LINEAR AND NON-LINEAR MECHANISTIC MODELING AND SIMULATION OF THE FORMATION OF CARBON ADSORBENTS

by

ALVARO ANDRES ARGOTI CAICEDO

B.S., Universidad Nacional de Colombia, Bogotá, 1998
M.S., Kansas State University, 2003

AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the requirements for the degree

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering
College of Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

2007

Abstract

Carbon adsorbents, namely, activated carbons and carbon molecular sieves, can be variously applied in the purification and separation of gaseous and liquid mixtures, e.g., in the separation of nitrogen or oxygen from air; often, carbon adsorbents also serve as catalysts or catalyst supports. The formation of carbon adsorbents entails the modification of the original internal surfaces of carbonaceous substrates by resorting to a variety of chemical or physical methods, thereby augmenting the carbonaceous substrates' adsorbing capacity. The formation of carbon adsorbents proceeds randomly, which is mainly attributable to the discrete nature, mesoscopic sizes, and irregular shapes of the substrates utilized as well as to their intricate internal surface configuration. Moreover, any process of carbon-adsorbent formation may fluctuate increasingly severely with time. It is desirable that such a process involving discrete and mesoscopic entities undergoing complex motion and behavior be explored by means of the statistical framework or a probabilistic paradigm.

This work aims at probabilistic analysis, modeling, and simulation of the formation of carbon adsorbents on the basis of mechanistic rate expressions. Specifically, the current work has formulated a set of linear and non-linear models of varied complexity; derived the governing equations of the models formulated; obtained the analytical solutions of the governing equations whenever possible; simulated one of the models by the Monte Carlo method; and validated the results of solution and simulation in light of the available experimental data for carbon-adsorbent formation from carbonaceous substrates, e.g., biomass or coal, or simulated data obtained by sampling them from a probability distribution. It is expected that the results from this work will be useful in establishing manufacturing processes for carbon adsorbents. For instance, they can be adopted in planning bench-scale or pilot-scale experiments; preliminary design and economic analysis of production facilities; and devising the strategies for operating and controlling such facilities.

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Co-Major Professor
L. T. Fan

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Dr. Walter P. Walawender

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Acknowledgements

The author wishes to express his most profound appreciation to Dr. L. T. Fan for his excellent guidance, constant encouragement, and invaluable advice in directing this work. Appreciation is extended to the author's co-major advisor, Dr. W. P. Walawender, for his advice and guidance; to Dr. K. Hohn of Department of Chemical Engineering and Dr. S.-S. Yang of Department of Statistics, for critically reviewing this dissertation and serving as members of the author's doctoral committee; and to Dr. Z. J. Pei of Department of Industrial and Manufacturing Systems Engineering, who served as the committee's chair. Special gratitude is also extended to Dr. S. T. Chou of Department of Finance and Banking, Kun Shan University of Technology, Taiwan, for his advice and assistance. The financial support provided by Kansas Agricultural Experiment Station, Department of Chemical Engineering, and Institute for Systems Design and Optimization of Kansas State University is gratefully acknowledged.

Dedication

To my parents, Alvaro and Betty, and my sisters, Marcela and Ximena.

CHAPTER 1 - Introduction

Carbon adsorbents, specifically, activated carbons (ACs) and carbon molecular sieves (CMSs), are highly porous materials that can be applied in the purification and separation of gaseous and liquid mixtures,[1-7] e.g., in the separation of nitrogen or oxygen from air. Various carbon adsorbents can also be effective as catalysts or catalyst supports.[8-19] The formation of carbon adsorbents entails the modification of the original internal surfaces of carbonaceous substrates by resorting to a variety of chemical or physical methods, thereby augmenting the carbonaceous substrates' adsorbing capacity.[20]

Activated carbons (ACs) can be manufactured from many varieties of carbonaceous substrates such as agricultural residues,[21-23] asphalt,[24] coal,[25-35] coffee bean husks,[36] corn and corn cobs,[37, 38] oil-palm and walnut shells,[39, 40] sorghum and wheat,[41, 42] and waste tire.[43] The activation of these carbonaceous substrates is carried out by physical or chemical methods, thereby leading to the formation of porosities on their internal surfaces. Physical activation of a carbonaceous substrate is usually performed by carbonizing it in an inert atmosphere at a temperature below 700 C, and subsequently activating it in the presence of steam, carbon dioxide, and/or air at a temperature between 800 C and 1000 C.[23, 44-49] Similarly, chemical activation of a carbonaceous substrate is generally carried out by impregnating it with a strong dehydrating agent, e.g., phosphoric acid, and subsequently heating this mixture to a temperature between 400 C and 800 C.[42, 50-54] The porosities on ACs can roughly be classified as micropores (< 2 nm), mesopores (2 – 50 nm), and macropores (> 50 nm)[20, 55] depending on the lengths of their diameters. Carbon molecular sieves (CMSs) are a special form of ACs whose pores have diameters of the order of molecular dimensions (0.4 – 0.9 nm);[56] they can be produced in two stages. In the first stage, ACs are manufactured from carbonaceous substrates as described earlier. In the second stage, very fine carbon particles are deposited on the pores' mouths of ACs to narrow them; some of the narrowed pores will eventually become blocked.[57-60] The carbon

particles are generated by decomposing gaseous organics of low-molecular weights, for instance, methane,[61] propylene and isobutylene,[62, 63] or benzene.[64-66]

Because of the discrete nature, mesoscopic sizes, irregular shapes, and intricate internal surface configuration of the carbonaceous substrates as well as the highly convoluted motion of the participating materials including reacting chemical species and carbon particles, the formation of carbon adsorbents tend to occur irregularly and randomly.

Objectives

It is natural or even desirable that the analysis and modeling of a process involving discrete and mesoscopic entities with convoluted motion and behavior, such as the formation of carbon adsorbents, be explored via the statistical framework or a probabilistic, i.e., stochastic paradigm. In fact, stochastic analysis and modeling are capable of revealing inherent fluctuations, or internal noises, of the phenomenon or system of interest.[67-69] Among various classes of stochastic processes, the birth-death process and its subclasses, the pure-birth and pure-death processes, have been most widely adopted.[69-72]

The work presented in this dissertation aims at stochastic analysis and modeling of the formation of carbon adsorbents on the basis of mechanistic rate expressions. Specific objectives of this work are as follows:

a. To formulate a series of linear and non-linear stochastic models of increasing sophistication based on the pure-birth and pure-death processes. In the pure-birth process, the population of interest only increases temporally; in other words, this population does not decrease, thereby indicating the absence of the death process. Naturally, the opposite is the case for the pure-death process, i.e., the population of concern only decreases as time progresses. [69, 71, 72]

b. To derive the governing equation for each of the models formulated, which is termed the master equation in the parlance of stochastic processes.[71, 73, 74]

c. To solve analytically or semi-analytically the master equations of the models derived.

d. To simulate one of the models by the Monte Carlo method.[74, 75]

e. To validate the results of solution and simulation in light of the available experimental data for carbon-adsorbent formation from carbonaceous substrates, such as biomass or coal, or simulated data obtained by sampling them from a probability distribution.

Rationale

As indicated earlier, the process of formation of carbon adsorbents tends to proceed randomly or stochastically. The randomness or stochasticity of the process is attributable to a variety of causes. For the formation of ACs, the causes of stochasticity include the following. First, the discreteness and mesoscopic nature of the carbonaceous substrates whose shapes are highly irregular and their internal surface configurations extremely intricate.[20, 76] Second, the random encounters between the activation agent, e.g., carbon dioxide or phosphoric acid, and the carbon atoms on the surfaces of the carbonaceous substrate: This is a chemical reaction, which is known to occur randomly.[77-85] Third, the random distribution of the pores formed on the carbonaceous substrate's internal surfaces whose sizes and shapes are also highly irregular.[20] A schematic of these phenomena is presented in Figure 1.1.

For the formation of CMSs, the causes of stochasticity include the following. First, the decomposition of a gaseous carbon source, e.g., methane or benzene, which is a randomly-occurring chemical reaction as mentioned above. Second, the generation of fine carbon particles from the decomposed carbon source; these carbon particles are discrete and mesoscopic in size and their motion in the gas phase is extremely convoluted. Third, the formation of large carbon clusters, or packets, through random collisions between these fine carbon particles. Fourth, the deposition of these carbon packets onto the pores' mouths of ACs, which progresses temporally and occurs as a consequence of random encounters between the depositing carbon packets and pores. A schematic of these phenomena is presented in Figure 1.2.

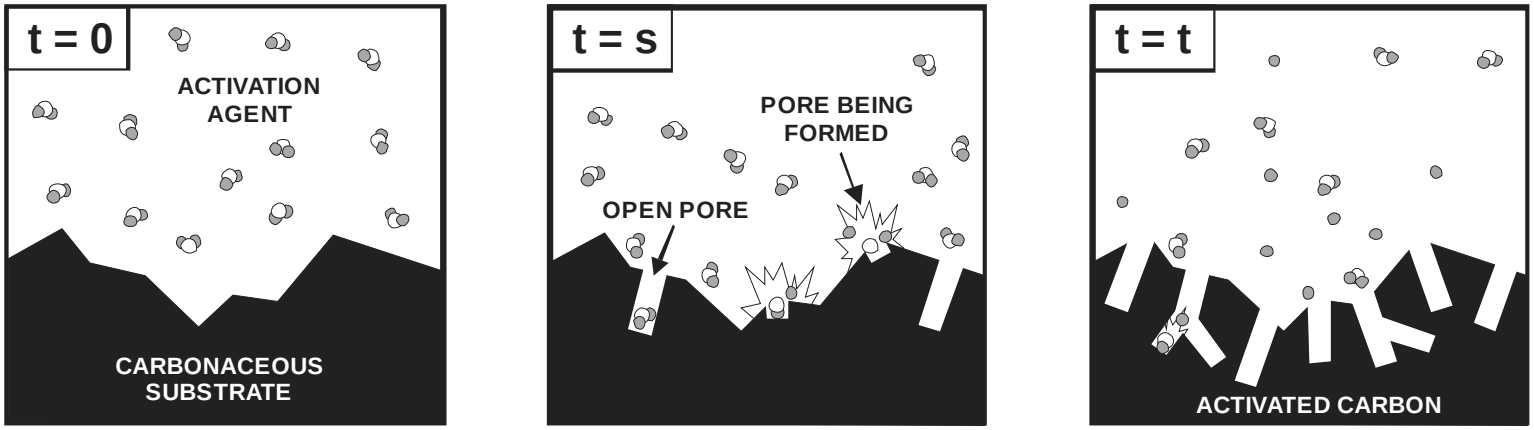


Figure 1.1. Schematic of the progression of activated-carbon (AC) formation: side view.

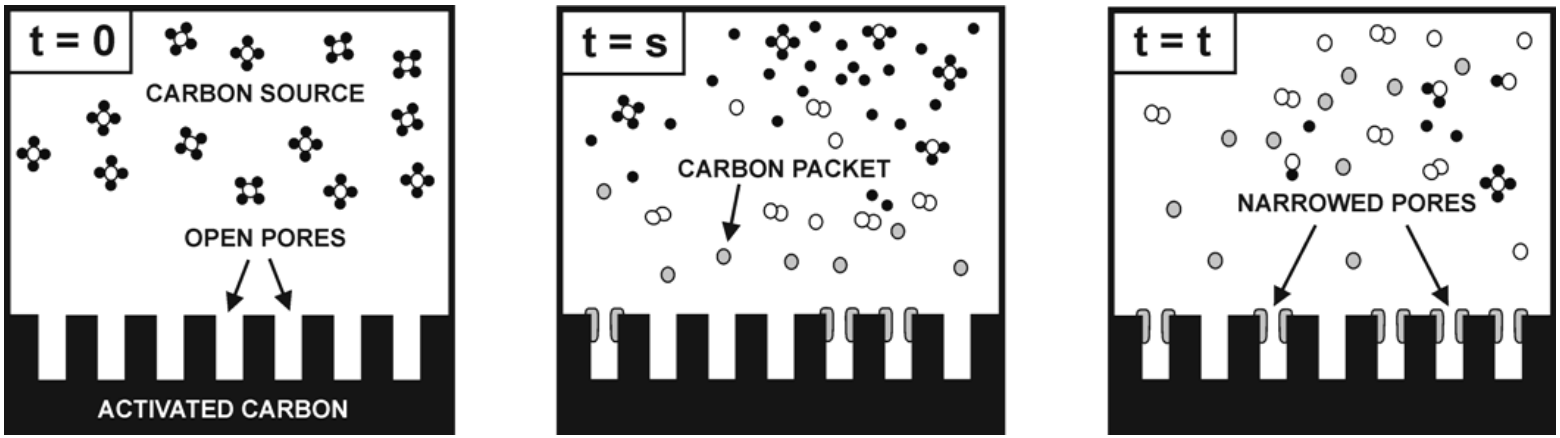


Figure 1.2. Schematic of the progression of carbon-molecular-sieve (CMS) formation: side view.

The randomness or stochasticity of any discrete or particulate system or process manifests itself in the form of incessant fluctuations in the macroscopic variables describing the system or process, which are inherent to it. These inherent fluctuations impede the prediction with certainty of any temporal or spatial variation in the evolution of the process. Such uncertainty can be accommodated by taking into account the probability distribution of the variables describing the process, thereby giving rise to the definition of random variables.[69, 71] Hence, the analysis and modeling of a process described by random variables must be performed in light of a stochastic paradigm. Unlike a deterministic model, a stochastic model renders it possible to predict the inherent fluctuations of a system or process; moreover, the mean component of the stochastic model is equivalent to the deterministic model.[67-69, 71]

The formation of ACs is essentially a fluid-solid reaction for which various mathematical models have been formulated;[86-93] their complexity ranges from linear[88] to highly non-linear.[90] In such models, the experimentally measurable variable is usually the conversion of the solid material as it reacts with the chemical species present in the fluid phase. Naturally, the kinetics of formation of ACs has been formulated in light of these models;[40, 94-101] nevertheless, they are deterministic in nature. So far, the stochastic formulation of the rate of formation of ACs has not been attempted; this work aims at providing it in the form of a linear stochastic model. Similarly, the formation of CMSs closely parallels the coke deposition process onto the pores of catalysts, thereby giving rise to their deactivation. A substantial number of works have been published on the deterministic analysis and modeling of coke deposition on catalysts.[102-108] These models have served as the starting point for the stochastic formulation of the rate of formation of CMSs on the basis of linear kinetic expressions.[109, 110] Hitherto, no effort has been made on the stochastic formulation of the formation of CMSs based on non-linear rate expressions, which is attempted in this work.

Stochastic analysis and modeling constitute viable tools that can greatly facilitate the development of an effective control strategy for randomly behaving systems and processes, e.g., the formation of carbon adsorbents. The mean component of the resultant stochastic model can be the basis for scaling up or designing the process; in addition, the inherent fluctuations predicted by the model are the limit of accuracy achievable by any control strategy.

Description of the Systems

To formulate the stochastic models for the formation of carbon adsorbents, including ACs and CMSs, the systems of concern must be properly identified; this is elaborated below.

Formation of activated carbons (ACs)

Figure 1.1 depicts the system of concern comprising the pores on the internal surfaces of a carbonaceous substrate being activated. The formation of pores is considered to be attributable exclusively to the chemical reaction between the carbon atoms constituting the carbonaceous substrate and the activation agent. Naturally, the number of pores being formed through the activation process increases temporally. In addition, these pores are randomly distributed over the internal surfaces of the carbonaceous substrate, thereby giving rise to a convoluted pore network. It is assumed that the reaction terminates prior to the collapse of the internal structure of the activated substrate.

Formation of carbon molecular sieves (CMSs)

Figure 1.2 exhibits the system of interest comprising carbon packets, or simply packets, and pores on ACs. These carbon packets are aggregates or clusters of fine carbon particles, which are generated by the decomposition of a gaseous carbon source. At the outset, the pores' mouths are completely open; subsequently, they are narrowed as time progresses by the deposition of packets onto them to a size suitable for effecting molecular sieving. Naturally, the number of narrowed pores increases and that of open pores decreases temporally. It is considered that a pore is narrowed by a single packet; moreover, the fraction of narrowed pores that become blocked by one packet is assumed to be negligible. The process of formation of CMSs as described herein is termed pore-narrowing for brevity.

Besides the current chapter, this dissertation contains four additional chapters, i.e., Chapters 2 through 5. Chapter 2 presents the analysis and modeling of the kinetics of formation of ACs as a pure-birth process with a linear intensity of transition, or intensity function, based on a single random variable. Chapter 3 focuses on the kinetics of formation of CMSs by carbon deposition, which is analyzed and modeled as a pure-birth process with a non-linear intensity function, based on a single random variable; in contrast, Chapter 4 views the formation of CMSs by carbon deposition as a pure-death process. Finally, the major conclusions are drawn and recommendations for possible extensions are proposed in Chapter 5.

CHAPTER 2 - Formation of Activated Carbons: Pure-Birth Process with a Linear Intensity of Transition Based on a Single Random Variable

As indicated in the introductory chapter, the formation of activated carbons (ACs) is analyzed and modeled in the current chapter as a pure-birth process with a linear intensity function based on a single random variable. In general, it is reasonable to consider that the driving force, or potential, of the formation of ACs is a function of the number of pores that have formed on the internal surfaces of a carbonaceous substrate being activated, which temporally increases. Naturally, one of the simplest forms of such a function is of the first-order. Thus, the corresponding intensity function is linear in the number of pores that have formed on the carbonaceous substrate's internal surfaces.

It is expected that the resultant model constitutes an insightful preliminary exploration of the stochastic nature of the formation of ACs. This exploration would improve the conceptual design of a reactor for manufacturing ACs of superior quality.

Identification of Random Variable and State Space

The available experimental data for the formation of ACs are given in terms of the conversion of a carbonaceous substrate into ACs at different temperatures.[40] It would be reasonable to equate the weight loss due to the reaction between the carbonaceous substrate and the activation agent to the number of pores that have formed on the carbonaceous substrate's internal surfaces. Thus, the number of pores that have already formed on the carbonaceous substrate's internal surfaces per unit weight of the activated substrate at time t is taken as the random variable of the process, N(t), whose realization is n. All possible values of N(t) are the states of the process and their collection, $\{ 0, 1, 2, \ldots, n_L - 1, n_L \}$, is its state space where n_L is the maximum number of pores that could form on the carbonaceous substrate's internal surfaces per unit weight of the activated substrate. Note that the random variable, N(t), in the current

model exclusively accounts for the number of pores that have already formed on the carbonaceous substrate's internal surfaces at any time t; hence, the analysis of the change in the pores' sizes or lengths would require the formulation of models with different variables designated as the random variables.

