Pitch Carbonization

by

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Introduction

A number of physical and chemical transformations occur during the carbonization of pitch between 300°C and 500°C, including: weight loss, evolution of gaseous reaction products, molecular weight increase and change in physical properties. Measurements of these parameters as a function of time and temperature can be used to derive kinetic information pertaining to the transformation of pitch to coke.

Such kinetic studies based on weight loss during pitch carbonization have been reported by a number of investigators.[1-3] Although the evolution of light gases is purely a chemical process, the release of total volatiles and, therefore, the weight loss, during pitch carbonization, is related to both chemical and physical effects.[4] In this study we have determined the kinetics of gas evolution from pitch when carbonized in a formed electrode. The results are used to clarify the carbonization process.

Experimental

The apparatus shown in Figure 1 was used to measure the evolution of volatiles during pitch carbonization. The apparatus allows separation of the volatiles into condensible and noncondensible gases. The experiments were performed on 2 1/2-inch diameter electrodes which contained 40 pph coal tar pitch (m.p. 120°C) as the binder. The electrodes were placed and packed in a cylindrical metal container which was sealed to prevent entrance of air. Thermocouples were placed at both the surface and the center of the electrode. The maximum temperature gradient observed across the sample was 8°C. Therefore, an average temperature was used as the sample temperature. Heat treatments were performed using both isothermal and nonisothermal conditions.

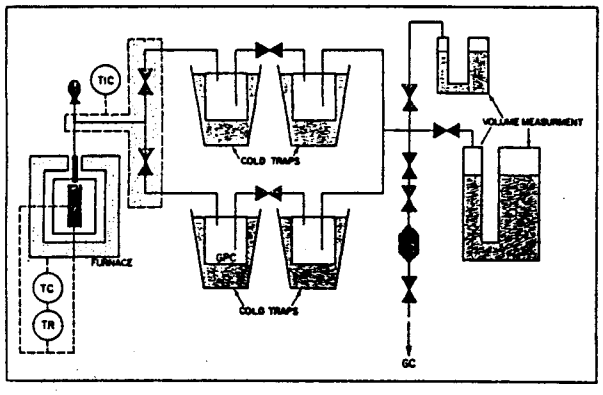

Figure 1. Baking Study Apparatus.

Results

Weight Loss

About 40% by weight of the pitch is lost as volatiles during carbonization to 750°C. Most of the weight loss involves distillation of low molecular weight pitch components. The rate of weight loss during nonisothermal heat treatment to 750°C is illustrated in Figure 2. Approximately 80% of the total weight loss occurs at temperatures between 350-500°C.

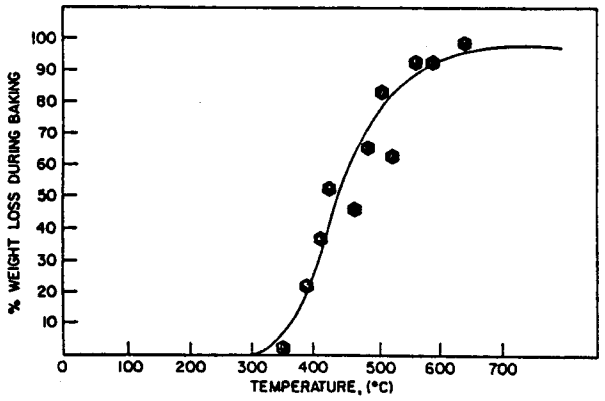

Figure 2. Cumulative Weight Loss During Baking Versus Temperature.

Isothermal Gas Evolution Studies

Measurements of gas evolution were performed at 449°C, 433°C and 410°C. The volume (moles) of noncondensible gases was measured as a function of time and the results are shown graphically in Figure 3. From this plot, it is evident that pitch carbonization follows a first order reaction. The rate constant K at the three temperatures can be determined from the slope of the lines in Figure 3, as:

$$k_{449°C} = 1.44 \times 10^{-4} \text{ sec}^{-1}$$
$$k_{433°C} = 0.63 \times 10^{-4} \text{ sec}^{-1}$$
$$k_{410°C} = 5.4 \times 10^{-6} \text{ sec}^{-1}$$

