petroleum pitches is slower due to the aliphatic carbon in mesophase which causes looseness of molecular planarity and increases the mesophase mobility. This behavior results in the narrowing of the characteristic peak for mesophase. In another study, it was shown (3) that the reacting molecules from petroleum pitch were in the 400-700 MW range and that these molecules undergo polymerization reaction to form dimers. Therefore, it is thought to be difficult to ascertain reaction order and mechanism for the reacting molecules. The model proposed here is purely empirical. It differs from the other models in the literature (1,2,9), since they were based on a particular type of reaction mechanism believed to be responsible for mesophase formation. The changing reaction order for different pitch precursors suggests that the reaction mechanism depends on the type and concentration of molecular species available in the pitch precursor materials.

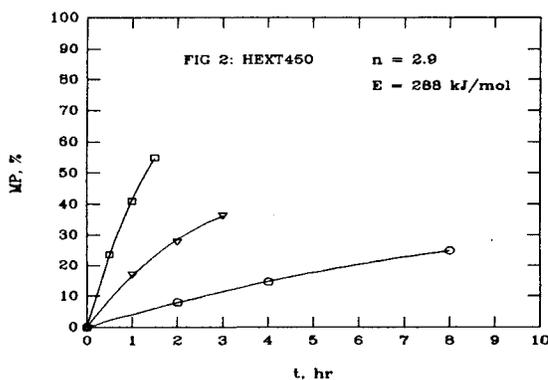
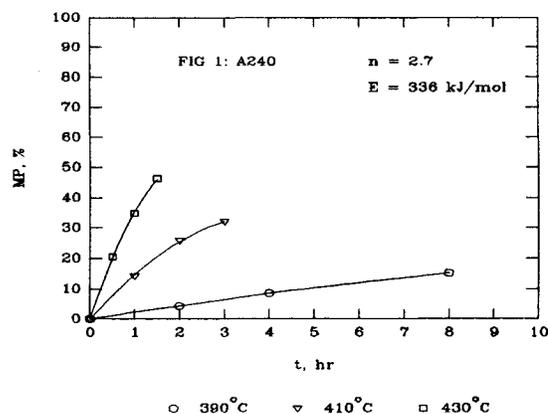
CONCLUSIONS

The kinetics of mesophase formation from petroleum pitch (A240) and coal-derived pitch (HEXT450) were studied. The coal-derived pitch was found to be more reactive than the petroleum pitch with a lower value of activation energy. An empirical kinetic model describes the mesophase formation from the pitches and the

reaction order is more than unity. The different reaction orders may be due to different molecular types in the pitch precursors.

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