Transition Diagram

The transition diagram of the process is presented in Figure 2.1. The circles indicate the system's possible states, which have already been identified in the preceding section, and the arrows describe transitions of the system at any moment.

Definition of Intensity of Transition

The intensity of transition, or simply intensity function, is defined as the instantaneous rate of change of the transition probability.[71] The intensity function for the pure-birth process of interest, which is termed intensity of birth, is given by

$$\lambda_n(t) = \frac{dn}{dt} = \kappa(n_L - n) \tag{2.1}$$

where κ is a proportionality constant whose dimension is inverse time (t^{-1}).

Master Equation

For the pure-birth process, the probability balance around state n leads to

$$\frac{d}{dt}p_n(t) = \lambda_{n-1}(t)p_{n-1}(t) - \lambda_n(t)p_n(t), \quad n = 0,\ 1,\ 2,...,\ n_L - 1,\ n_L \tag{2.2}$$

which is the master, i.e., governing, equation of the process;[71, 73] its derivation is detailed in Appendix A. The term, $p_n(t)$, in the above expression denotes the probability that n pores have formed at time t. Inserting the expression for the intensity of birth, $\lambda_n(t)$, into the above expression yields

$$\frac{d}{dt}p_n(t) = \{\kappa[n_L - (n-1)]\}p_{n-1}(t) - [\kappa(n_L - n)]p_n(t) \tag{2.3}$$

Clearly, this equation is dependent on realization n but independent of time t.

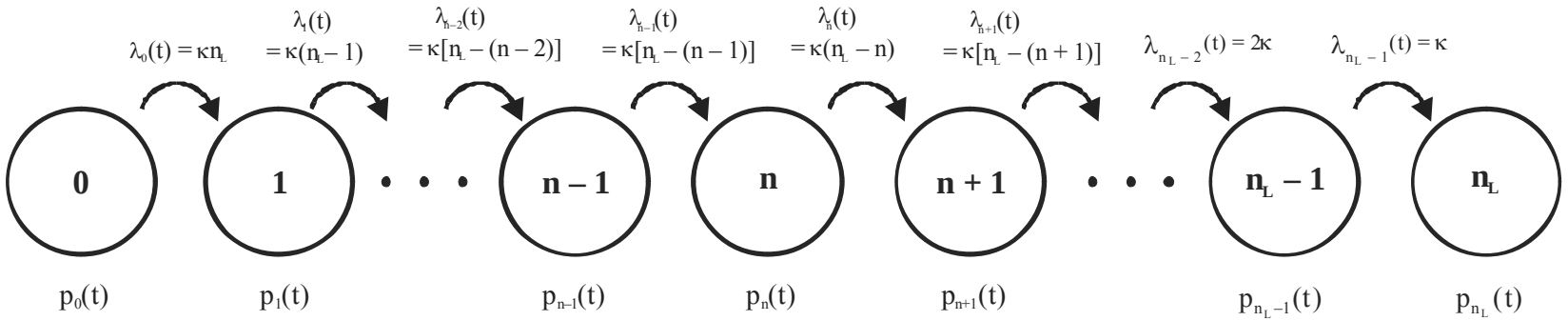


Figure 2.1. Transition diagram of the pure-birth process representing the formation of pores on a carbonaceous substrate: The symbols, 0, 1, 2, …, (n – 1), n, (n + 1), …, (n_L – 1), n_L, are the states of the process; $p_0(t)$, $p_1(t)$, …, $p_{n-1}(t)$, $p_n(t)$, $p_{n+1}(t)$, …, $p_{n_L-1}(t)$, $p_{n_L}(t)$, are the corresponding state probabilities; and $\lambda_n(t) = \kappa(n_L - n)$ is the intensity of birth, which is a linear function of n for each transition.

Mean and Variance

The mean, i.e., and higher moments about the mean can be computed from the master equation of the pure-birth process, Eq. (2.3). Among these higher moments, the second moment about the mean, i.e., the variance, is of special importance: It signifies the fluctuations or scatterings of the random variable about its mean,[69, 111] which should be the focus of any stochastic analysis and modeling.

Mean

As detailed in Appendix B, the mean, or expected value, of N(t) is obtained as

$$m(t) = n_L[1 - \exp(-\kappa t)] \tag{2.4}$$

where κ is a proportionality constant. From this expression, the normalized form of the mean, denoted by $\eta(\tau)$, is given by

$$\eta(\tau) = \frac{m(\tau)}{n_L} = [1 - \exp(-\tau)] \tag{2.5}$$

where $\tau = (\kappa t)$ is the dimensionless time. Note that this expression is solely a function of τ.

Variance

The variance, Var[N(t)] or $\sigma^2(t)$, of N(t), which is also derived in Appendix B, is given by

$$\sigma^2(t) = n_L[1 - \exp(-\kappa t)]\exp(-\kappa t) \tag{2.6}$$

In terms of dimensionless time τ, this expression becomes

$$\sigma^2(\tau) = n_L[1 - \exp(-\tau)]\exp(-\tau) \tag{2.7}$$

The standard deviation, $\sigma(t)$, is the square root of the variance, $\sigma^2(t)$; thus,

$$\sigma(t) = n_L^{1/2}\left\{[1 - \exp(-\kappa t)]\exp(-\kappa t)\right\}^{1/2} \tag{2.8}$$

From this equation, the normalized form of the standard deviation, $\zeta(\tau)$, is obtained as

$$\zeta(\tau) = \frac{\sigma(\tau)}{n_L} = \frac{1}{n_L^{1/2}}\left\{[1 - \exp(-\tau)]\exp(-\tau)\right\}^{1/2} \tag{2.9}$$

Note that this expression is a function of τ and n_L. The standard deviation relative to the mean, termed the coefficient of variation, is defined as[112]

$$CV(t)=\frac{\sigma(t)}{m(t)} \tag{2.10}$$

Inserting Eqs. (2.4) and (2.8) for m(t) and σ(t), respectively, into the above equation yields the coefficient of variation, CV(t), of the pure-birth process as

$$CV(t)=\left\{\frac{\exp(-\kappa t)}{n_L[1-\exp(-\kappa t)]}\right\}^{1/2} \tag{2.11}$$

or in terms of τ,

$$CV(\tau)=\left\{\frac{\exp(-\tau)}{n_L[1-\exp(-\tau)]}\right\}^{1/2} \tag{2.12}$$

Note that this expression is also a function of τ and n_L.

Analysis of Experimental Data

The available experimental data are presented in terms of the temporal evolution of the conversion of oil-palm shell char, a carbonaceous substrate, into ACs via physical activation with carbon dioxide at five temperatures.[40] The data are illustrated in

Figure 2.2, and also listed in Table 2.1. Naturally, the model derived in this work is validated with these data. To fit the model to the data, the random variable, N(t), i.e., the number of pores that have already formed on the carbonaceous substrate's internal surfaces per unit weight of the activated substrate, needs to be related to the experimentally measurable variable, Y(t), signifying the conversion of the carbonaceous substrate into ACs, which is defined as

$$Y(t)=\frac{W(t)}{W_L} \tag{2.13}$$

where W(t) is the amount of carbon that has reacted with the activation agent at any time t, and W_L, the maximum amount of carbon that reacts before the internal structure of the carbonaceous substrate collapses. By assuming that the formation of pores on the carbonaceous substrate's internal surfaces is only attributable to the reaction between the carbon in the substrate and the activation agent, we have

$$W(t)=\delta N(t) \tag{2.14}$$

where δ is the amount of carbon that reacts, thereby giving rise to the formation of a single pore. In light of this equation, W_L can be related to n_L as

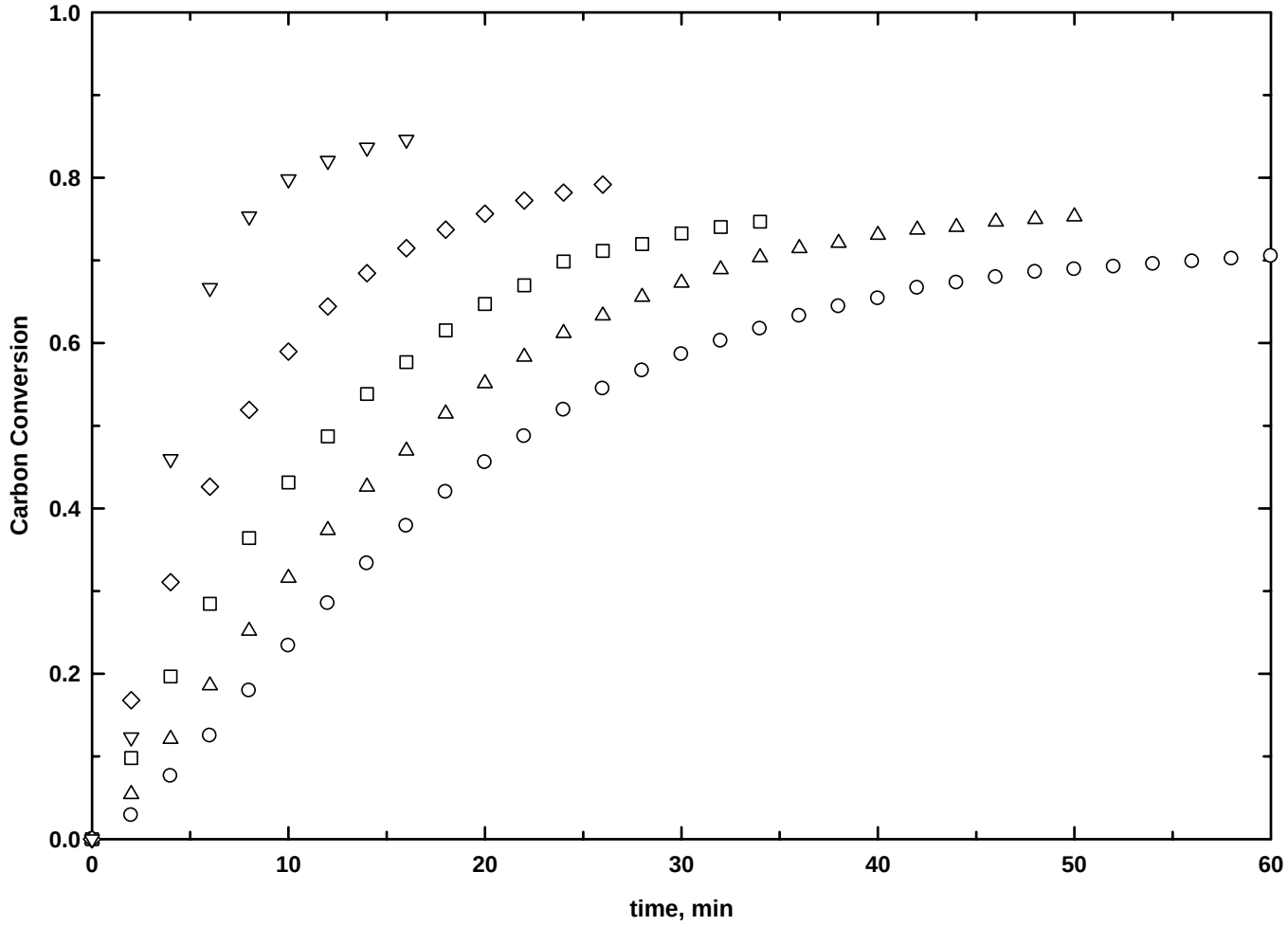


Figure 2.2. Experimentally measured conversion of a carbonaceous substrate into ACs at different temperatures.*

* Data were obtained with oil-palm-shell char.[40]

Table 2.1. Experimentally Measured Fractional Conversion of a Carbonaceous Substrate into ACs at Different Temperatures*

time, min	Carbon Conversion				
	T = 973 K	T = 1023 K	T = 1073 K	T = 1123 K	T = 1173 K
0.0	0.000	0.000	0.000	0.000	0.000
2.0	0.029	0.054	0.098	0.168	0.123
4.0	0.076	0.121	0.197	0.311	0.460
6.0	0.125	0.186	0.285	0.426	0.667
8.0	0.179	0.252	0.364	0.519	0.753
10.0	0.234	0.316	0.431	0.590	0.798
12.0	0.285	0.374	0.487	0.644	0.821
14.0	0.333	0.426	0.538	0.685	0.837
16.0	0.379	0.470	0.577	0.715	0.846
18.0	0.420	0.515	0.615	0.737	
20.0	0.456	0.551	0.647	0.756	
22.0	0.487	0.583	0.670	0.772	
24.0	0.519	0.612	0.699	0.782	
26.0	0.545	0.633	0.712	0.792	
28.0	0.567	0.656	0.720		
30.0	0.587	0.673	0.733		
32.0	0.603	0.689	0.740		
34.0	0.617	0.704	0.747		
36.0	0.633	0.715			
38.0	0.644	0.721			
40.0	0.654	0.731			
42.0	0.667	0.737			
44.0	0.673	0.740			
46.0	0.679	0.747			
48.0	0.686	0.750			
50.0	0.689	0.753			
52.0	0.692				
54.0	0.696				
56.0	0.699				
58.0	0.702				
60.0	0.705				

* Data were obtained with oil-palm shell char.[40]

$$W_L = (\delta n_L) \tag{2.15}$$

The mean value of Y(t), denoted by $m_Y(t)$, is obtained from this equation in conjunction with Eqs. (2.13) and (2.14) as follows:

$$\begin{aligned} m_Y(t) &= E[Y(t)] \\ &= E\left[\frac{W(t)}{W_L}\right] \\ &= \frac{1}{W_L} E[\delta N(t)] \end{aligned}$$

or

$$m_Y(t) = \frac{\delta}{W_L} E[N(t)]$$

or

$$m_Y(t) = \frac{\delta}{W_L} m(t)$$

Substituting Eq. (2.4) for m(t) into this equation yields

$$m_Y(t) = \left(\frac{\delta}{W_L}\right) n_L [1 - \exp(-\kappa t)]$$

Because $W_L = (\delta n_L)$, this expression reduces to

$$m_Y(t) = [1 - \exp(-\kappa t)] \tag{2.16}$$

In terms of dimensionless time τ, the above equation can be rewritten as

$$m_Y(\tau) = [1 - \exp(-\tau)] \tag{2.17}$$

Note that this expression is identical to Eq. (2.5) for $\eta(\tau)$. Similarly, the variance of Y(t), denoted by $\sigma_Y^2(t)$, is obtained from Eqs. (2.13), (2.14), and (2.15) as

$$\begin{aligned} \sigma_Y^2(t) &= \mathrm{Var}\left[\frac{W(t)}{W_L}\right] \\ &= \mathrm{Var}\left[\frac{\delta N(t)}{W_L}\right] \\ &= \left(\frac{\delta}{\delta n_L}\right)^2 \mathrm{Var}[N(t)] \end{aligned}$$

or

$$\sigma_Y^2(t) = \frac{1}{n_L^2}[\sigma^2(t)]$$

Substituting Eq. (2.6) for $\sigma^2(t)$ into the above expression yields

$$\sigma_Y^2(t) = \frac{1}{n_L^2}\{n_L[1-\exp(-\kappa t)]\exp(-\kappa t)\}$$

or

$$\sigma_Y^2(t) = \frac{1}{n_L}[1-\exp(-\kappa t)]\exp(-\kappa t)$$

Naturally, the standard deviation of Y(t), i.e., $\sigma_Y(t)$, is given by

$$\sigma_Y(t) = \frac{1}{n_L^{1/2}}\{[1-\exp(-\kappa t)]\exp(-\kappa t)\}^{1/2} \tag{2.18}$$

In terms of τ, this equation can be transformed into

$$\sigma_Y(\tau) = \frac{1}{n_L^{1/2}}\{[1-\exp(-\tau)]\exp(-\tau)\}^{1/2} \tag{2.19}$$

Note that this expression is identical to Eq. (2.9) for $\zeta(\tau)$. From Eqs. (2.16) and (2.18), the coefficient of variation, $CV_Y(\tau)$, is obtained as

$$CV_Y(t) = \frac{\sigma_Y(t)}{m_Y(t)} = \left\{\frac{\exp(-\kappa t)}{n_L[1-\exp(-\kappa t)]}\right\}^{1/2} \tag{2.20}$$

or in terms of τ

$$CV_Y(\tau) = \left\{\frac{\exp(-\tau)}{n_L[1-\exp(-\tau)]}\right\}^{1/2} \tag{2.21}$$

Note that this equation is identical to Eq. (2.12) for $CV(\tau)$.

