Diffusion in Porous Carbon Artifacts

by

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Introduction

Several of the steps in the manufacture of graphite and carbon articles involve simultaneous heat transfer, chemical reaction with gaseous by-products, and diffusion of gases through the pores. The problem of the flow of gases through porous media has been studied extensively.[1-3] However, for carbon processes, the addition of simultaneous heat transfer and chemical reaction imposes special complications in the modeling of the gas flow. Since the reaction rate is temperature-dependent, a temperature gradient within the porous carbon artifact will cause spatial dependence of the rate of gas production. Although carbon articles exhibit some permeability, the allowable free gas flow through the existing pores is finite. The bigger the difference between the rate of gas generation and the allowable gas flow rate at any point in the article, the higher the pressure developed at that point. In this paper, the problem of pressure distribution in a carbon article as functions of space and time is addressed by applying the principles of mass, energy, and momentum conservations.

Model Formulation

Gas evolution curves as a function of temperature during pitch carbonization have been obtained and reported elsewhere.[4] The main volume of gases are evolved above 550°C, after the pitch has transformed to coke. The gases evolved during this stage (550-850°C) have been identified[4] as mainly H_2 and CH_4 with a volumetric ratio of H_2/CH_4 equal to 4:1. In this temperature region, carbon articles are infusible solids with some developed permeability. If the gas generation rate is higher than the allowable flow rate through this permeability, some pressure will be developed within the carbon article. A model for calculating this pressure is developed in this paper.

Conservation of Mass

The continuity equation for the flow of gases through a porous medium is:[3]

$$\frac{\partial(\varepsilon\rho)}{\partial t} = -\nabla \cdot \rho\vec{v}_o + S \qquad (1)$$

where: ε is the porosity of the carbon artifact;
v_o is the volume flow rate through a unit cross-sectional area; and
S is the rate of gas generation.

Conservation of Momentum

The general equation of motion (Navier-Stokes equation[3]) is very complicated and unsurmountable difficulties would be encountered if we tried to incorporate it in the model. Instead, an empirical correlation, known as Darcy's Law,[1] will be used:

$$\vec{v}_o = \frac{\kappa}{\mu}(\nabla P - \rho\vec{g}) \qquad (2)$$

where: κ is the permeability of the carbon artifact; and
μ is the viscosity of the gas generated.

Conservation of Energy

The heat transfer equation is:[3]

$$\frac{\partial T}{\partial t} = \nabla \cdot \alpha\nabla T \qquad (3)$$

where: α is the thermal diffusivity of the carbon artifact.

Equation of State

The ideal gas equation of state has been used. At high temperatures (> 550°C), this equation should hold with a good approximation:

$$p = \frac{PW}{RT} \qquad (4)$$

where: W is the average molecular weight of the outgoing gases; and
R is the ideal gas constant.

Combining Equations (1), (2), and (4) and neglecting the gravity term, we get:

$$\frac{\partial}{\partial t}\left(\frac{\varepsilon WP}{\mu T}\right) = \nabla \cdot \left(\frac{W\kappa P}{\mu T}\right)\nabla P + S \cdot \bar{R} \qquad (5)$$

The initial and boundary conditions for a cylindrical article heated at the surface with a heating rate h are (Figure 1):

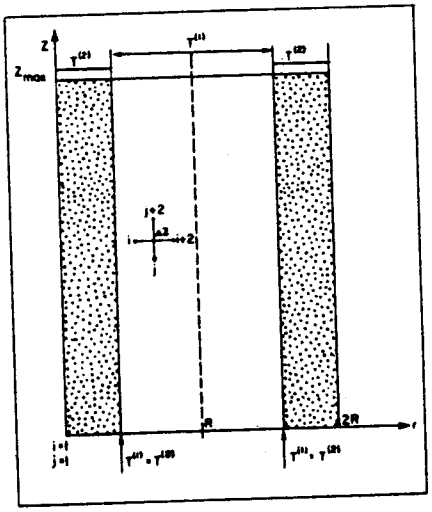

Figure 1. Two-Dimensional Grid.

At $t=0$ and $0 \leq r \leq R$: $T=T_0$, P=1 Atm.
At $t \geq 0$ and $r=0$: $dT/dr=0$, P=Finite.
At $t \geq 0$ and $r=R$: $T=T_0 + ht$, P=1 Atm.
At $t \geq 0$ and $z=\pm L$: $T=T_0 + ht$, P=1 Atm.

Equation (5) combined with the equation of heat transfer (Equation (3)) should give the pressure distribution as functions of time and space.

