

STOCHASTIC MODELING OF CARBON GASIFICATION

*Wei-Yin Chen, Advait Kulkarni and Jeremy L. Milum
Department of Chemical Engineering, Anderson Hall
University of Mississippi, University, MS 38677*

and

*L. T. Fan
Department of Chemical Engineering, Durland Hall
Kansas State University, Manhattan, KS 66506*

Introduction

The need to predict fluctuations in the conversion of the reactant during carbon gasification is being increasingly recognized [1]; this is attributable to the disordered nature of most carbonaceous materials. The current paper demonstrates that modeling carbon gasification by the master-equation approach gives rise to such prediction.

Model Formulation

The two-site, Langmuir-Hinshelwood model of Nagle and Strickland-Constable [2], or the NSC model in short, has been widely adopted for modeling carbon gasification. The model's applicability and limitations have been reviewed by Suuberg [3]. Various features of the NSC model, including the two-site concept, has been generally accepted and verified [4]. The present work assumes, as in the NSC model, that the two forms of carbons, edge and basal carbons, undergo three types of reactions: the gasification of edge carbon, the gasification of basal carbon, and the conversion of edge carbon to basal carbon due to thermal annealing. Moreover, we have visualized that the gasification of a cluster of either basal or edge carbon will instantaneously result in a conversion of another cluster of basal carbon to that of edge carbon.

Derivation of the master equation follows what has been established by Oppenheim [5] and van Kampen [6]. Let us assume that the numbers of clusters of the basal, edge and gasified carbons are the three time-dependent random variables, N_1 , N_2 and N_3 , of the system of interest. These three random variables form a random vector, i.e., $\mathbf{N}(t)=[N_1(t), N_2(t), N_3(t)]$. The corresponding realization vector is $\mathbf{n}=[n_1, n_2, n_3]$. The cluster distribution can be characterized by the joint probability distribution, $P(\mathbf{n}; t)$, or $P(n_1, n_2, n_3; t)$, denoting the probability that the carbon system has the number distribution, \mathbf{n} , at time t . The transition of the system from one state, i.e., the number distribution of the clusters of different carbon forms, to another is characterized by a set of intensity functions or the rates of reactions, i.e.,

Pr [a basal cluster will gasify during the time interval, $(t, t+\Delta t)]=\lambda_1\Delta t+o(\Delta t)$ (1)

Pr [an edge cluster will gasify during the time interval, $(t, t+\Delta t)]=\lambda_2\Delta t+o(\Delta t)$ (2)

Pr [an edge cluster will convert to a basal cluster due to thermal annealing during the time interval, $(t, t+\Delta t)]=\lambda_3\Delta t+o(\Delta t)$ (3)

A complete process leading to the evolution of the cluster distribution comprises four mutually exclusive events, the probabilities of which are given below.

Pr [the number distribution will transform into \mathbf{n} from another state due to the gasification of a basal cluster during the time interval, $(t, t+\Delta t)$]
 $= (n_1 + 2)\lambda_1 \Delta t P_{n_1+2, n_2-1, n_3-1}(t)$ (4)

Pr [the number distribution will transform into \mathbf{n} from another state due to the gasification of an edge cluster during the time interval, $(t, t+\Delta t)$]
 $= n_2 \lambda_2 \Delta t P_{n_1+1, n_2, n_3-1}(t)$ (5)

Pr [the number distribution will transform into \mathbf{n} from another state due to the annealing of an edge cluster to a basal cluster during the time interval, $(t, t+\Delta t)$]
 $= (n_2 + 1)\lambda_3 \Delta t P_{n_1-1, n_2+1, n_3}(t)$ (6)

Pr [all clusters in the system will remain invariant, or the number distribution will remain at \mathbf{n} during the time interval, $(t, t+\Delta t)$]
 $= (1 - n_1 \lambda_1 - n_2 \lambda_2 - n_2 \lambda_3) \Delta t P_{n_1, n_2, n_3}(t)$ (7)

By taking into account all the four mutually exclusive events discussed above, we have

$$\begin{aligned} P_{n_1, n_2, n_3}(t + \Delta t) &= (n_1 + 2) \lambda_1 \Delta t P_{n_1+2, n_2-1, n_3-1}(t) \\ &+ n_2 \lambda_2 \Delta t P_{n_1+1, n_2, n_3-1}(t) \\ &+ (n_2 + 1) \lambda_3 \Delta t P_{n_1-1, n_2+1, n_3}(t) \\ &+ (1 - n_1 \lambda_1 - n_2 \lambda_2 - n_2 \lambda_3) \Delta t P_{n_1, n_2, n_3}(t) \\ &+ o(\Delta t) \end{aligned} \quad (8)$$

Rearranging the above equation and taking the limit as $\Delta t \rightarrow 0$ result in the following master equation of the system.

$$\begin{aligned} \frac{dP_n(t)}{dt} = & (n_1 + 2)\lambda_1 P_{n_1+2, n_2-1, n_3-1}(t) + n_2 \lambda_2 P_{n_1+1, n_2, n_3-1}(t) \\ & + (n_2 + 1)\lambda_3 P_{n_1-1, n_2+1, n_3}(t) \\ & - (n_1 \lambda_1 + n_2 \lambda_2 + n_3 \lambda_3) P_{n_1, n_2, n_3}(t) \end{aligned} \quad (9)$$