Results and Discussion

The model formulated, in terms of $m_Y(\tau)$ as given in Eq. (2.16), has been regressed on the available experimental data[40] by resorting to the adaptive random search procedure.[113, 114] The regression has resulted in the values of κ, which are listed in Table 2.2. These values have rendered it possible to evaluate the dimensionless time, $\tau = (\kappa t)$, as well as the mean, $m_Y(\tau)$, from Eq. (2.17), whose values are plotted in Figure 2.3 as a function of τ. The corresponding experimentally measured values of the fractional conversion of the carbonaceous substrate into

Table 2.2. Values of κ for the Formation of ACs at Different Temperatures.

temperature, K (C)	κ, $s^{-1} \cdot 10^4$ (min^{-1})
973 (699.85)	4.38 (0.026)
1023 (749.85)	5.94 (0.036)
1073 (799.85)	8.36 (0.050)
1123 (849.85)	13.16 (0.079)
1173 (899.85)	24.93 (0.150)

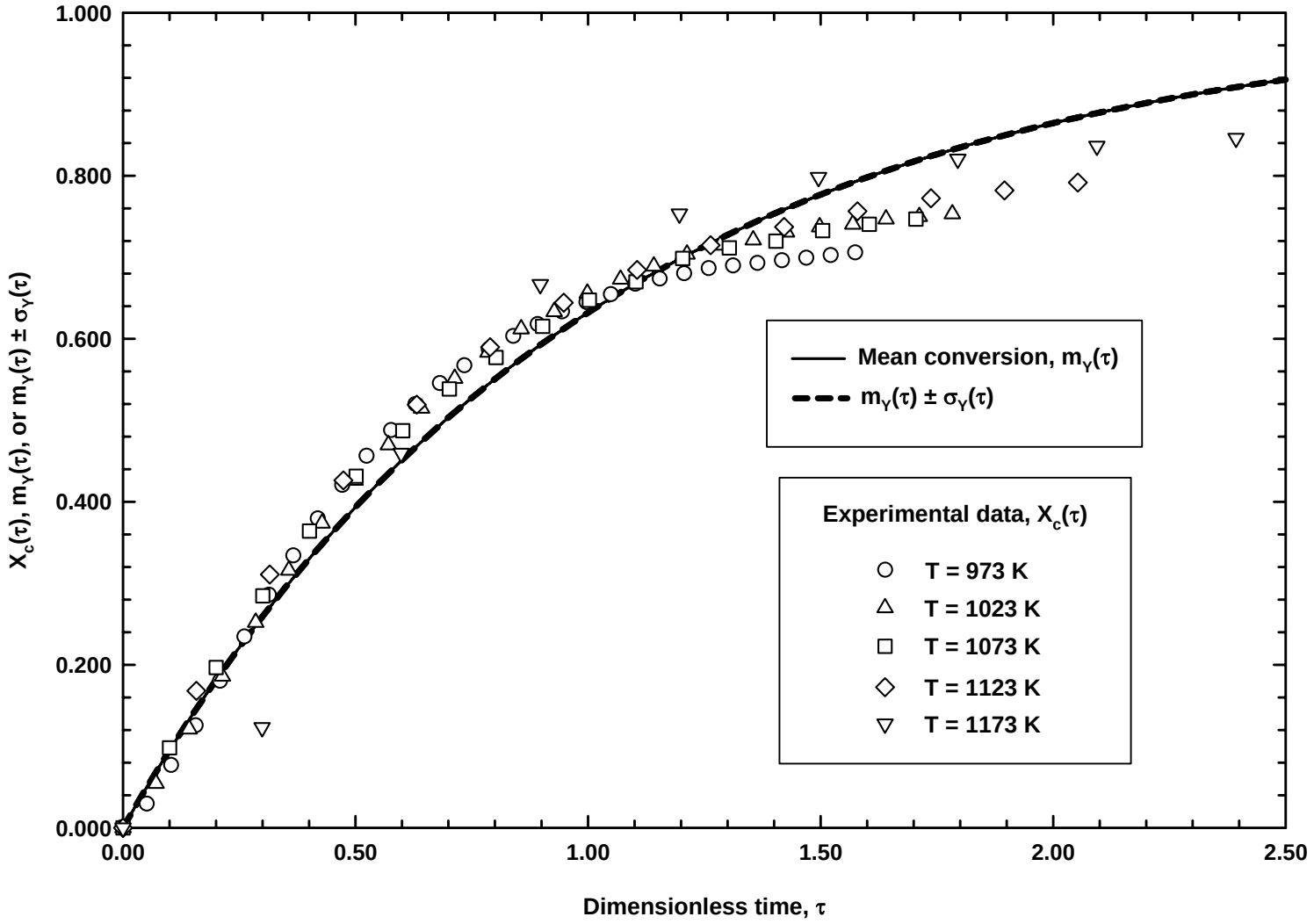


Figure 2.3. Mean fractional conversion $m_Y(\tau)$ and standard deviation envelope [$m_Y(\tau) \pm \sigma_Y(\tau)$] as functions of dimensionless time τ for the formation of ACs.

ACs, denoted as $X_c(\tau)$, are superimposed in the same figure for comparison. Clearly, $m_Y(\tau)$ increases and asymptotically approaches to 1 as τ progresses; this asymptotic value for $m_Y(\tau)$ can be discerned from Eq. (2.17). The normalized standard deviation, $\sigma_Y(\tau)$, as computed by Eq. (2.19), signifies the deviations attributable to the internal or characteristic noises of the process as predicted by the stochastic model.[109] The standard deviation envelope, i.e., $m_Y(\tau) \pm \sigma_Y(\tau)$, is plotted in Figure 2.3. Note that the majority of the experimental data[40] lie appreciably beyond the expected variation, or scattering; this is almost always the case: The overall deviations of the experimental data include not only those attributable to the internal noises of the process as predicted by the model, but also to the external noises due to unavoidable measurement errors and instrumental deficiencies that can never be totally eliminated. The coefficient of variation, CV(t), as defined by Eq. (2.11), provides a more meaningful relative measurement of the variability or dispersion of the values of a random variable about their mean than the standard deviation, $\sigma(t)$. In general, the smaller the values of random variable N(t), i.e., the population size, the greater the extent of the expected fluctuations about their mean.

Clearly, Eq. (2.19) for $\sigma_Y(\tau)$ depends on n_L, i.e., the maximum number of pores that could form on the carbonaceous substrate's internal surfaces per unit weight of activated substrate. The number of pores on ACs is profoundly large;[115, 116] thus, it is reasonable to expect that the value of n_L be enormous. The order of magnitude estimate of n_L is obtained by dividing the total volume of pores per unit weight of ACs by the volume of a single pore. The former can be obtained from the experimental characterization of ACs produced from a carbonaceous substrate under specific activation conditions, and the latter can be computed under the assumption that the shape of the pore is perfectly cylindrical. For illustration, the total volume of pores for ACs prepared at 873 K is 0.96 cm^3 per gram of ACs.[40] Moreover, the volume of a single pore is given by

$$v_p = \pi(\bar{r})^2 \ell \tag{2.22}$$

where $\bar{r}$ and ℓ are the pore's average radius and the pore's length, respectively. For a perfectly cylindrical pore, $\bar{r}$ can be expressed as[117]

$$\bar{r} = \frac{2\varepsilon_s}{\rho_s S_g} \tag{2.23}$$

where ε_s, ρ_s, and S_g are structural properties of ACs, specifically, their porosity, apparent density, and surface area per unit weight of ACs, respectively. For ACs prepared at 873 K, the corresponding values of these properties are 0.66, 0.69 g · cm^{-3}, and 1,366 m^2 · g^{-1}, [40] thereby yielding $\bar{r}$ as 1.40 nm. By changing ℓ from 1 nm to 50 nm, the volume of a single pore, v_p, varies from $6.16 \cdot 10^{-21}$ cm^3 to $3.08 \cdot 10^{-19}$ cm^3 as computed from Eq. (2.22). Thus, the value of n_L falls within the range between $3.12 \cdot 10^{18}$ and $1.56 \cdot 10^{20}$ pores per gram of ACs.

The parameter, κ, in Eq. (2.16) has the connotation of kinetic constant. Thus, it is temperature dependent and varies according to the Arrhenius law; hence,

$$\kappa = \kappa_0 \exp\left(-\frac{E_a}{RT}\right) \tag{2.24}$$

where κ_0 is the frequency factor and E_a the activation energy.

Figure 2.4 exhibits the Arrhenius plot of the values of κ against their corresponding values of inverse temperature for the available experimental data.[40] From this plot, κ_0 and E_a are computed as 7.88 s^{-1} and 80.2 kJ · mol^{-1}, respectively. These values differ from those obtained by Guo and Lua[40] of $1.26 \cdot 10^{-3}$ s^{-1} and 38.7 kJ · mol^{-1}, respectively, on the basis of a non-linear kinetic model.

Summary

A stochastic model has been derived for the formation of ACs from carbonaceous substrates. Specifically, the model is based on a pure-birth process with a linear intensity of transition. The mean and variance of the conversion of a carbonaceous substrate into ACs, have been computed from the master equation of the pure-birth process. The model has been validated by fitting it to the available experimental data. The mean values of the model at various times follow the general trend of these data. As expected, the data's fluctuations around the mean values are more noticeable than those predicted by the model: In addition to the process' internal noises, the deviations of the experimental data also account for the external noises due to unavoidable measurement errors.

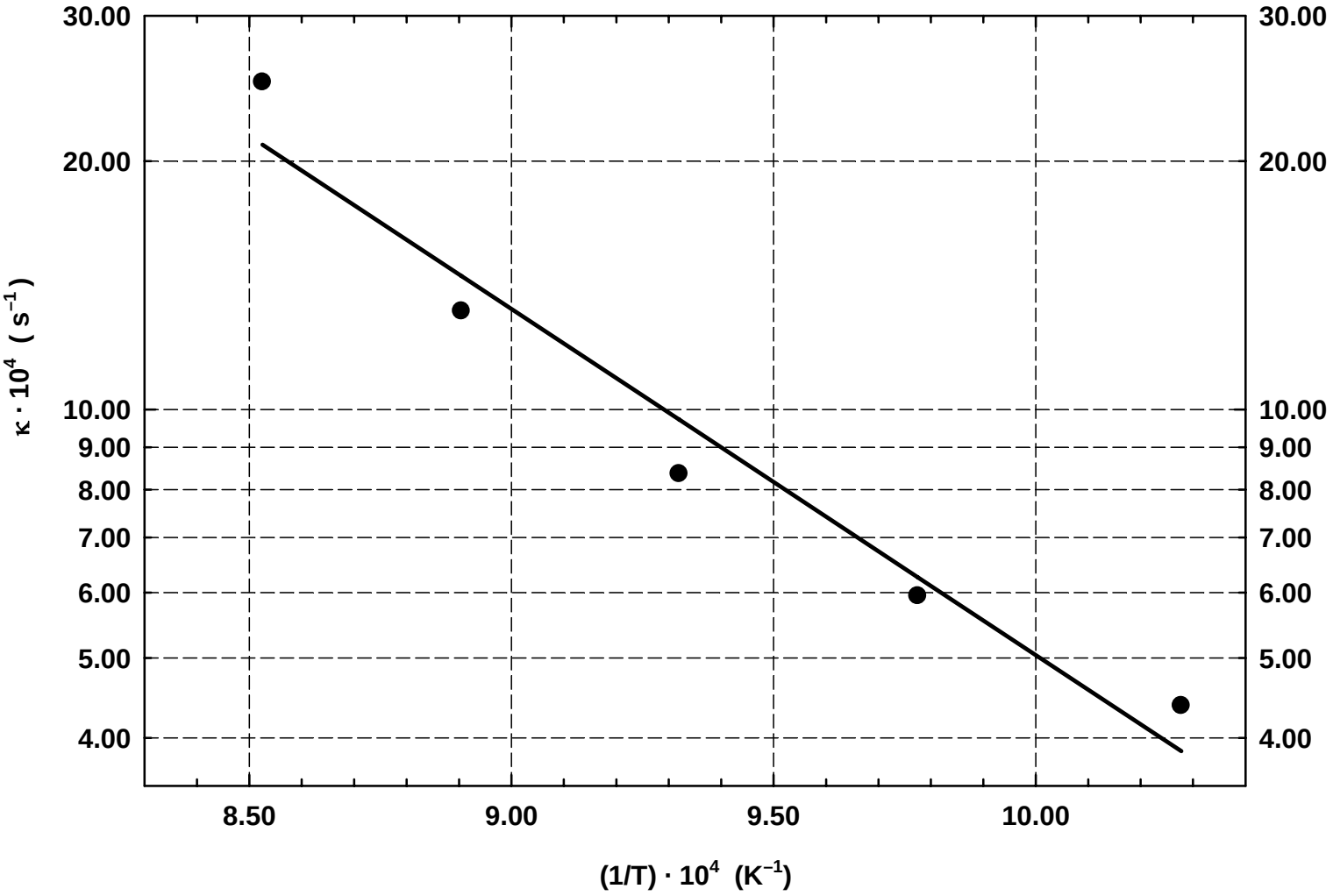


Figure 2.4. Arrhenius plot for the kinetic constant, κ.

Notation

$m(t)$ = mean of the random variable, N(t)

$m_Y(t)$ = mean of the experimental measurable variable, Y(t), mg C

$N(t)$ = random variable representing the number of pores that have already formed on the internal surfaces of ACs at time t

n = realization of the random variable, N(t)

$p_n(t)$ = probability that n pores have formed at time t

t = time

$Y(t)$ = experimentally measurable variable representing the conversion of a carbonaceous substrate into ACs

Greek letters

κ = kinetic constant in the intensity of birth, $(t)^{-1}$

$\lambda_n(t)$ = intensity of birth for the pure-birth process in state n at time t

$\sigma^2(t)$ = variance of the random variable, N(t)

$\sigma_Y^2(t)$ = variance of the experimentally measurable variable, Y(t)

τ = dimensionless time

CHAPTER 3 - Formation of Carbon Molecular Sieves by Carbon Deposition: Pure-Birth Process with a Non-Linear Intensity of Transition Based on a Single Random Variable

As indicated in the introductory chapter, the formation of CMSs due to the narrowing of pores by carbon deposition is analyzed and modeled herein as a pure-birth process with a non-linear intensity of transition based on a single random variable. In general, it is reasonable to consider that the driving force, or potential, of the pore-narrowing process by carbon deposition is a function of the number of carbon packets, or packets, that deposit onto the pores' mouths, which increases with time.[109] In this chapter, the form of such a function is of the second-order, thereby incorporating into the model the effect of collisions or interactions between pairs of carbon packets as they deposit onto the pores' mouths of ACs. Hence, the corresponding intensity function is non-linear in the number of packets to be deposited. For brevity, the pore-narrowing process under consideration is referred to as pore-narrowing hereafter.

Identification of Random Variable and State Space

The available experimental data for formation of CMSs are usually given in terms of the weight of carbon aggregates, or packets, deposited on ACs.[8, 65, 118, 119] It would be plausible to equate the weight gain due to the deposition of carbon packets to the number of such packets.[109, 110] In this connection, the number of packets that have already deposited onto the pores' mouths, thereby causing them to narrow, at time t is taken as the random variable of the process, N(t), whose realization is n. All possible values of N(t) are the states of the process and their collection, $\{ 0, 1, 2, \ldots, n_M - 1, n_M \}$, is its state space where n_M is the number of packets that would deposit onto the maximum number of pores susceptible to narrowing. Note that the random variable, N(t), in the current model exclusively accounts for the number of packets that have already deposited onto the pores' mouths at any time t; hence, the analysis of the change in

the pores' sizes or lengths would require the formulation of models with different variables designated as the random variables.

Transition Diagram

The transition diagram of the process is presented in Figure 3.1. The circles indicate the system's possible states as identified in the preceding section, and the arrows describe transitions of the system at any moment.

Master Equation

For the pure-birth process, the probability balance around state n leads to

$$\frac{d}{dt}p_n(t) = \lambda_{n-1}(t)p_{n-1}(t) - \lambda_n(t)p_n(t), \quad n = 0,\ 1,\ 2,...,\ n_M - 1,\ n_M \tag{3.1}$$

which is the master, i.e., governing, equation of the process;[71, 73] see Appendix A. The term, $p_n(t)$, in the above expression denotes the probability that n carbon packets, or packets, have deposited at time t. Moreover, the intensity of birth, $\lambda_n(t)$, in Eq. (3.1) is given by

$$\lambda_n(t) = \frac{dn}{dt} = \alpha(n_M - n)^2 \tag{3.2}$$

where α is a proportionality constant. In this equation, the term, $(n_M - n)$, is the number of packets yet to deposit onto the pores' mouths at time t. Inserting Eq. (3.2) into Eq. (3.1) yields

$$\frac{d}{dt}p_n(t)$$

$$= \{\alpha[n_M - (n-1)]^2\}p_{n-1}(t) - [\alpha(n_M - n)^2]p_n(t), \quad n = 0,\ 1,\ 2,...,\ n_M - 1,\ n_M \tag{3.3}$$

Clearly, the above equation depends on realization n but is independent of time t.

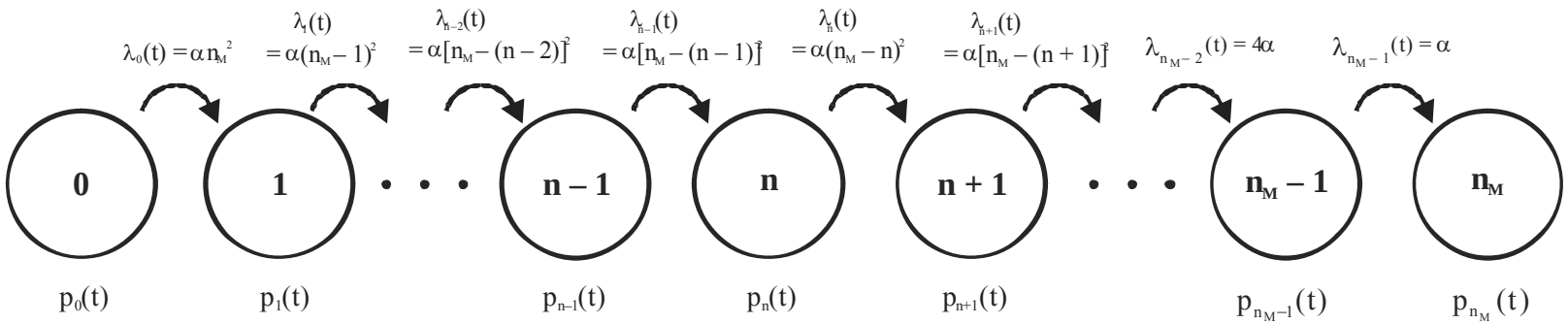


Figure 3.1. **Transition diagram of the pure-birth process representing pore-narrowing on ACs: The symbols, 0, 1, 2, …, (n – 1), n, (n + 1), …, (n_M – 1), n_M, are the states of the process; $p_0(t)$, $p_1(t)$, …, $p_{n-1}(t)$, $p_n(t)$, $p_{n+1}(t)$, …, $p_{n_M-1}(t)$, $p_{n_M}(t)$, are the corresponding state probabilities; and $\lambda_n(t) = \alpha(n_M - n)^2$ is the intensity of birth, which is a non-linear function of n for each transition.**

Mean and Variance

The mean and variance of the process are evaluated by solving the process' master equation, Eq. (3.3). Clearly, the intensity of birth, $\lambda_n(t)$, is embedded in the master equation; for the process of concern, $\lambda_n(t)$ is non-linear as given by Eq. (3.2). The non-linearity arising from the intensity of birth renders the solution of the master equation exceedingly complex to obtain. Nevertheless, this complexity can be circumvented by resorting to a rational approximation method, the system-size expansion of the master equation; see Appendix C. The system-size expansion entails that the random variable, N(t), be expressed as the sum of the macroscopic term, $\Omega\varphi(t)$, and the fluctuation term, $\Omega^{1/2}\Xi(t)$. The symbol, Ω, is the system's size, which is n_M in this work. Hence, the system-size expansion of the master equation yields the macroscopic equation in terms of $\varphi(t)$ governing the overall, i.e., mean, behavior of the process, and the equation in terms of $\Xi(t)$ governing the fluctuations of the process around the macroscopic values. Integration of the macroscopic equation results in an explicit expression for $\varphi(t)$. This expression, in turn, yields the mean of N(t), E[N(t)] or m(t), of the pore-narrowing as

$$m(t)= n_M\left(\frac{\alpha' t}{\alpha' t+1}\right) \tag{3.4}$$

where $\alpha' = (\alpha n_M)$. From this expression, the normalized form of the mean, $\eta(\tau)$, is

$$\eta(\tau)=\frac{m(\tau)}{n_M}=\left(\frac{\tau}{\tau+1}\right) \tag{3.5}$$

where $\tau = (\alpha' t)$ is the dimensionless time. Similarly, from the equation governing the fluctuations, the variance of N(t), Var[N(t)] or $\sigma^2(t)$, of the pore-narrowing is

$$\sigma^2(t)=\frac{n_M}{3(\alpha' t+1)}\left[1-\frac{1}{(\alpha' t+1)^3}\right] \tag{3.6}$$

or in terms of dimensionless time τ,

$$\sigma^2(\tau)=\frac{n_M}{3(\tau+1)}\left[1-\frac{1}{(\tau+1)^3}\right] \tag{3.7}$$