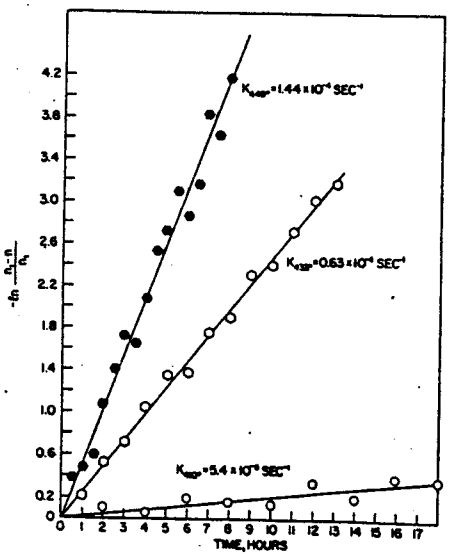

Figure 3. Moles of Gases Generated During Isothermal Heat Treatment Versus Temperature.

Using the Arrhenius relationship, the activation energy E was determined as 52.3 kcal/mole. This activation energy is essentially identical to that reported in the literature for pitch polymerization.[5]

Nonisothermal Gas Evolution Studies

Gas evolution data were obtained as the electrode was heated from room temperature to 850°C at a rate of 120°C/hour. As shown in Figure 4, the nonisothermal gas evolution exhibited two peaks with the first occurring at about 460°C and the second at about 730°C with a minimum at about 580°C. These data can be used to calculate the pressure distribution within a carbon artifact.[6]

Noncondensible Gas Analysis Results

Samples of the noncondensible gases were collected at different temperatures and analyzed by gas chromatography. The composition of the gas stream as a function of temperature is shown in Figure 5. The main gases produced are H_2 and CH_4 with a volumetric ratio of 4:1. The ratio of H_2/CH_4 is fairly constant from 500-800°C and then increases above 800°C.

Discussion of Results

The evolution of noncondensible gases up to 450°C follows first order kinetics with an activation energy of 52 Kcal/mole. The evolution of these gases can likely be associated with the pitch polymerization reactions which exhibit similar kinetics. Above 500°C, the gas evolution rate decreases. This change in rate (Figure 4) may be related to the solidification process in transformation of pitch to coke. At this

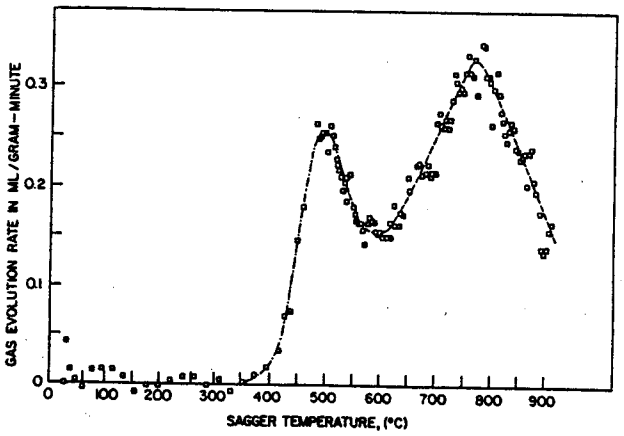

Figure 4. Rate of Gas Evolution Versus Temperature.

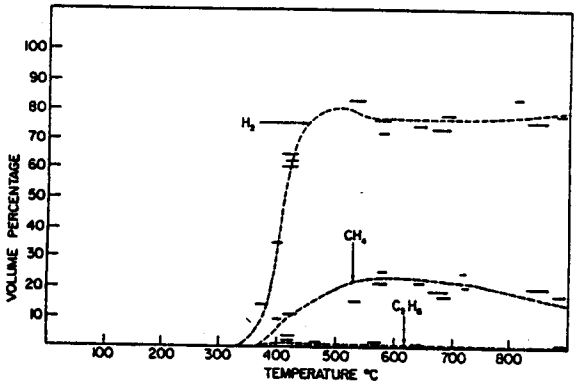

Figure 5. Composition of Gases Generated During Baking Versus Temperature.

temperature, chemical changes are occurring in the solid rather than in the liquid state. Similar results have been obtained by Greinke[7] from molecular weight measurements. Some of our preliminary studies indicate that a different reaction mechanism is associated with the second gas evolution peak that occurs at 730°C.

References

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