For convenience, the one-step operator, D, is introduced here; it is defined through its effect on the arbitrary function, f(n), as [6]

$$D f(n) = f(n+1) \quad \text{and} \quad D^{-1} f(n) = f(n-1) \quad (10)$$

In the light of the above definition of D, Eq. 9 simplifies to

$$\begin{aligned} \frac{dP_n(t)}{dt} = & \lambda_1 (D_{n_1}^{-2} D_{n_2}^{-1} D_{n_3}^{-1} - 1) n_1 P_n(t) \\ & + \lambda_2 (D_{n_1} D_{n_3}^{-1} - 1) n_2 P_n(t) \\ & + \lambda_3 (D_{n_1}^{-1} D_{n_2} - 1) n_3 P_n(t) \end{aligned} \quad (11)$$

By generating the first and second moments of the master equation, we obtain the governing equations, 3 each, for the means, variances and covariances of N_1 , N_2 , and N_3 . For brevity, only one each of these quantities is shown here.

$$\frac{dE[N_1(t)]}{dt} = -2\lambda_1 E[N_1(t)] - \lambda_2 E[N_2(t)] + \lambda_3 E[N_3(t)] \quad (12)$$

$$\begin{aligned} \frac{dE[N_1^2(t)]}{dt} = & -4\lambda_1 (E[N_1^2(t)] - E[N_1(t)]^2) - \lambda_2 (2E[N_1(t)N_2(t)] \\ & - E[N_2(t)]^2) + \lambda_3 (2E[N_1(t)N_3(t)] + E[N_3(t)]^2) \end{aligned} \quad (13)$$

$$\begin{aligned} \frac{dE[N_1(t)N_2(t)]}{dt} = & \lambda_1 (-2E[N_1(t)N_2(t)] - 2E[N_1(t)]^2 + E[N_1^2(t)] \\ & + \lambda_2 (E[N_1(t)N_2(t)] - E[N_2^2(t)] - E[N_2(t)]^2) \\ & + \lambda_3 (-E[N_1(t)N_2(t)] + E[N_2^2(t)] - E[N_2(t)]^2) \end{aligned} \quad (14)$$

Simulations

The master equation derived renders it possible to simulate the number evolutions of carbon clusters. Simulations has been performed according to two procedures.

The first procedure involves solving simultaneously the differential equations governing the means, variances, and covariances. The three transition-intensity functions defining the probabilities, or fractions, of cluster conversions per unit time, Eqs. 1 through 3, have been estimated from the deterministic rate expressions, i.e., the NSC model [1]. For instance, by considering that the number of edge clusters varies as a result of gasification during the time interval, (t, t+Δt), we obtain the rate expression

$$-r_{2,3} = \lim_{\Delta t \rightarrow 0} \frac{n_2 - [n_2 - n_2 \lambda_2 \Delta t + \alpha(\Delta t)]}{A \Delta t} = \frac{\lambda_2 n_2}{A} \quad (15)$$

where A stands for the surface area, and $-r_{2,3}$ is the rate of gasification of edge clusters [6]. At a temperature of 1800K and under an O_2 partial pressure of 0.23atm, the resultant

values of the three transition-intensity functions are:

$$\lambda_1 = 6.264 \times 10^2 s^{-1}, \quad \lambda_2 = 2.809 \times 10^3 s^{-1}, \quad \text{and} \quad \lambda_3 = 12.49 s^{-1}.$$

The second procedure resorts to an event-driven Monte Carlo technique [7]. The number of simulations corresponds to the total number of carbon clusters at t=0. In each simulation, two random numbers, both between (0, 1), have been generated. The first random number, r_1 , is for estimating the waiting time, τ , i.e., the expected time that one of the three possible reactions will take place [6]; mathematically,

$$\tau = 1/(\lambda_1 + \lambda_2 + \lambda_3) \ln(1/r_1).$$

The second random number, r_2 , is for predicting the type of reaction taking place. The ratios of occurrences of the three reactions is proportional to the reaction rates in the normalized domain (0, 1), i.e., $[0, \lambda_1/(\lambda_1 + \lambda_2 + \lambda_3)]$, $[\lambda_1/(\lambda_1 + \lambda_2 + \lambda_3), (\lambda_1 + \lambda_2)/(\lambda_1 + \lambda_2 + \lambda_3)]$ and $[(\lambda_1 + \lambda_2)/(\lambda_1 + \lambda_2 + \lambda_3), 1]$; hence, the value of r_2 determines the type of reaction. Then, the numbers of various clusters are updated, and a new iteration initiated.

The two procedures for simulation have generated nearly identical results. Figure 1 illustrates the number evolutions of the three types of clusters and their standard-deviation envelopes. The initial numbers of basal and edge carbons have been assumed to be 70 and 30, respectively.

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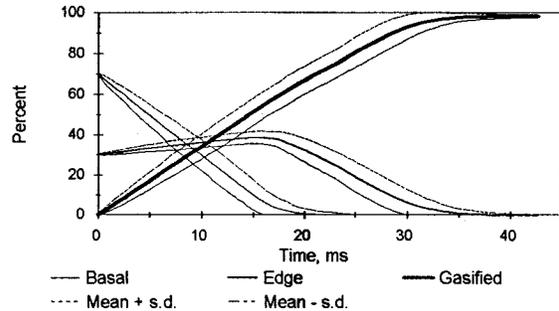


Figure 1. Number evolutions of the three types of carbon clusters and their standard-deviation envelopes.