The standard deviation, $\sigma(t)$, is the square root of the variance, $\sigma^2(t)$; thus,

$$\sigma(t)=\left\{\frac{n_M}{3(\alpha' t+1)}\left[1-\frac{1}{(\alpha' t+1)^3}\right]\right\}^{1/2} \tag{3.8}$$

From this equation, the normalized form of the standard deviation, $\zeta(\tau)$, is obtained as

$$\zeta(\tau) = \frac{\sigma(\tau)}{n_M} = \left\{ \frac{1}{3n_M(\tau+1)} \left[1 - \frac{1}{(\tau+1)^3} \right] \right\}^{1/2} \tag{3.9}$$

Note that this expression is a function of τ and n_M. The standard deviation relative to the mean, termed the coefficient of variation, is defined as[112]

$$CV(t) = \frac{\sigma(t)}{m(t)} \tag{3.10}$$

Inserting Eqs. (3.4) and (3.8) for m(t) and $\sigma(t)$, respectively, into the above equation yields the coefficient of variation, CV(t), of the pore-narrowing as

$$CV(t) = \frac{1}{(\alpha' t)} \left\{ \frac{(\alpha' t+1)}{3n_M} \left[1 - \frac{1}{(\alpha' t+1)^3} \right] \right\}^{1/2} \tag{3.11}$$

or in terms of dimensionless time τ,

$$CV(\tau) = \frac{1}{\tau} \left\{ \frac{(\tau+1)}{3n_M} \left[1 - \frac{1}{(\tau+1)^3} \right] \right\}^{1/2} \tag{3.12}$$

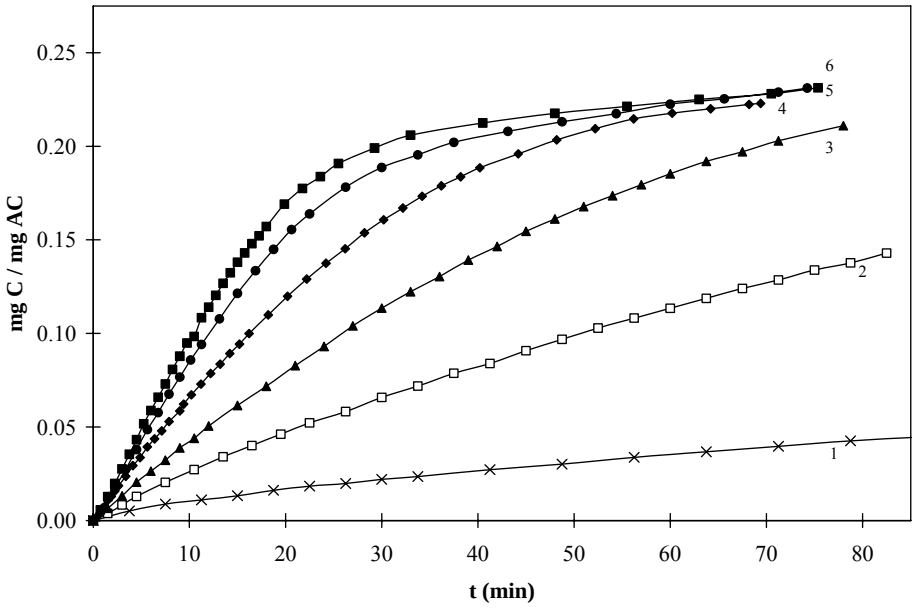
Note that this expression is also a function of τ and n_M.

Analysis of Experimental Data

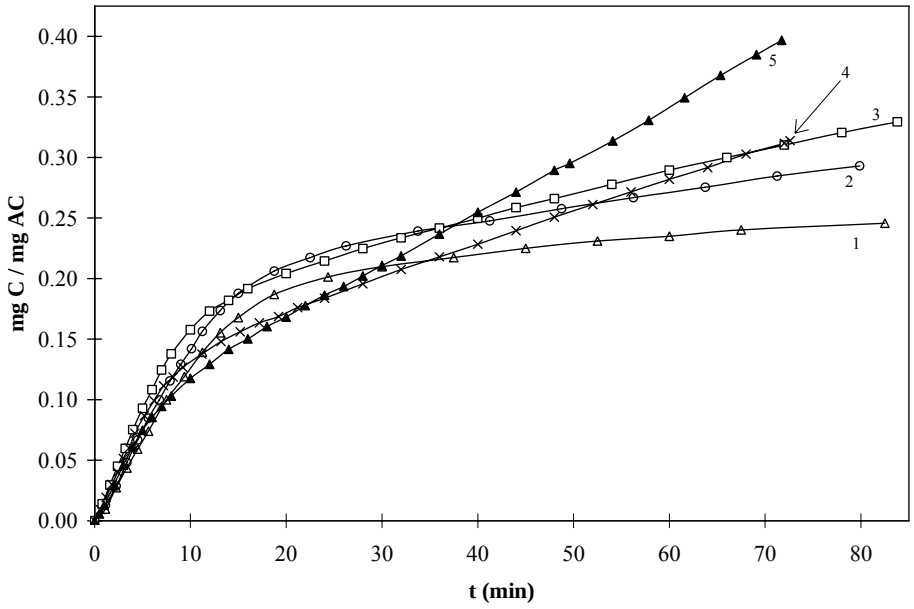
As illustrated in Figure 3.2, the available experimental data are presented in terms of the temporal increase in the amount of carbon deposited per unit weight of ACs at eleven temperatures. Specifically, they are given in the unit of milligrams of carbon per milligram of ACs, i.e., mg C/mg AC,[65] as listed in Table 3.1. The model derived in this work is validated with these data. To fit the model to the data, the number of carbon packets that have narrowed the pores, which is the random variable, N(t), needs to be related to the experimentally measurable variable, W(t), representing the weight of carbon already deposited on ACs. At any time t, W(t) should be proportional to N(t); thus,

$$W(t) = \omega N(t) \tag{3.13}$$

where ω is the weight of a single packet of carbon. The mean value of W(t), denoted by $m_W(t)$, is obtained from the above expression as follows:



(a)



(b)

Figure 3.2. Experimentally measured weights of carbon deposited (C) on activated carbon (AC) at different temperatures: (a) 1 – 873 K, 2 – 923 K, 3 – 948 K, 4 – 973 K, 5 – 1023 K, and 6 – 1048 K; (b) 1 – 1073 K, 2 – 1098 K, 3 – 1123 K, 4 – 1173 K, and 5 – 1223 K.*

* Data were obtained with activated carbon ACW.[65]

Table 3.1. Experimentally Measured Weights of Carbon Deposited (C) on Activated Carbon (AC) at Different Temperatures*

T = 873 K		T = 923 K		T = 948 K		T = 973 K	
t, min	mg C/mg AC	t, min	mg C/mg AC	t, min	mg C/mg AC	t, min	mg C/mg AC
0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000
3.75	0.005	1.50	0.004	1.50	0.007	0.38	0.002
7.50	0.009	3.00	0.008	3.00	0.013	0.75	0.004
11.25	0.011	4.50	0.013	4.50	0.021	1.13	0.007
15.00	0.013	7.50	0.020	6.00	0.026	1.50	0.011
18.75	0.016	10.50	0.027	7.50	0.032	1.88	0.013
22.50	0.018	13.50	0.034	9.00	0.039	2.25	0.016
26.25	0.020	16.50	0.040	10.50	0.044	2.63	0.019
30.00	0.022	19.50	0.046	12.00	0.051	3.38	0.024
33.75	0.024	22.50	0.052	15.00	0.062	4.13	0.029
41.25	0.027	26.25	0.058	18.00	0.072	4.88	0.034
48.75	0.030	30.00	0.066	21.00	0.083	5.63	0.039
56.25	0.034	33.75	0.072	24.00	0.093	6.38	0.044
63.75	0.037	37.50	0.079	27.00	0.104	7.13	0.048
71.25	0.040	41.25	0.084	30.00	0.114	7.88	0.053
78.75	0.043	45.00	0.091	33.00	0.122	9.00	0.059
86.25	0.045	48.75	0.097	36.00	0.130	9.40	0.062
93.75	0.048	52.50	0.103	39.00	0.139	10.20	0.067
101.25	0.051	56.25	0.108	42.00	0.147	11.20	0.073
104.25	0.051	60.00	0.113	45.00	0.155	12.20	0.079
		63.75	0.119	48.00	0.161	13.20	0.084
		67.50	0.124	51.00	0.168	14.20	0.089
		71.25	0.129	54.00	0.174	15.20	0.094
		75.00	0.134	57.00	0.179	16.20	0.100
		78.75	0.138	60.00	0.185	18.20	0.110
		82.50	0.143	63.75	0.192	20.20	0.120
				67.50	0.197	22.20	0.129
				71.25	0.203	24.20	0.138
				78.00	0.211	26.20	0.145
						28.20	0.154
						30.20	0.161
						32.20	0.167
						34.20	0.173
						36.20	0.179
						38.20	0.184
						40.20	0.189
						44.20	0.196
						48.20	0.203
						52.20	0.209
						56.20	0.215
						60.20	0.218
						64.20	0.220
						68.20	0.222
						69.40	0.223

* Data were obtained with activated carbon ACW.[65]

Table 3.1. (Cont'd.)

T = 1023 K		T = 1048 K		T = 1073 K		T = 1098 K	
t, min	mg C/mg AC	t, min	mg C/mg AC	t, min	mg C/mg AC	t, min	mg C/mg AC
0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000
1.13	0.007	0.75	0.006	1.13	0.010	1.13	0.013
2.25	0.017	1.50	0.013	2.25	0.027	2.25	0.029
3.38	0.027	2.25	0.020	3.38	0.044	3.38	0.048
4.50	0.038	3.00	0.028	4.50	0.059	4.50	0.067
5.63	0.049	3.75	0.035	5.63	0.074	5.63	0.085
6.75	0.058	4.50	0.043	7.50	0.100	6.75	0.100
7.88	0.068	5.25	0.052	9.38	0.119	7.88	0.116
9.00	0.077	6.00	0.059	11.25	0.139	9.00	0.129
10.13	0.086	6.75	0.066	13.13	0.155	10.13	0.142
11.25	0.094	7.50	0.073	15.00	0.168	11.25	0.156
13.13	0.108	8.25	0.081	18.75	0.187	13.13	0.174
15.00	0.121	9.00	0.088	24.38	0.201	15.00	0.188
16.88	0.134	9.75	0.095	30.00	0.210	18.75	0.206
18.75	0.145	10.50	0.098	37.50	0.217	22.50	0.217
20.63	0.156	11.25	0.108	45.00	0.225	26.25	0.227
22.50	0.164	12.00	0.114	52.50	0.231	33.75	0.239
26.25	0.178	12.75	0.120	60.00	0.235	41.25	0.248
30.00	0.189	13.50	0.127	67.50	0.240	48.75	0.258
33.75	0.195	14.25	0.132	82.50	0.246	56.25	0.267
37.50	0.202	15.00	0.138			63.75	0.275
43.13	0.208	15.75	0.143			71.25	0.285
48.75	0.213	16.50	0.148			79.88	0.293
54.38	0.217	17.25	0.152				
60.00	0.223	18.00	0.157				
65.63	0.225	19.88	0.169				
71.25	0.229	21.75	0.178				
74.25	0.231	23.63	0.184				
		25.50	0.191				
		29.25	0.199				
		33.00	0.206				
		40.50	0.212				
		48.00	0.218				
		55.50	0.221				
		63.00	0.225				
		70.50	0.228				
		75.38	0.231				

Table 3.1. (Cont'd.)

T = 1123 K		T = 1173 K		T = 1223 K	
t, min	mg C/mg AC	t, min	mg C/mg AC	t, min	mg C/mg AC
0.00	0.000	0.00	0.000	0.00	0.000
0.80	0.014	0.60	0.009	0.50	0.006
1.60	0.029	1.20	0.019	1.00	0.013
2.40	0.045	1.80	0.030	2.00	0.029
3.20	0.060	2.40	0.040	3.00	0.046
4.00	0.075	3.00	0.051	4.00	0.061
5.00	0.093	3.60	0.060	5.00	0.075
6.00	0.108	4.20	0.072	6.00	0.085
7.00	0.125	5.20	0.087	7.00	0.095
8.00	0.138	6.20	0.099	8.00	0.103
10.00	0.158	7.20	0.111	10.00	0.118
12.00	0.173	8.20	0.119	12.00	0.129
14.00	0.182	9.20	0.127	14.00	0.142
16.00	0.192	11.20	0.138	16.00	0.150
20.00	0.204	13.20	0.148	18.00	0.160
24.00	0.214	15.20	0.156	20.00	0.168
28.00	0.225	17.20	0.163	22.00	0.178
32.00	0.234	19.20	0.169	24.00	0.186
36.00	0.242	21.20	0.176	26.00	0.193
40.00	0.250	24.00	0.184	28.00	0.202
44.00	0.259	28.00	0.196	30.00	0.211
48.00	0.266	32.00	0.208	32.00	0.219
54.00	0.278	36.00	0.218	36.00	0.237
60.00	0.290	40.00	0.228	40.00	0.255
66.00	0.300	44.00	0.240	44.00	0.271
72.00	0.310	48.00	0.251	48.00	0.289
78.00	0.321	52.00	0.261	49.60	0.295
83.80	0.329	56.00	0.272	54.10	0.314
		60.00	0.282	57.85	0.331
		64.00	0.292	61.60	0.349
		68.00	0.303	65.35	0.368
		72.00	0.312	69.10	0.385
		72.60	0.314	71.73	0.397

$$m_W(t) = E[W(t)]$$
$$= E[\omega N(t)]$$
$$= \omega E[N(t)]$$

or

$$m_W(t) = \omega m(t)$$

Substituting Eq. (3.4) for m(t) into this equation yields

$$m_W(t) = \omega n_M \left(\frac{\alpha' t}{\alpha' t + 1} \right)$$

or

$$m_W(t) = W_M \left(\frac{\alpha' t}{\alpha' t + 1} \right) \tag{3.14}$$

where W_M, or (ωn_M), is the weight of carbon that would deposit onto the maximum number of pores susceptible to narrowing. In terms of dimensionless time τ, the above equation can be rewritten as

$$m_W(\tau) = W_M \left(\frac{\tau}{\tau + 1} \right) \tag{3.15}$$

From this expression, the normalized form of the mean, $\eta_W(\tau)$, is,

$$\eta_W(\tau) = \frac{m_W(\tau)}{W_M} = \left(\frac{\tau}{\tau + 1} \right) \tag{3.16}$$

Note that this expression is identical to Eq. (3.5) for $\eta(\tau)$. Similarly, the variance of W(t), $\sigma_W^2(t)$, is obtained from Eq. (3.13) as

$$\sigma_W^2(t) = Var[W(t)]$$
$$= Var[\omega N(t)]$$
$$= \omega^2 Var[N(t)]$$

or

$$\sigma_W^2(t) = \omega^2 [\sigma^2(t)]$$

Substituting Eq. (3.6) for $\sigma^2(t)$ into the above expression yields

$$\sigma_W^2(t) = \frac{\omega^2 n_M}{3(\alpha' t + 1)} \left[1 - \frac{1}{(\alpha' t + 1)^3} \right]$$

From this equation, the standard deviation of W(t), $\sigma_W(t)$, is,

$$\sigma_W(t) = \omega\left\{\frac{n_M}{3(\alpha' t+1)}\left[1-\frac{1}{(\alpha' t+1)^3}\right]\right\}^{1/2}$$

or

$$\sigma_W(t) = W_M\left\{\frac{1}{3n_M(\alpha' t+1)}\left[1-\frac{1}{(\alpha' t+1)^3}\right]\right\}^{1/2}$$

In terms of dimensionless time τ, this equation can be transformed into

$$\sigma_W(\tau) = W_M\left\{\frac{1}{3n_M(\tau+1)}\left[1-\frac{1}{(\tau+1)^3}\right]\right\}^{1/2} \tag{3.17}$$

From this expression, the normalized form of the standard deviation, $\zeta_W(\tau)$, is,

$$\zeta_W(\tau) = \frac{\sigma_W(\tau)}{W_M} = \left\{\frac{1}{3n_M(\tau+1)}\left[1-\frac{1}{(\tau+1)^3}\right]\right\}^{1/2} \tag{3.18}$$

Note that this equation is identical to Eq. (3.9) for $\zeta(\tau)$. From Eqs. (3.15) and (3.17), the coefficient of variation, $CV_W(\tau)$, is obtained as

$$CV_W(\tau) = \frac{\sigma_W(\tau)}{m_W(\tau)} = \frac{1}{\tau}\left\{\frac{(\tau+1)}{3n_M}\left[1-\frac{1}{(\tau+1)^3}\right]\right\}^{1/2} \tag{3.19}$$

Note that this equation is identical to Eq. (3.12) for $CV(\tau)$.

Monte Carlo Simulation

The master equation of the pure-birth process, Eq. (3.1), is stochastically simulated by means of the Monte Carlo method. The two basic procedures to implement the method, one resorting to the event-driven approach[74, 79, 120-127] and the other resorting to the time-driven approach,[124, 128] are described in detail; these two approaches differ in the manner of updating the simulation clock of the process' temporal evolution.

Event-driven approach

The event-driven approach advances the simulation clock by a random waiting time, ν, which has an exponential distribution.[74, 122] No event takes place during the time interval, $(t, t+\nu)$, and only one event occurs at the end of this time interval at which the state of the

system is specified by the probability of transition corresponding to each event. For the pure-birth process of interest, the series of steps to perform the Monte Carlo simulation via the event-driven approach is given below.

Step 1. Define the initial number of carbon packets, n_0, the total number of simulations, Z_f, and the length of each simulation, t_f. Initialize the simulation counter as $Z \leftarrow 1$.