Numerical Solution

Equations (3) and (5) can be decoupled and solved independently. The thermal diffusivity α has been treated as a function of temperature ($\alpha = \alpha$ (T)). The solution derived is of the following general form:

$$T = T(\alpha, h, t, r, z) \qquad (6)$$

The parameters of Equation (5) have been expressed as functions of temperature:

1. Porosity $\epsilon = (0.0355 \times T + 0.46)/100$
   $T > 550°C$.

2. Permeability $\mu = 0.023$ Darcy's
   $T > 550°C$

3. Molecular weight of gaseous products: $W = W(T)$. Previous work[4] has determined that the gaseous products between 550-850°C are H_2 and CH_4, the mole fraction H_2/CH_4 is constant in this temperature range and equals 4:1. Therefore, we can calculate:

   $$W = 0.80 \times 2 + 0.20 \times 16 = 5 \quad T > 550°C$$

4. Viscosity of the gas products: $\mu = \mu(T)$ can be obtained from the component viscosities which are derived from Arnold's correlations.[5]

5. Rate of reaction (mass of gases produced/time/volume of carbon article): [$S = S(T)$]. The rate of reaction has been measured and reported before.[4]

Since every term of Equation (5) has been expressed as a function of temperature and the temperature has been expressed as a function of time and space (Equation (6)), numerical solution of Equation (5) will give the pressure distribution.

Results and Discussion

Two examples are cited for the case of a cylindrical carbon artifact. In the first example, the temperature throughout the article is assumed to be changing with time only ($T = T(t)$). As expected, the maximum pressure is developed at the center and at the peak of the gas evolution.[4] Thereafter, the pressure drops because of the decrease in the gas evolution rate (Figure 2).

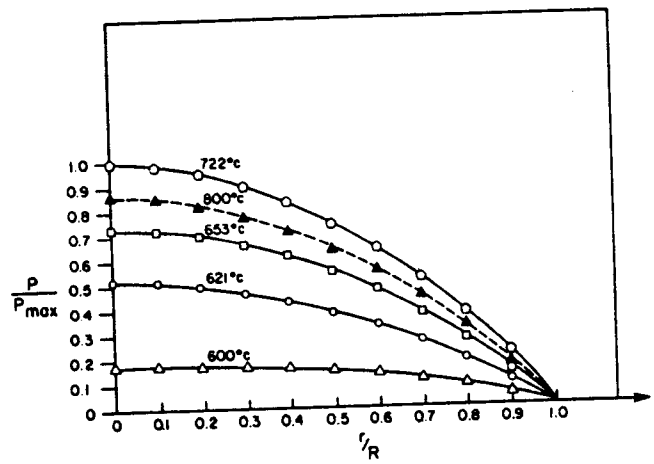

Figure 2. Pressure Distribution (No T Gradient).

In the second example, the temperature profile is obtained first as function of time and space. Thereafter, the pressure profile has been obtained and results are shown in Figure 3. Some interesting features appear in this figure. As we raise the temperature from 550°C, the outer surface and its vicinity are at higher temperatures and, therefore, the rate of gas evolution is higher than it is at the center.[4] This fact can explain why the maximum pressure is developed initially close to the surface. As long as the center is at a temperature lower than the peak of gas evolution[4] (about 730°C), the

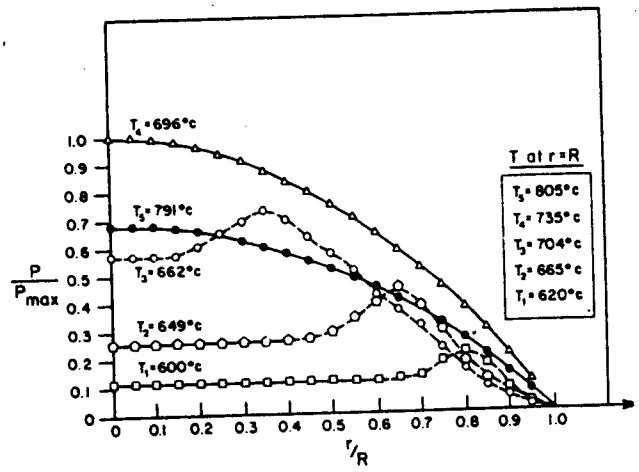

Figure 3. Pressure Distribution.

above pattern will be followed and the peak will appear at a position between the center and the surface, moving in the direction towards the center of the article. As soon as the center reaches the maximum gas evolution rate temperature (about 730°C), the maximum pressure will be developed at the center. Thereafter, due to the continuous decrease of gas evolution at all the points, the maximum pressure starts dropping, but the peak always remains at the center.

References

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