Step 2. Initialize clock time t, data-recording time θ,[129] the realization of N(t) at time t for simulation Z, $n_Z(t)$, and the realization of $N(\theta)$ at time θ for simulation Z, $n_Z(\theta)$, as follows:

$$t \leftarrow t_0$$

$$\theta_0 \leftarrow t_0$$

$$n_Z(t_0) \leftarrow n_0$$

$$n_Z(\theta_0) \leftarrow n_Z(t_0)$$

Step 3. Sample a realization u from the uniform random variable, U, on interval (0, 1). Estimate ν according to the following expression; [74]

$$\nu = \frac{-1}{[\alpha(n_M - n)^2]} \ell n(1-u) \tag{3.20}$$

with $n = n_Z(t)$. Note that the denominator on the right-hand side of this expression is the intensity of birth, $\lambda_n(t)$, as given by Eq. (3.2); see Appendices E and F.

Step 4. Advance clock time as $t \leftarrow (t + \nu)$.

Step 5. If ($\theta < t$), then continue to the next step; otherwise, continue to Step 8.

Step 6. Compute the sample mean, variance, and standard deviation at time θ as follows:

a. Record the value of realization at θ:

$$n_Z(\theta) \leftarrow n_Z(t - \nu)$$

b. Store the sum of realizations at θ:

$$\Xi_Z(\theta) \leftarrow \sum_{Z=1}^{Z} n_Z(\theta)$$

c. Store the sum of squares of realizations at θ:

$$\Phi_Z(\theta) \leftarrow \sum_{Z=1}^{Z} n_Z^2(\theta)$$

d. Store the square of sum of realizations at θ:

$$\Psi_Z(\theta) \leftarrow \left[\sum_{Z=1}^{Z} n_Z(\theta)\right]^2 = \left[\Xi_Z(\theta)\right]^2$$

e. Compute the sample mean at θ: [75, 122, 123]

$$m_Z(\theta) \leftarrow \frac{1}{Z}\sum_{Z=1}^{Z} n_Z(\theta) = \frac{1}{Z}\Xi_Z(\theta) \tag{3.21}$$

f. If $1 < Z \le Z_f$, then compute the sample variance and standard deviation at θ: [75, 122, 123]

$$s_Z^2(\theta) \leftarrow \frac{1}{(Z-1)}\left\{\sum_{Z=1}^{Z} n_Z^2(\theta) - \frac{1}{Z}\left[\sum_{Z=1}^{Z} n_Z(\theta)\right]^2\right\} = \frac{1}{(Z-1)}\left\{\Phi_Z(\theta) - \frac{1}{Z}\Psi_Z(\theta)\right\} \tag{3.22}$$

$$s_Z(\theta) \leftarrow [s_Z^2(\theta)]^{1/2} \tag{3.23}$$

Step 7. Advance θ by a conveniently small Δθ as $\theta \leftarrow (\theta + \Delta\theta)$. If $(\theta \le t_f)$, then return to Step 5; otherwise, continue to Step 10.

Step 8. Determine the state of the system at the end of time interval $(t, t+\nu)$. At this juncture, a birth event occurs, i.e., the population of carbon packets increases by one; thus,

$$n_Z(t) \leftarrow [n_Z(t-\nu) + 1]$$

$$n_Z(\theta) \leftarrow n_Z(t)$$

Step 9. Repeat Steps 3 through 8 until t_f is reached.

Step 10. Update simulation counter as $Z \leftarrow (Z + 1)$.

Step 11. Repeat Steps 2 through 10 until Z_f is reached.

Given in Appendix G is the computer code for performing Monte Carlo simulation of the pure-birth process via the event-driven approach as presented above.

Time-driven approach

As briefly indicated at the outset of this section, the time-driven approach[124, 128] differs from the event-driven approach: It advances the simulation clock by a fixed time increment of Δt, which is sufficiently small so that at most one or no event occurs during time interval $(t, t+\Delta t)$. At the end of this interval, the state of the process is determined by the probability of

transition corresponding to each event. For the pure-birth process of interest, the series of steps to perform the Monte Carlo simulation via the time-driven approach is given below.

Step 1. Define the initial number of carbon packets, n_0, the total number of simulations, Z_f, and the length of each simulation, t_f. Initialize the simulation counter as $Z \leftarrow 1$. Compute time increment Δt as follows:

$$\Delta t = \frac{1}{[c\ \lambda_n^M(t)]} \tag{3.24}$$

where c is a constant greater than 1,[124] and $\lambda_n^M(t)$, the maximum possible value of the intensity of birth; for the pure-birth process, $\lambda_n^M(t) = \alpha n_M^2$.

Step 2. Initialize clock time t, and the realization of N(t) at time t for simulation Z, $n_Z(t)$, as follows:

$$t \leftarrow t_0$$

$$n_Z(t_0) \leftarrow n_0$$

Step 3. Compute the sample mean, variance, and standard deviation at time t as follows:

a. Record the value of realization at t:

$$n_Z(t) \leftarrow n_Z$$

b. Store the sum of realizations at t:

$$\Xi_Z(t) \leftarrow \sum_{Z=1}^{Z} n_Z(t)$$

c. Store the sum of squares of realizations at t:

$$\Phi_Z(t) \leftarrow \sum_{Z=1}^{Z} n_Z^2(t)$$

d. Store the square of sum of realizations at t:

$$\Psi_Z(t) \leftarrow \left[\sum_{Z=1}^{Z} n_Z(t)\right]^2 = \left[\Xi_Z(t)\right]^2$$

e. Compute the sample mean at t:

$$m_Z(t) \leftarrow \frac{1}{Z}\sum_{Z=1}^{Z} n_Z(t) = \frac{1}{Z}\Xi_Z(t) \tag{3.25}$$

f. If $1 < Z \leq Z_f$, then compute the sample variance and standard deviation at t:

$$s_Z^2(t) \leftarrow \frac{1}{(Z-1)}\left\{\sum_{Z=1}^{Z} n_Z^2(t) - \frac{1}{Z}\left[\sum_{Z=1}^{Z} n_Z(t)\right]^2\right\} = \frac{1}{(Z-1)}\left\{\Phi_Z(t) - \frac{1}{Z}\Psi_Z(t)\right\} \qquad (3.26)$$

$$s_Z(t) \leftarrow [s_Z^2(t)]^{1/2} \qquad (3.27)$$

Step 4. Advance time as $t \leftarrow (t + \Delta t)$.

Step 5. Estimate the probability of transition for the birth event as $\{[\lambda_n(t)]\Delta t\}$ with $n = n_Z(t)$.

Step 6. Determine the state of the system at the end of time interval $(t, t + \Delta t)$. In this connection, sample a realization u from the uniform random variable U on interval (0, 1) and compare it with $\{[\lambda_n(t)]\Delta t\}$. If $u < \{[\lambda_n(t)]\Delta t\}$, then a birth event occurs; thus,

$$n_Z(t) \leftarrow [n_Z(t - \Delta t) + 1]$$

Otherwise, no event occurs; hence,

$$n_Z(t) \leftarrow n_Z(t - \Delta t)$$

Step 7. Repeat Steps 3 through 6 until t_f is reached.

Step 8. Update the simulation counter as $Z \leftarrow (Z + 1)$.

Step 9. Repeat Steps 2 through 8 until Z_f is reached.

Given in Appendix G is the computer code for performing Monte Carlo simulation of the pure-birth process via the time-driven approach as presented above.

Results and Discussion

The model formulated, in terms of $m_W(t)$ as given in Eq. (3.14), has been regressed on the available experimental data[65] by resorting to the adaptive random search procedure;[113, 114] it has resulted in the values of W_M and those of α' listed in Table 3.2. These values have rendered it possible to evaluate the dimensionless time, $(\alpha' t)$, i.e., τ, and the normalized mean, $\eta_W(\tau)$, from Eq. (3.16), the values of which are plotted in Figure 3.3 as a function of τ. The corresponding experimentally measured weights in milligrams of carbon deposited per milligram of ACs are normalized by dividing them by W_M; the values of the resultant quantity, denoted as $w(\tau)$, are superimposed in the same figure for comparison. Clearly, $\eta_W(\tau)$ increases and asymptotically

Table 3.2. Values of α' and W_M for the Pore-narrowing at Different Temperatures.

temperature, K (C)	α', $s^{-1} \cdot 10^4$ (min^{-1})	W_M (mg C)
873 (599.85)	1.48 (0.009)	0.105
923 (649.85)	1.04 (0.006)	0.419
948 (674.85)	1.62 (0.010)	0.501
973 (699.85)	3.70 (0.022)	0.385
1023 (749.85)	6.68 (0.040)	0.322
1048 (774.85)	8.25 (0.050)	0.312
1073 (799.85)	12.21 (0.073)	0.296
1098 (824.85)	11.13 (0.067)	0.346
1123 (849.85)	11.17 (0.067)	0.362
1173 (899.85)	7.73 (0.046)	0.378
1223 (949.85)	2.77 (0.017)	0.680

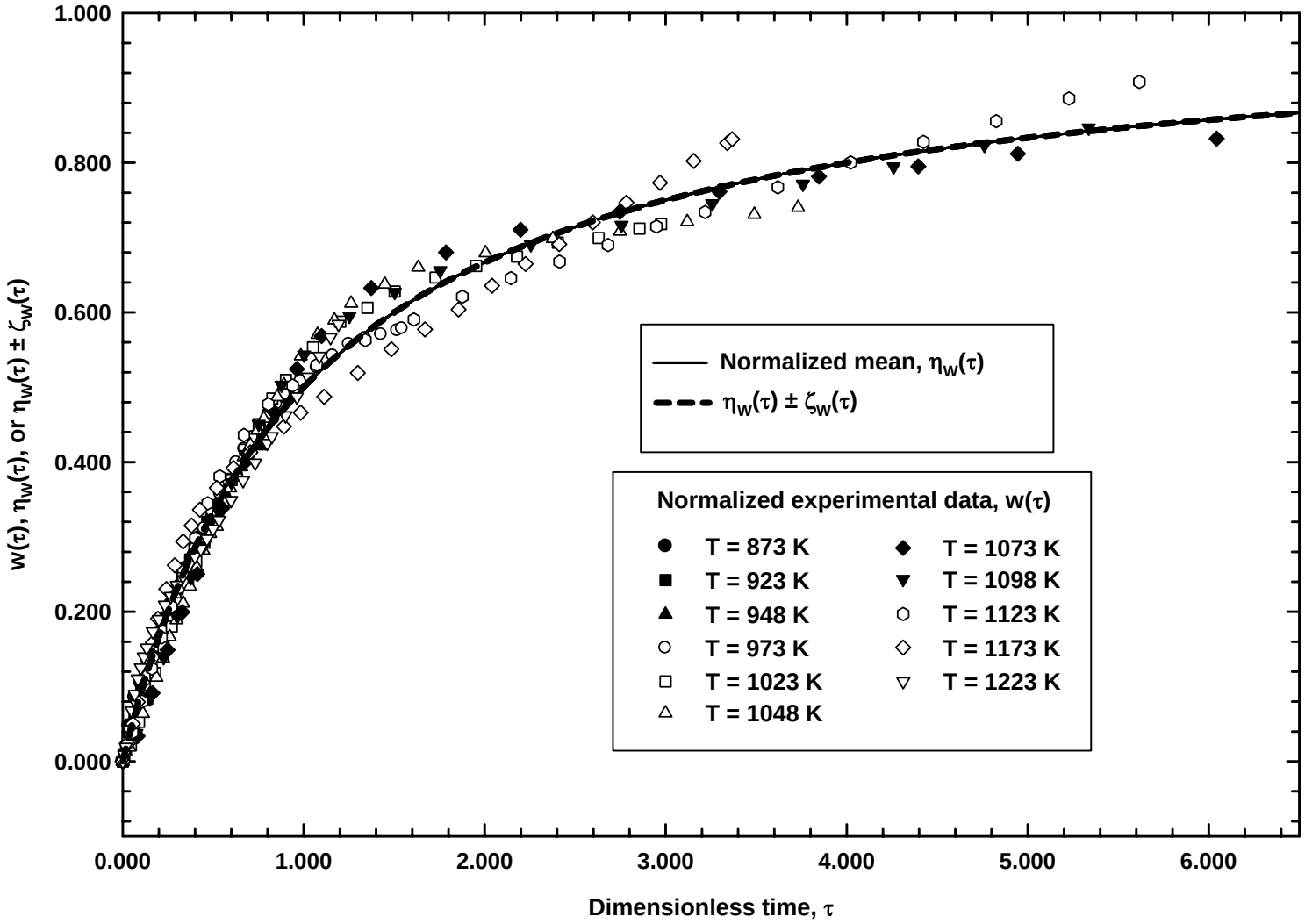


Figure 3.3. Normalized mean $\eta_W(\tau)$ and normalized standard deviation envelope $[\eta_W(\tau) \pm \zeta_W(\tau)]$ as functions of dimensionless time τ for the pore-narrowing.

approaches to 1 as τ progresses; this asymptotic value for $\eta_W(\tau)$ can be discerned from Eq. (3.16). The normalized standard deviation, $\zeta_W(\tau)$, as computed by Eq. (3.18), signifies the deviations attributable to the internal or characteristic noises of the process as predicted by the stochastic model.[109] The normalized standard deviation envelope, i.e., $\eta_W(\tau) \pm \zeta_W(\tau)$, is plotted in Figure 3.3. Note that many of the experimental data[65] lie appreciably beyond the expected variation, or scattering; this is almost always the case: The overall deviations of the experimental data include not only those attributable to the internal noises of the process as predicted by the model, but also to the external noises due to unavoidable measurement errors and instrumental deficiencies that can never be totally suppressed. The coefficient of variation, CV(t), as defined by Eq. (3.11), provides a more meaningful relative measurement of the variability or dispersion of the values of a random variable about their mean than the standard deviation, $\sigma(t)$. In general, the smaller the values of random variable N(t), i.e., the population size, the greater the extent of the expected fluctuations about their mean.

As evident from Eqs. (3.18) and (3.19), the value of n_M must be estimated in view of the uncertainty involved in its actual value. The order of magnitude estimate of n_M is obtained by dividing the weight of carbon that would deposit onto the maximum number of pores susceptible to narrowing, W_M, at a temperature of reference by the weight of a single packet of carbon, ω. For illustration, the temperature of reference is selected as 973 K, and thus, the value of W_M is 0.385 mg C as listed in Table 3.2. The order of magnitude estimate for ω is obtained by multiplying the volume of a single ideal carbon packet by the density of carbon. The former is assumed to be equivalent to that of a single ideal mesopore, which has been estimated approximately as $3 \cdot 10^{-17}$ cm^3,[109] and the latter is 2.1 $g \cdot cm^{-3}$;[130] thus, the value of ω is estimated as $0.63 \cdot 10^{-13}$ mg C. These values of W_M and ω yield the estimate of n_M as $6.12 \cdot 10^{12}$ packets per milligram of ACs.

Figure 3.4 shows the normalized mean, $\eta_W(\tau)$, and the normalized standard deviation envelope, $\eta_W(\tau) \pm \zeta_W(\tau)$, resulting from Monte Carlo simulation via the event-driven and time-driven approaches; these values have been computed by averaging 200 iterations, i.e., Z = 200.

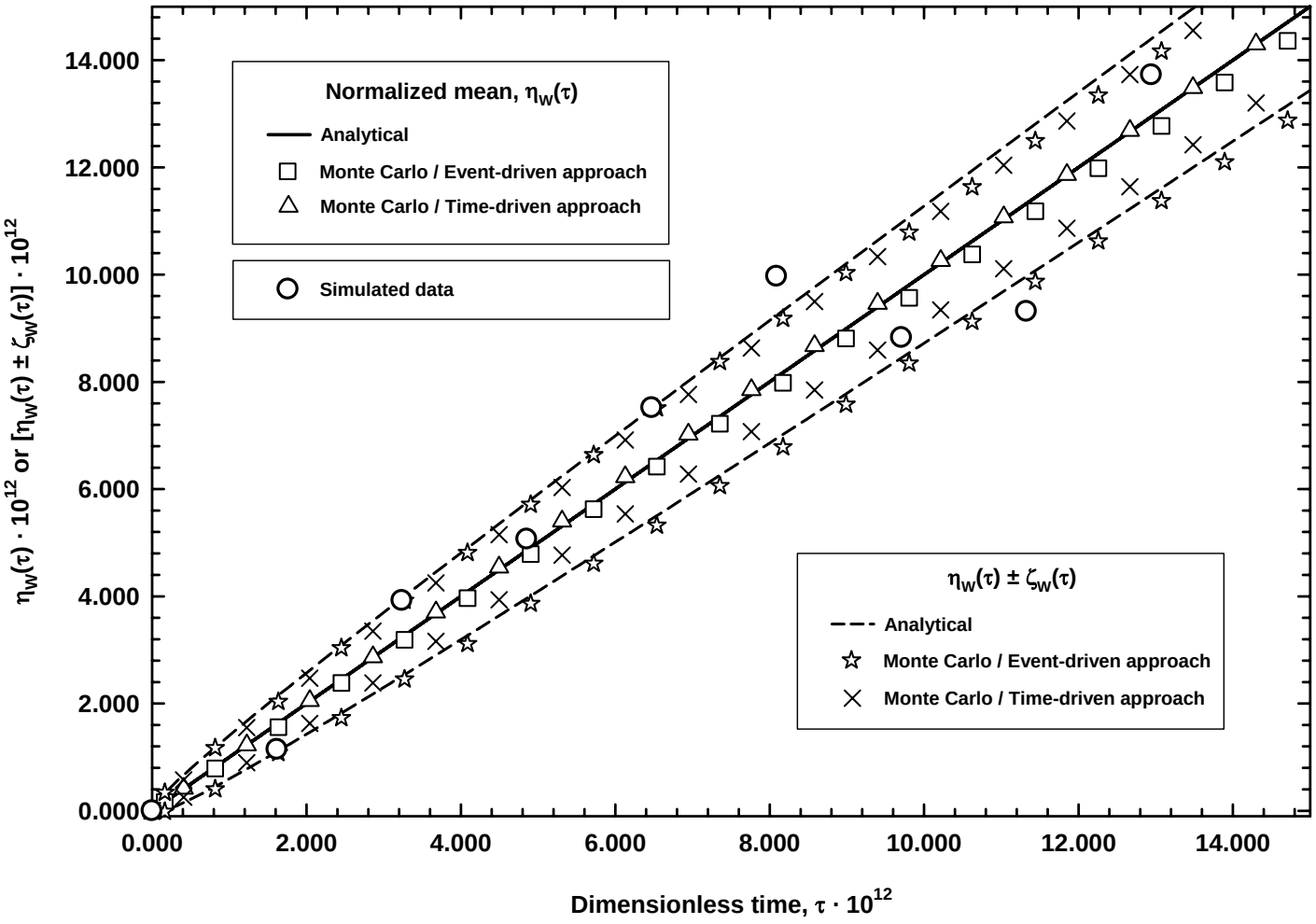


Figure 3.4. **Normalized mean $\eta_W(\tau)$ and normalized standard deviation envelope $[\eta_W(\tau) \pm \zeta_W(\tau)]$ as functions of dimensionless time τ at the early stage of the pore-narrowing at 973 K: The average of 200 Monte Carlo simulations via the event-driven and time-driven approaches are compared with the analytical solutions resulting from the system-size expansion of the master equation.**

As an example, the simulation has been carried out until the time when approximately 100 carbon packets have deposited onto the mouths of an equal number of open pores on activated carbons at 973 K; this time has been estimated as $7.44 \cdot 10^{-10}$ min; see Appendix H. Thus, the time span of the simulation corresponds to the very outset of the pore-narrowing where the number of carbon packets is small, thereby magnifying the fluctuations of the process about its mean value. Figure 3.4 also presents simulated experimental data to illustrate the process' inherent fluctuations; they have been generated according to the procedure outlined in Appendix H. Moreover, the values of $\eta_W(\tau)$ and $[\eta_W(\tau) \pm \zeta_W(\tau)]$ computed analytically from the system-size expansion of the master equation are superimposed in the same figure for comparison. Note that the results from Monte Carlo simulation are in accord with the corresponding analytical results.

Summary

A stochastic model has been derived for the formation of CMSs by carbon deposition on ACs. Specifically, the model is based on a pure-birth process with a non-linear intensity of transition. The complexity in solving the resultant master equation has been circumvented by resorting to a rational approximation method, system-size expansion. The mean and variance of the amount of carbon deposited onto the open pores of ACs have been computed on the basis of expressions derived from the system-size expansion of the master equation. The model has been validated by fitting it to the available experimental data. The mean values of the model at various times are in good accord with these data. As expected, the data's fluctuations around the mean values are more noticeable than those predicted by the model: In addition to the process' internal noises, the deviations of the experimental data also account for the external noises due to unavoidable measurement errors. Moreover, the non-linear master equation of the model based on the pure-birth process has been simulated by the Monte Carlo method via the event-driven and time-driven approaches at the very outset of the pore-narrowing. The model's mean and variance resultant from Monte Carlo simulation are in line with those obtained analytically based on the system-size expansion of the master equation.

Notation

$m(t)$ = mean of the random variable, N(t)

$m_W(t)$ = mean of the experimental measurable variable, W(t), mg C

$N(t)$ = random variable representing the number of carbon packets that have already deposited onto the pores' mouths of ACs at time t

n = realization of the random variable, N(t)

$p_n(t)$ = probability that n carbon packets have deposited at time t

t = time

$W(t)$ = experimentally measurable variable representing the weight of carbon already deposited on ACs, mg C

Greek letters

α = proportionality constant in the intensity of birth, $(\text{number})^{-1} \cdot (t)^{-1}$

$\lambda_n(t)$ = intensity of birth for the pure-birth process in state n at time t

$\sigma^2(t)$ = variance of the random variable, N(t)

$\sigma_W^2(t)$ = variance of the experimentally measurable variable, W(t)

τ = dimensionless time

CHAPTER 4 - Formation of Carbon Molecular Sieves by Carbon Deposition: Pure-Death Process with a Non-Linear Intensity of Transition Based on a Single Random Variable

In this chapter, the formation of CMSs due to the narrowing of pores by carbon deposition is analyzed and modeled as a pure-death process with a non-linear intensity of transition based on a single random variable. This is in contrast to Chapter 3, where the formation of CMSs has been analyzed and modeled as a pure-birth process. In this chapter, it is considered that the driving force of the pore-narrowing process by carbon deposition is a function of not only the number of pores susceptible to narrowing, or open pores, but also of the number of pores that have already been narrowed at any time. Herein, the form of such a function is of the second-order; as a result, the corresponding intensity function is non-linear.

Identification of Random Variable and State Space

As discerned from the prologue, the random variable of the process, N(t), with realization n is identified as the number of pores susceptible to narrowing, i.e., the open pores, at time t. All possible values of N(t) are the states of the process and their collection, $\{ n_0, n_0 - 1, \ldots, 2, 1, 0 \}$, is its state space where n_0 is the initial number of open pores, i.e., n at $t = 0$. Note that the random variable, N(t), in the current model exclusively accounts for the number of open pores at any time t; thus, the analysis of the change in the pores' sizes or lengths would require the formulation of models with different variables designated as the random variables.

Transition Diagram

Figure 4.1 illustrates the transition diagram of the pure-death process under consideration. Note that the transitions of the system in the pure-death process occur in the opposite direction of those in the pure-birth process as presented in Figure 3.1.

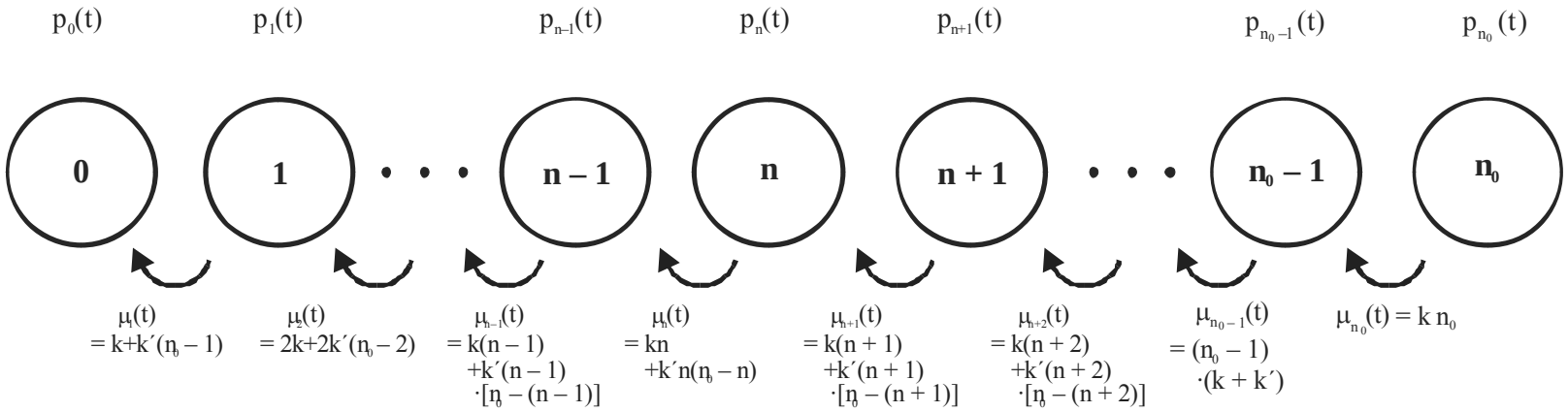


Figure 4.1. **Transition diagram of the pure-death process representing pore-narrowing on ACs: The symbols, n_0, $(n_0 - 1)$, …, $(n + 1)$, n, $(n - 1)$, …, 2, 1, 0, are the states of the process; $p_{n_0}(t)$, $p_{n_0-1}(t)$, …, $p_{n+1}(t)$, $p_n(t)$, $p_{n-1}(t)$, …, $p_1(t)$, $p_0(t)$, are the corresponding state probabilities; and $\mu_n(t) = kn + k'n(n_0 - n)$ is the intensity of death, which is a non-linear function of n for each transition.**

Master Equation

For the pure-death process, the probability balance around state n leads to

$$\frac{d}{dt}p_n(t) = \mu_{n+1}p_{n+1}(t) - \mu_n p_n(t), \quad n = n_0, n_0 - 1, \ldots, 2, 1, 0 \tag{4.1}$$

which is the master, i.e., governing, equation of the process;[71, 73] see Appendix I. The term, $p_n(t)$, in the above expression denotes the probability that n pores are open at time t. Moreover, the term, $\mu_n(t)$, is the intensity function or intensity of death, which is given by

$$\mu_n(t) = -\frac{dn}{dt} = kn + k'n(n_0 - n) \tag{4.2}$$

where k and k' are proportionality constants. In this equation, the term, $(n_0 - n)$, i.e., the difference between the maximum number of open pores and the number of open pores at any time t, is the number of pores that have already been narrowed at time t. Thus, the intensity of death, Eq. (4.2), is a function of not only the number of open pores but also the number of pores that have already been narrowed at time t. Inserting Eq. (4.2) into Eq. (4.1) gives rise to

$$\begin{aligned}&\frac{d}{dt}p_n(t)\\ &= \left\{k(n+1) + k'(n+1)[n_0 - (n+1)]\right\}p_{n+1}(t)\\ &\quad -[kn + k'n(n_0 - n)]p_n(t), \qquad n = n_0, n_0 - 1, \ldots, 2, 1, 0\end{aligned} \tag{4.3}$$

Clearly, this equation depends on realization n but is independent of time t.

Mean and Variance

The intensity of death, $\mu_n(t)$, as given by Eq. (4.2) is non-linear, thereby rendering the solution of the master equation, Eq. (4.3), exceedingly complex. Thus, the mean and variance of the process need be evaluated via the system-size expansion of the master equation; see Appendix J. Upon expansion, the mean of N(t), E[N(t)] or m(t), for the pore-narrowing is obtained from Eq. (4.3) as

$$m(t) = n_0\left\{\frac{1}{1 + \beta[\exp(\alpha t) - 1]}\right\} \tag{4.4}$$

where $\alpha = (k + k'n_0)$ and $\beta = k(k + k'n_0)^{-1}$. From this expression, the normalized, or dimensionless, form of the mean, $\eta(\tau)$, is

$$\eta(\tau) = \frac{m(\tau)}{n_0} = \frac{1}{1 + \beta[\exp(\tau) - 1]} \tag{4.5}$$

where $\tau = (\alpha t)$ is the dimensionless time. Similarly, the variance of N(t), Var[N(t)] or $\sigma^2(t)$, of the pore-narrowing is

$$\sigma^2(t) = n_0 \frac{\beta \exp(\alpha t)}{\{1 + \beta[\exp(\alpha t) - 1]\}^4} \cdot \left(2\beta - 1 + \exp(\alpha t)\left\{1 - 2\beta[1 + (\beta - 1)(\alpha t)] + 2\beta^2 \sinh(\alpha t)\right\}\right) \tag{4.6}$$

or in terms of dimensionless time τ,

$$\sigma^2(\tau) = n_0 \frac{\beta \exp(\tau)}{\{1 + \beta[\exp(\tau) - 1]\}^4} \cdot \left(2\beta - 1 + \exp(\tau)\left\{1 - 2\beta[1 + (\beta - 1)\tau] + 2\beta^2 \sinh(\tau)\right\}\right) \tag{4.7}$$

From Eq. (4.6), the standard deviation, $\sigma(t)$, is obtained as

$$\sigma(t) = n_0^{1/2} \frac{[\beta \exp(\alpha t)]^{1/2}}{\{1 + \beta[\exp(\alpha t) - 1]\}^2} \cdot \left(2\beta - 1 + \exp(\alpha t)\left\{1 - 2\beta[1 + (\beta - 1)(\alpha t)] + 2\beta^2 \sinh(\alpha t)\right\}\right)^{1/2} \tag{4.8}$$

The normalized form of the standard deviation, $\zeta(\tau)$, is obtained from Eq. (4.7) as

$$\zeta(\tau) = \frac{\sigma(\tau)}{n_0} = \frac{1}{n_0^{1/2}} \cdot \frac{[\beta \exp(\tau)]^{1/2}}{\{1 + \beta[\exp(\tau) - 1]\}^2} \cdot \left(2\beta - 1 + \exp(\tau)\left\{1 - 2\beta[1 + (\beta - 1)\tau] + 2\beta^2 \sinh(\tau)\right\}\right)^{1/2} \tag{4.9}$$

From Eqs. (4.4) and (4.8), the coefficient of variation, CV(t), is

$$\begin{aligned} CV(t) &= \frac{\sigma(t)}{m(t)} \\ &= \frac{1}{n_0^{1/2}} \cdot \frac{[\beta \exp(\alpha t)]^{1/2}}{\{1+\beta[\exp(\alpha t)-1]\}} \\ &\quad \cdot \left(2\beta - 1 + \exp(\alpha t)\left\{1 - 2\beta[1+(\beta-1)(\alpha t)] + 2\beta^2 \sinh(\alpha t)\right\}\right)^{1/2} \end{aligned} \tag{4.10}$$

or in terms of τ,

$$\begin{aligned} CV(\tau) &= \frac{1}{n_0^{1/2}} \cdot \frac{[\beta \exp(\tau)]^{1/2}}{\{1+\beta[\exp(\tau)-1]\}} \\ &\quad \cdot \left(2\beta - 1 + \exp(\tau)\left\{1 - 2\beta[1+(\beta-1)\tau] + 2\beta^2 \sinh(\tau)\right\}\right)^{1/2} \end{aligned} \tag{4.11}$$

Note that this expression is a function of n_0.

Analysis of Experimental Data

The available experimental data[65] are listed in Table 3.1 and also exhibited in Figure 3.2 in the preceding chapter; they are given in the unit of milligrams of carbon per milligram of ACs, i.e., mg C/mg AC. The model derived in this chapter is also validated with the same set of data; this validation is carried out by relating the number of open pores at time t, which is the random variable, N(t), to the experimentally measurable variable, W(t). This variable represents the weight of carbon already deposited on ACs at time t. Accordingly, it is assumed that a fixed amount of carbon, δ, deposits onto an open pore and its surroundings, thus causing the pore to narrow. Hence, at any time t,

$$W(t) = \delta[n_0 - N(t)] \tag{4.12}$$

where the term, $[n_0 - N(t)]$, is the number of narrowed pores at any time t. The mean value of W(t), denoted by $m_W(t)$, is obtained from the above expression as follows:

$$\begin{aligned} m_W(t) &= E[W(t)] \\ &= E\{\delta\,[n_0 - N(t)]\} \\ &= \delta\{n_0 - E[N(t)]\} \end{aligned}$$

or

$$m_W(t) = \delta[n_0 - m(t)] \tag{4.13}$$

Substituting (4.4) for m(t) into this equation gives

$$m_W(t) = \delta n_0 \left\{ 1 - \frac{1}{1+\beta[\exp(\alpha t)-1]} \right\}$$

or

$$m_W(t) = W_0 \left\{ \frac{\beta[\exp(\alpha t)-1]}{1+\beta[\exp(\alpha t)-1]} \right\} \tag{4.14}$$

where W_0, or (δn_0), is the weight of carbon that would deposit onto the initial number of open pores. From the above expression, the dimensionless form of the mean, $\eta_W(\tau)$, is

$$\eta_W(\tau) = \frac{m_W(\tau)}{W_0} = \frac{\beta[\exp(\tau)-1]}{1+\beta[\exp(\tau)-1]} \tag{4.15}$$

Note that $\eta_W(\tau) \to 1$ as $\tau \to \infty$. Multiplying both sides of this equation by $\beta^{-1}\{1+\beta[\exp(\tau)-1]\}$ gives rise to

$$\eta_W^*(\tau) = \exp(\tau) - 1 \tag{4.16}$$

where $\eta_W^*(\tau) = \beta^{-1}\{1+\beta[\exp(\tau)-1]\}\eta_W(\tau)$. Note that $\eta_W^*(\tau) \to \infty$ as $\tau \to \infty$.

Similarly, the variance of W(t), $\sigma_W^2(t)$, is obtained from (4.12) as

$$\begin{aligned} \sigma_W^2(t) &= \mathrm{Var}[W(t)] \\ &= \mathrm{Var}\{\delta[n_0 - N(t)]\} \\ &= \delta^2 \mathrm{Var}[N(t)] \end{aligned}$$

or

$$\sigma_W^2(t) = \delta^2[\sigma^2(t)] \tag{4.17}$$

Substituting (4.6) for $\sigma^2(t)$ into the above expression leads to

$$\begin{aligned} \sigma_W^2(t) = \delta^2 n_0 &\frac{\beta\exp(\alpha t)}{\{1+\beta[\exp(\alpha t)-1]\}^4} \\ &\cdot\left(2\beta - 1 + \exp(\alpha t)\{1 - 2\beta[1+(\beta-1)(\alpha t)] + 2\beta^2\sinh(\alpha t)\}\right) \end{aligned} \tag{4.18}$$

From this equation, the standard deviation, $\sigma^2(t)$, is

$$\sigma_W(t) = \delta n_0^{1/2} \frac{[\beta \exp(\alpha t)]^{1/2}}{\{1+\beta[\exp(\alpha t)-1]\}^2} \cdot \left(2\beta - 1 + \exp(\alpha t)\{1 - 2\beta[1+(\beta-1)(\alpha t)] + 2\beta^2 \sinh(\alpha t)\}\right)^{1/2} \tag{4.19}$$

The dimensionless form of σ_W^2, i.e., $\zeta_W(\tau)$, is given by

$$\zeta_W(\tau) = \frac{\sigma_W(\tau)}{W_0} = \frac{1}{n_0^{1/2}} \cdot \frac{[\beta \exp(\tau)]^{1/2}}{\{1+\beta[\exp(\tau)-1]\}^2} \cdot \left(2\beta - 1 + \exp(\tau)\{1 - 2\beta[1+(\beta-1)\tau] + 2\beta^2 \sinh(\tau)\}\right)^{1/2} \tag{4.20}$$

Note that this equation is identical to (4.9) for $\zeta(\tau)$; moreover, $\zeta_W(\tau) \to 0$ as $\tau \to \infty$. By multiplying both sides of this equation by $\beta^{-1}\{1+\beta[\exp(\tau)-1]\}$, we have

$$\zeta_W^*(\tau) = \frac{1}{n_0^{1/2}} \cdot \frac{1}{\beta^{1/2}} \cdot \frac{[\exp(\tau)]^{1/2}}{\{1+\beta[\exp(\tau)-1]\}} \cdot \left(2\beta - 1 + \exp(\tau)\{1 - 2\beta[1+(\beta-1)\tau] + 2\beta^2 \sinh(\tau)\}\right)^{1/2} \tag{4.21}$$

where $\zeta_W^*(\tau) = \beta^{-1}\{1+\beta[\exp(\tau)-1]\}\zeta_W(\tau)$. Note that $\zeta_W^*(\tau) \to \infty$ as $\tau \to \infty$. The coefficient of variation, $CV_W(\tau)$, is obtained as

$$CV_W(\tau) = \frac{\sigma_W(\tau)}{m_W(\tau)} = \frac{1}{n_0^{1/2}} \cdot \frac{[\beta \exp(\tau)]^{1/2}}{\beta[\exp(\tau)-1]\{1+\beta[\exp(\tau)-1]\}} \cdot \left(2\beta - 1 + \exp(\tau)\{1 - 2\beta[1+(\beta-1)\tau] + 2\beta^2 \sinh(\tau)\}\right)^{1/2} \tag{4.22}$$

Note that this equation is also a function of n_0.

Results and Discussion

The model formulated, in terms of the temporal mean given in Eq. (4.14), has been fitted to the available experimental data[65] through regression without linearization via the adaptive

random search procedure.[113, 114] The regression has resulted in the values of W_0 and those of α and β, which are listed in Table 4.1. These values have rendered it possible to evaluate the dimensionless time, (αt), i.e., τ, as well as the dimensionless mean, $\eta_W(\tau)$, from Eq. (4.15). The values of $\eta_W^*(\tau)$ computed from Eq. (4.16) as a function of τ are presented in Figure 4.2 at the eleven temperature levels. The corresponding experimentally measured weights in milligrams of carbon deposited per milligram of ACs are rendered dimensionless by dividing them by W_0 and multiplying them by $\beta^{-1}\{1+\beta[\exp(\tau)-1]\}$; the values of the resultant quantity, denoted as w*(τ), are superimposed in the same figure for comparison. As indicated earlier, note that $\eta_W^*(\tau)$ increases boundlessly as τ progresses.

The standard deviation signifies the deviations attributable to the internal or characteristic noises of the process as predicted by the stochastic model.[110] The values of $\zeta_W^*(\tau)$ around $\eta_W^*(\tau)$, i.e., $\eta_W^*(\tau)\pm\zeta_W^*(\tau)$, are also plotted in Figure 4.2. As expected, many of the experimental data[65] lie appreciably beyond the expected variation, or scattering, which is almost always the case: The overall deviations of the experimental data include not only those attributable to the internal noises of the process as predicted by the model, but also to the external noises due to inevitable measurement errors and instrumental deficiencies that can never be totally eliminated. As evident from Eq. (4.21), the expression for $\zeta_W^*(\tau)$ depends on the initial number of open pores per milligram of ACs, i.e., n_0, whose order of magnitude estimate is $1.67 \cdot 10^{13}$ pores.[110]

Table 4.1. Values of α, β, and W_0 for the Pore-narrowing at Different Temperatures.

temperature, K (C)	α, $s^{-1} \cdot 10^4$ (min^{-1})	β, (–)	W_0 (mg C)
873 (599.85)	2.73 (0.016)	0.817	0.064
923 (649.85)	2.90 (0.017)	0.683	0.206
948 (674.85)	4.00 (0.024)	0.698	0.267
973 (699.85)	8.65 (0.052)	0.569	0.235
1023 (749.85)	13.45 (0.081)	0.485	0.226
1048 (774.85)	17.75 (0.107)	0.397	0.225
1073 (799.85)	16.83 (0.101)	0.637	0.235
1098 (824.85)	12.13 (0.073)	0.916	0.277
1123 (849.85)	6.85 (0.038)	1.862	0.308
1173 (899.85)	1.78 (0.011)	4.712	0.344
1223 (949.85)	1.10 (0.007)	2.950	0.577

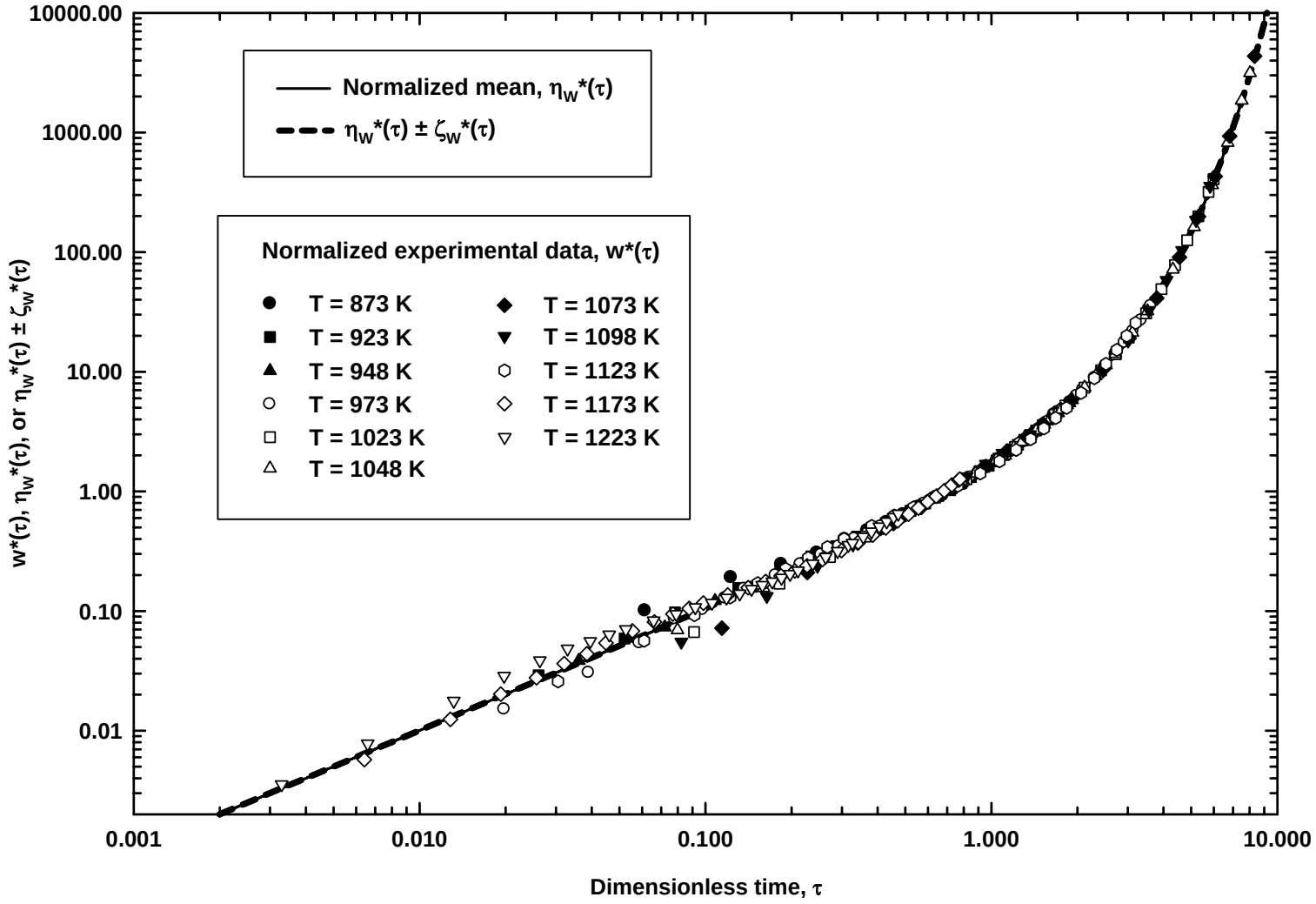


Figure 4.2. Normalized mean $\eta_W^*(\tau)$ and normalized standard deviation envelope $[\eta_W^*(\tau) \pm \zeta_W^*(\tau)]$ as functions of dimensionless time τ for the pore-narrowing: The values on both axes are presented in logarithmic scale to facilitate their visualization.

Summary

A stochastic model has been derived for the formation of CMSs by the deposition of carbon particles on ACs as a pure-death process based on a non-linear intensity function. The complexity in solving the resultant master equation of the process has been circumvented by resorting to a rational approximation method, system-size expansion. The mean and variance of the amount of carbon deposited onto the pores susceptible to narrowing, i.e., the open pores, have been computed from the master equation. The model derived has been validated by fitting it to the available experimental data. The mean value of the model is in excellent accord with these data. As expected, the data's fluctuations around their mean are more noticeable than those predicted by the model: In addition to the process' internal noises, the deviations of the experimental data also account for the external noises due to unavoidable measurement errors.

Notation

k = proportionality constant in the intensity of death, $(t)^{-1}$

$(k'n_0)$ = proportionality constant in the intensity of death, $(t)^{-1}$

$m(t)$ = mean of the random variable, N(t)

$m_W(t)$ = mean of the experimental measurable variable, W(t), mg C

$N(t)$ = random variable representing the number of pores susceptible to narrowing, i.e., the number of open pores, at time t

n = realization of the random variable, N(t)

$p_n(t)$ = probability that n pores are open at time t

t = time

$W(t)$ = experimentally measurable variable representing the weight of carbon already deposited on ACs, mg C

Greek letters

α = constant $(k + k'n_0)$, $(t)^{-1}$

β = dimensionless constant, $k(k + k'n_0)^{-1}$

$\mu_n(t)$ = intensity of death for the pure-death process in state n at time t

$\sigma^2(t)$ = variance of the random variable, N(t)

$\sigma_W^2(t)$ = variance of the experimentally measurable variable, W(t)

τ = dimensionless time

CHAPTER 5 - Conclusions and Recommendations for Future Work

In this dissertation, the formation of carbon adsorbents, including activated carbons (ACs) and carbon molecular sieves (CMSs), has been analyzed and modeled by resorting to stochastic processes. What follows are the significant conclusions reached as well as recommendations for future work.

Conclusions

The formation of activated carbons (ACs) from a carbonaceous substrate has been stochastically analyzed and modeled as a pure-birth process with a linear intensity function based on a single random variable. The solution of the master equation of the process yields the mean and variance of the number of pores that have been formed on the internal surfaces of the carbonaceous substrate; this number is regarded as the process' random variable. The model has been validated with the available experimental data for the formation of ACs from a carbonaceous substrate. In general, the model's mean value follows the trend of these data; moreover, the model's kinetic constant obeys the Arrhenius law. It is expected that the linear stochastic model for the formation of ACs be an insightful preliminary exploration of the process of concern.

Subsequently, two stochastic models for the formation of carbon molecular sieves (CMSs) on ACs have been derived; each of them is based on a single random variable. The first of the two models has been formulated as a pure-birth process with a non-linear intensity function. The random variable of the process is identified as the number of packets that have already deposited onto the pores' mouths of ACs, which increases temporally. Naturally, the resultant master equation is non-linear; the complexity in solving it is circumvented via a rational approximation method, the system-size expansion. The mean and variance of the amount of carbon deposited onto the pores' mouth of ACs have been computed from expressions obtained from the system-size expansion of the master equation. In general, the model is in accord with

the available experimental data for the formation of CMSs on ACs. Moreover, the non-linear master equation of the process has been simulated with the Monte Carlo method via the event-driven as well as time-driven approaches. The simulation has been carried out at the process' early stage where the number of carbon packets depositing onto the pores of ACs is exceedingly small, thereby magnifying the fluctuations of the process around its mean. The mean and variance computed from simulation are in line with their corresponding analytical results. Simulating the process' non-linear master equation with the Monte Carlo method is of special significance: In some instances, this might be the only viable avenue for reliably estimating the means and variances of highly non-linear processes. In contrast, the second of the two models has been formulated as a pure-death process; its random variable is the number of open pores on ACs, which decreases temporally as they are narrowed. The non-linear intensity function accounts for the number of pores that have already been narrowed as well as that of open pores. Because the resultant master equation is non-linear, it has also been solved by resorting to the system-size expansion, thereby resulting in expressions for the process' mean and variance. The model's mean values at various times are in good accord with the available experimental data.

Recommendations

The stochastic analysis and modeling of the kinetics of formation of ACs is far from complete. A natural sequel of the linear stochastic model presented in this dissertation would be a stochastic model with a non-linear intensity function based on single random variable. Various forms of such an intensity function could be investigated by including a second-order function or an exponential-like function. It would be desirable that the non-linear intensity function incorporates several structural parameters of the carbonaceous materials from which ACs are manufactured. An expression in light of the random pore model for fluid-solid reactions might offer an alternative for the definition of the non-linear intensity function.

The stochastic analysis and modeling of the formation of CMSs could be further extended by formulating a stochastic model that couples the pore-narrowing with the subsequent pore-blocking. Naturally, the resultant model including both pore-narrowing and pore-blocking would involve two random variables and two intensity functions. For a given stochastic model, these two intensity functions could be linear, non-linear, or their combination thereof.

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Appendix A - Derivation of the Master Equation of a Pure-Birth Process

Suppose that a system comprising a population of particulate or discrete entities in a given space is to be stochastically modeled as a pure-birth process. The random variable characterizing this process is denoted by N(t) with realization n; moreover, the intensity of birth is denoted by $\lambda_n(t)$. Thus, one of the following two events is considered to occur during time interval $(t, t+\Delta t)$. First, the number of entities increases by one, which is a birth event, with conditional probability $\{[\lambda_n(t)]\Delta t + o(\Delta t)\}$. Second, the number of entities changes by a number other than one with conditional probability o(Δt), which is defined such that

$$\lim_{\Delta t \to 0} \frac{o(\Delta t)}{\Delta t} = 0 \tag{A.1}$$

Naturally, the conditional probability of no change in the number of entities during this time interval is $(1 - \{[\lambda_n(t)]\Delta t + o(\Delta t)\})$.

Let the probability that exactly n entities are present at time t be denoted as $p_n(t) = \Pr[N(t) = n]$, where $n \in (0, 1, 2, ..., n_\infty - 1, n_\infty)$; n_∞ is the maximum possible number of entities in the system. For the two adjacent time intervals, (0, t) and $(t, t+\Delta t)$, the occurrence of exactly n entities being present at time $(t+\Delta t)$ can be realized in the following mutually exclusive ways; see Figure A.1.

(1) With a probability of $\{[\lambda_{n-1}(t)]\Delta t + o(\Delta t)\}p_{n-1}(t)$, the number of entities will increase by one during time interval $(t, t+\Delta t)$, provided that exactly $(n-1)$ entities are present at time t.

(2) With a probability of o(Δt), the number of entities will change by exactly j entities during time interval $(t, t+\Delta t)$, provided that exactly $(n-j)$ entities are present at time t, where $2 \le j \le n_\infty$.

(3) With a probability of $(1 - \{[\lambda_n(t)]\Delta t + o(\Delta t)\})p_n(t)$, the number of entities will remain unchanged during time interval $(t, t+\Delta t)$, provided that n entities are present at time t.

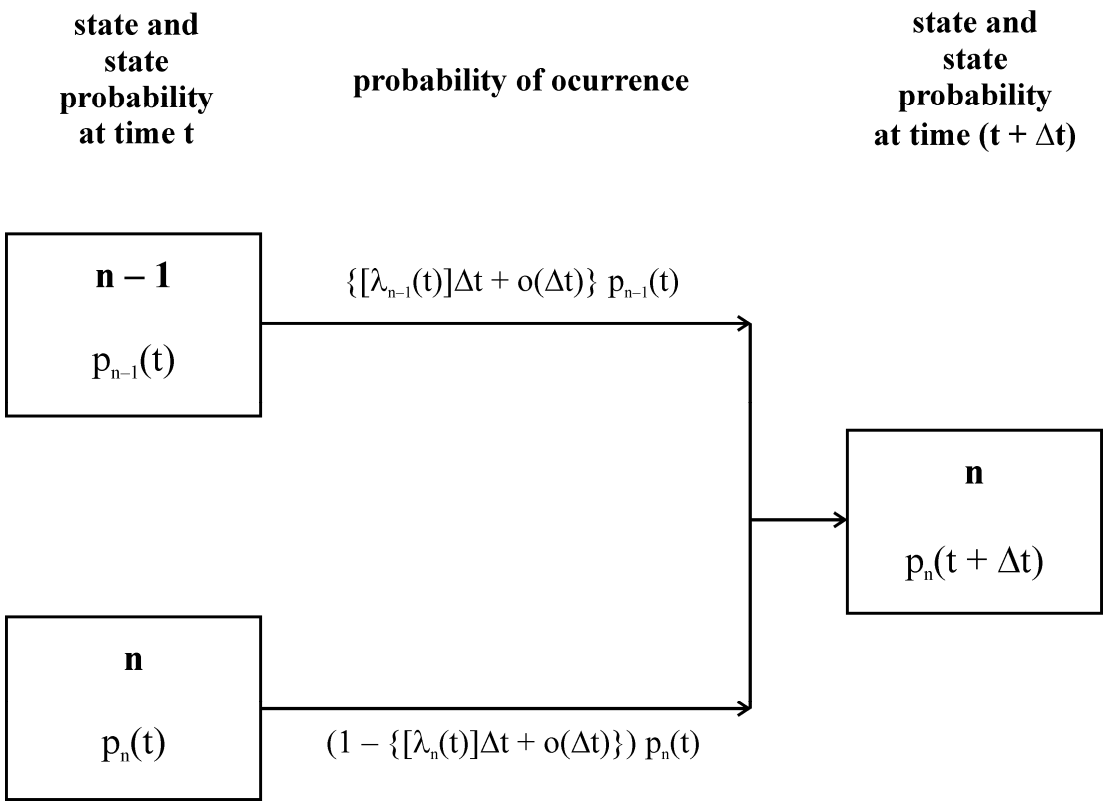

Figure A.1. Probability balance for the pure-birth process involving the mutually exclusive events in the time interval, (t, t + Δt).

Summing all these probabilities and consolidating all quantities of o(Δt) yield

$$p_n(t+\Delta t) = \{[\lambda_{n-1}(t)]\Delta t\}\, p_{n-1}(t) + \{1-[\lambda_n(t)]\Delta t\}\, p_n(t) + o(\Delta t) \tag{A.2}$$

Rearranging this equation, dividing it by Δt, and taking the limit as $\Delta t \to 0$ yield the master equation of the pure-birth process as[71, 73]

$$\frac{d}{dt} p_n(t) = \lambda_{n-1}(t)\, p_{n-1}(t) - \lambda_n(t)\, p_n(t) \tag{A.3}$$

This is Eq. (2.2) in Chapter 2 with $n \in \left(0, 1, 2, ..., n_L - 1, n_L\right)$, and also Eq. (3.1) in Chapter 3 with $n \in \left(0, 1, 2, ..., n_M - 1, n_M\right)$.

Appendix B - Formation of Activated Carbons: Derivation of Mean and Variance of the Pure-Birth Process with Linear Intensity of Transition Based on a Single Random Variable

The master equation of the pure-birth process of interest is given by Eq. (2.2) in the text as

$$\frac{d}{dt}p_n(t) = \lambda_{n-1}(t)p_{n-1}(t) - \lambda_n(t)p_n(t), \quad n = 0,\ 1,\ 2,...,\ n_L - 1,\ n_L \tag{B.1}$$

The mean and variance of the pure-birth process can be computed from this equation by resorting to the one-step operator, $\mathbb{E}$. This operator is defined by its effect on an arbitrary function, f(n), as

$$\mathbb{E}f(n) = f(n+1) \quad \text{and} \quad \mathbb{E}^{-1}f(n) = f(n-1) \tag{B.2}$$

In light of this definition, Eq. (B.1) becomes

$$\frac{d}{dt}p_n(t) = \mathbb{E}^{-1}\,\lambda_n(t)\,p_n(t) - \lambda_n(t)\,p_n(t)$$

or

$$\frac{d}{dt}p_n(t) = (\mathbb{E}^{-1} - 1)\,\lambda_n(t)\,p_n(t) \tag{B.3}$$

For any arbitrary functions, f(n) and g(n), of integer n, the following expression holds

$$\sum_{n=0}^{n_L-1}[g(n)\,\mathbb{E}\,f(n)] = \sum_{n=1}^{n_L}[f(n)\,\mathbb{E}^{-1}g(n)]$$

When $g(-1) = f(n_L + 1) = 0$, this equation becomes

$$\sum_{n=0}^{n_L}[g(n)\,\mathbb{E}\,f(n)] = \sum_{n=0}^{n_L}[f(n)\,\mathbb{E}^{-1}g(n)] \tag{B.4}$$

This property of $\mathbb{E}$ facilitates the evaluation of the mean and variance of the pure-birth process of interest from its master equation.

Mean

The mean, E[N(t)] or m(t), which is the expected value (first moment) of the distribution of random variable N(t) is defined as

$$E[N(t)] = \sum_{n} np(n;t) \tag{B.5}$$

The mean or expected value, E[N(t)], is the weighted sum of the realizations of random variable N(t) where the weights are the corresponding probabilities to those realizations.[111] By multiplying both sides of Eq. (B.3) by n and summing over the state space of N(t), i.e., all values of n, we have

$$\sum_{n=0}^{n_L} n \frac{d}{dt} p_n(t) = \sum_{n=0}^{n_L} n(\mathbb{E}^{-1} - 1)\lambda_n(t)\, p_n(t)$$

By virtue of Eq. (B.4), this equation can be rewritten as

$$\sum_{n=0}^{n_L} n \frac{d}{dt} p_n(t) = \sum_{n=0}^{n_L} \lambda_n(t)\, p_n(t)(\mathbb{E} - 1)\, n$$

or

$$\sum_{n=0}^{n_L} n \frac{d}{dt} p_n(t) = \sum_{n=0}^{n_L} \lambda_n(t)\, p_n(t) \tag{B.6}$$

Inserting Eq. (2.1) in text for $\lambda_n(t)$ into the above equation gives

$$\sum_{n=0}^{n_L} n \frac{d}{dt} p_n(t) = \sum_{n=0}^{n_L} \kappa(n_L - n)\, p_n(t) \tag{B.7}$$

or

$$\sum_{n=0}^{n_L} n \frac{d}{dt} p_n(t) = \kappa n_L \sum_{n=0}^{n_L} p_n(t) - \kappa \sum_{n=0}^{n_L} n\, p_n(t) \tag{B.8}$$

By definition,

$$\sum_{n=0}^{n_L} p_n(t) = 1 \tag{B.9}$$

Moreover, the mean of N(t), E[N(t)] or m(t), is given by

$$E[N(t)] = \sum_{n=0}^{n_L} n\, p_n(t) \tag{B.10}$$

and thus,

$$\frac{d}{dt} E[N(t)] = \sum_{n=0}^{n_L} n \frac{d}{dt} p_n(t) \tag{B.11}$$

By virtue of Eqs. (B.9) through (B.11), Eq. (B.8) reduces to

$$\frac{d}{dt} E[N(t)] = \kappa\, n_L - \kappa\, E[N(t)]$$

or

$$\frac{d}{dt} E[N(t)] + \kappa\, E[N(t)] = \kappa\, n_L \tag{B.12}$$

From the initial conditions for the pure-birth process,

$$p_n(0) = \begin{cases} 0 & \text{if} \quad n \neq 0 \\ \\ 1 & \text{if} \quad n = 0\ , \end{cases} \tag{B.13}$$

and the definition of E[N(t)], Eq. (B.10), we have

$$E[N(0)] = 0 \tag{B.14}$$

Integrating Eq. (B.12) subject to this initial condition yields

$$E[N(t)] = n_L[1 - \exp(-\kappa t)] \tag{B.15}$$

or

$$m(t) = n_L[1 - \exp(-\kappa t)]\,, \tag{B.16}$$

This is Eq. (2.4) in the text.

Variance

The variance, Var[N(t)] or $\sigma^2(t)$, is the second moment of the distribution of random variable N(t) about the mean, E[N(t)]; thus,

$$\mathrm{Var}[N(t)] = \sigma^2(t) = E[\{N(t) - E[N(t)]\}^2]$$

or

$$\sigma^2(t) = \sum_n \{n - E[N(t)]\}^2 p(n;t) \tag{B.17}$$

By expanding the above equation, $\sigma^2(t)$ can be related to the mean, E[N(t)], as follows:

$$\sigma^2(t) = E[N^2(t)] - \{E[N(t)]\}^2 \tag{B.18}$$

In this expression, $E[N^2(t)]$ is the second moment of N(t), i.e.,

$$E[N^2(t)] = \sum_n n^2 p(n;t) \tag{B.19}$$

By multiplying both sides of Eq. (B.3) by n^2 and summing over all values of n, we obtain

$$\sum_{n=0}^{n_L} n^2 \frac{d}{dt} p_n(t) = \sum_{n=0}^{n_L} n^2 (\mathbb{E}^{-1} - 1)\lambda_n(t)\, p(n;t) \tag{B.20}$$

By virtue of Eq. (B.4), this equation can be transformed into

$$\sum_{n=0}^{n_L} n^2 \frac{d}{dt} p_n(t) = \sum_{n=0}^{n_L} \lambda_n(t)\, p_n(t)(\mathbb{E} - 1)n^2$$

or

$$\sum_{n=0}^{n_L} n^2 \frac{d}{dt} p_n(t) = \sum_{n=0}^{n_L} \lambda_n(t)\, p_n(t)(2n + 1)$$

Expanding and rearranging the right-hand side of this expression yield

$$\sum_{n=0}^{n_L} n^2 \frac{d}{dt} p(n;t) = 2\sum_{n=0}^{n_L} [\lambda_n(t)]\, n\, p_n(t) + \sum_{n=0}^{n_L} [\lambda_n(t)]\, p_n(t) \tag{B.21}$$

Inserting Eq. (2.1) in text for $\lambda_n(t)$ into the above equation gives rise to

$$\sum_{n=0}^{n_L} n^2 \frac{d}{dt} p(n;t) = 2\sum_{n=0}^{n_L} [\kappa(n_L - n)]\, n\, p_n(t) + \sum_{n=0}^{n_L} [\kappa(n_L - n)]\, p_n(t) \tag{B.22}$$

or

$$\sum_{n=0}^{n_L} n^2 \frac{d}{dt} p_n(t) = -2\kappa \sum_{n=0}^{n_L} n^2 p_n(t) + \kappa(2n_L - 1)\sum_{n=0}^{n_L} n p(t) + \kappa n_L \sum_{n=0}^{n_L} p_n(t) \tag{B.23}$$

By definition,

$$\sum_{n=0}^{n_L} p_n(t) = 1 \tag{B.24}$$

and

$$E[N(t)] = \sum_{n=0}^{n_L} n\, p_n(t) \tag{B.25}$$

Moreover,

$$E[N^2(t)] = \sum_{n=0}^{n_L} n^2 p_n(t) \tag{B.26}$$

and thus,

$$\frac{d}{dt} E[N^2(t)] = \sum_{n=0}^{n_L} n^2 \frac{d}{dt} p_n(t) \tag{B.27}$$

In light of Eqs. (B.24) through (B.27), Eq. (B.23) can be transformed into

$$\frac{d}{dt} E[N^2(t)] = -2\kappa E[N^2(t)] + \kappa(2n_L - 1)E[N(t)] + \kappa n_L$$

or

$$\frac{d}{dt} E[N^2(t)] + 2\kappa E[N^2(t)] = \kappa(2n_L - 1)E[N(t)] + \kappa n_L \tag{B.28}$$

The expression for $E[N^2(t)]$, Eq. (B.26), in conjunction with the initial conditions for the birth-death process, Eq. (B.13), lead to

$$E[N^2(0)] = 0 \tag{B.29}$$

Inserting Eq. (B.15) for E[N(t)] into Eq. (B.28) and integrating the resulting expression subject to the initial condition given above yield

$$E[N^2(t)] = n_L^2 - 2n_L^2 \exp(-\kappa t) + n_L \exp(-\kappa t) + n_L^2 \exp(-2\kappa t) - n_L \exp(-2\kappa t) \tag{B.30}$$

Consequently, this equation in conjunction with Eqs. (B.15) and (B.18) give rise to

$$\sigma^2(t) = n_L[1 - \exp(-\kappa t)]\exp(-\kappa t) \tag{B.31}$$

This is Eq. (2.6) in the text.

Appendix C - Formation of Carbon Molecular Sieves: System-Size Expansion of the Master Equation of the Pure-Birth Process with a Non-Linear Intensity of Transition Based on a Single Random Variable

The master equation of the pure-birth process of interest is given by Eq. (3.1) in the text as

$$\frac{d}{dt}p_n(t) = \lambda_{n-1}(t)p_{n-1}(t) - \lambda_n(t)p_n(t), \quad n = 0,\ 1,\ 2,...,\ n_M - 1,\ n_M \tag{C.1}$$

In light of the one-step operator, $\mathbb{E}$, as defined by Eq. (B.2), this equation can be transformed into

$$\frac{d}{dt}p_n(t) = (\mathbb{E}^{-1} - 1)\lambda_n(t)p_n(t), \quad n = 0, 1, 2, \ldots, n_M - 1, n_M \tag{C.2}$$

The intensity of birth, $\lambda_n(t)$, in this expression is given by Eq. (3.2) in the text as

$$\lambda_n(t) = \frac{dn}{dt} = \alpha(n_M - n)^2 \tag{C.3}$$

where α is a proportionality constant. Substituting the above expression into Eq. (C.2) yields

$$\frac{d}{dt}p_n(t) = \alpha(\mathbb{E}^{-1} - 1)[(n_M - n)^2]p_n(t) \tag{C.4}$$

It is expected that at later time t, the probability distribution of N(t), $p_n(t)$ or p(n;t), exhibits a sharp peak at some position of order Ω, while its width is of order $\Omega^{1/2}$; see Figure C.1. The symbol, Ω, signifies the system's size, which is n_M in this case. To formulate this formally, N(t) is expressed as the sum of the macroscopic term, $\Omega\varphi(t)$, and the fluctuation term, $\Omega^{1/2}\Xi(t)$ as

$$N(t) = \Omega\varphi(t) + \Omega^{1/2}\Xi(t)$$

or

$$N(t) = n_M\varphi(t) + n_M^{1/2}\Xi(t) \tag{C.5}$$

whose realization is

$$n = n_M\varphi(t) + n_M^{1/2}\xi \tag{C.6}$$

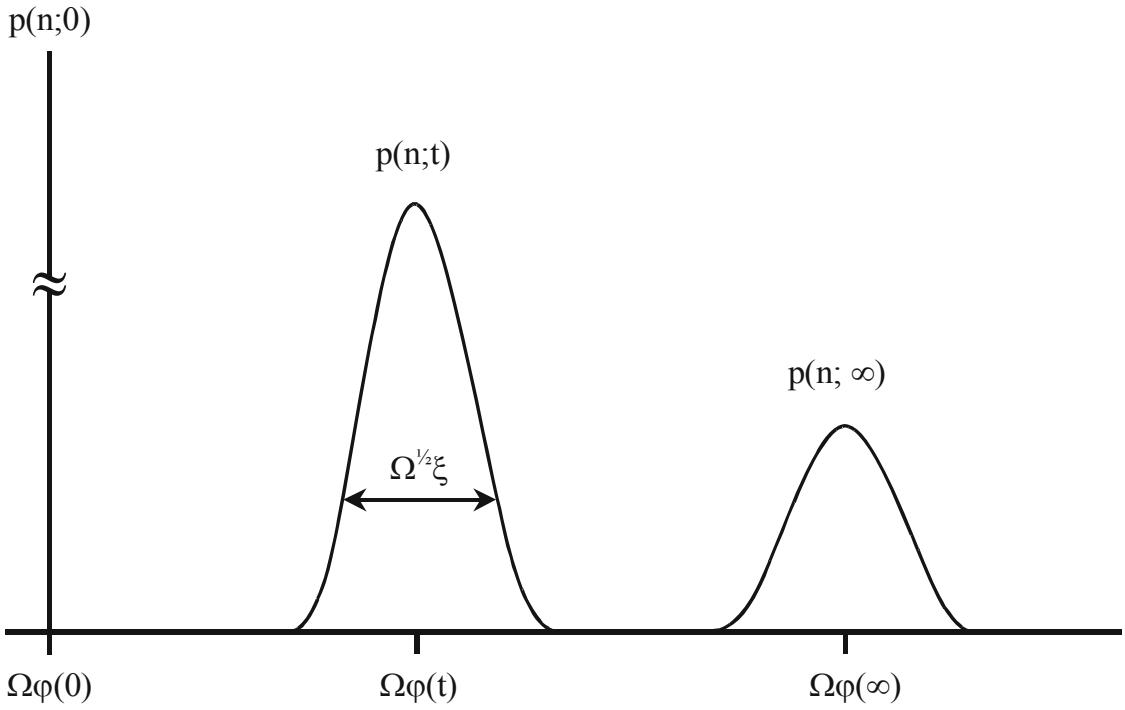

Figure C.1. Temporal evolution of the probability distribution, $p_n(t)$ or p(n;t).

The function, $\varphi(t)$, in these two equations is adjusted to follow the motion of the peak in time; consequently, $p(n;t)$ is transformed into function $\pi(\xi;t)$, which depends on realization ξ of $\Xi(t)$, as

$$p(n;t) = \pi(\xi;t) \tag{C.7}$$

where $\pi(\xi;t) = \Pr[\Xi(t) = \xi]$. From Eq. (C.6), we have

$$\xi = n(n_M^{-1/2}) - n_M^{1/2}\varphi(t) \tag{C.8}$$

Given that n is fixed, the time derivative of the above expression is obtained as

$$\frac{d\xi}{dt} = -n_M^{1/2}\frac{d\varphi}{dt} \tag{C.9}$$

where $\varphi = \varphi(t)$. Differentiating Eq. (C.7) with respect to time leads to

$$\frac{d}{dt}p(n;t) = \frac{\partial}{\partial t}\pi(\xi;t)$$

or

$$\frac{d}{dt}p(n;t) = \frac{\partial\pi}{\partial t} + \frac{\partial\pi}{\partial\xi}\left(\frac{d\xi}{dt}\right) \tag{C.10}$$

where $\pi = \pi(\xi;t)$. By inserting Eq. (C.9) into this equation, we obtain

$$\frac{d}{dt}p(n;t) = \frac{\partial\pi}{\partial t} - n_M^{1/2}\left(\frac{d\varphi}{dt}\right)\frac{\partial\pi}{\partial\xi} \tag{C.11}$$

In light of the one-step operator, $\mathbb{E}$, we have

$$\mathbb{E}^{-1}n = n - 1$$

Substituting Eq. (C.6) for n on the right-hand side of this equation gives rise to

$$\begin{aligned}\mathbb{E}^{-1}n &= [n_M\varphi(t) + n_M^{1/2}\xi] - 1 \\ &= [n_M\varphi(t) + n_M^{1/2}\xi] - [n_M^{1/2}n_M^{-1/2}]\end{aligned}$$

or

$$\mathbb{E}^{-1}n = n_M\varphi(t) + n_M^{1/2}(\xi - n_M^{-1/2})$$

In other words, $\mathbb{E}^{-1}$ transforms n into $(n-1)$, and therefore, ξ into $(\xi - n_M^{-1/2})$; as a result, from Eq. (C.7),

$$\mathbb{E}^{-1}p(n;t) = \mathbb{E}^{-1}\pi(\xi;t)$$

or

$$p(n-1;t)=\pi(\xi-n_M^{-1/2};t) \tag{C.12}$$

The Taylor expansion of $\pi(\xi-n_M^{-1/2};t)$ about ξ, is obtained as

$$\pi(\xi-n_M^{-1/2};t)=\pi(\xi;t)+(-n_M^{-1/2})\frac{\partial}{\partial\xi}\pi(\xi;t)+\frac{1}{2!}(-n_M^{-1/2})^2\frac{\partial^2}{\partial\xi^2}\pi(\xi;t)+...$$

or

$$\pi(\xi-n_M^{-1/2};t)=\left(1-n_M^{-1/2}\frac{\partial}{\partial\xi}+\frac{1}{2}n_M^{-1}\frac{\partial^2}{\partial\xi^2}-...\right)\pi(\xi;t) \tag{C.13}$$

In view of Eqs. (C.7) and (C.12), the above expression can be transformed to

$$p(n-1;t)=\left(1-n_M^{-1/2}\frac{\partial}{\partial\xi}+\frac{1}{2}n_M^{-1}\frac{\partial^2}{\partial\xi^2}-...\right)p(n;t)$$

or

$$\mathbb{E}^{-1}p(n;t)=\left(1-n_M^{-1/2}\frac{\partial}{\partial\xi}+\frac{1}{2}n_M^{-1}\frac{\partial^2}{\partial\xi^2}-...\right)p(n;t)$$

By comparing both sides of this expression, we have

$$\mathbb{E}^{-1}=1-n_M^{-1/2}\frac{\partial}{\partial\xi}+\frac{1}{2}n_M^{-1}\frac{\partial^2}{\partial\xi^2}-... \tag{C.14}$$

Substituting this expression in conjunction with Eqs. (C.6), (C.7), and (C.11) into the master equation, Eq. (C.4), leads to

$$\frac{\partial\pi}{\partial t}-n_M^{1/2}\left(\frac{d\varphi}{dt}\right)\frac{\partial\pi}{\partial\xi}$$

$$=\alpha n_M^2\left(-n_M^{-1/2}\frac{\partial}{\partial\xi}+\frac{1}{2}n_M^{-1}\frac{\partial^2}{\partial\xi^2}-...\right)[1-(\varphi+n_M^{-1/2}\xi)]^2\pi \tag{C.15}$$

Absorbing the system's size, n_M, into the time variable, t, as

$$n_M t=\gamma$$

and truncating the terms after the second-order derivative for large n_M give

$$\frac{\partial \pi}{\partial \gamma} - n_M^{1/2}\left(\frac{d\varphi}{d\gamma}\right)\frac{\partial \pi}{\partial \xi}$$

$$= \alpha n_M\left(-n_M^{-1/2}\frac{\partial}{\partial \xi} + \frac{1}{2}n_M^{-1}\frac{\partial^2}{\partial \xi^2}\right)\left(1-\varphi-n_M^{-1/2}\xi\right)^2 \pi \tag{C.16}$$

By expanding the right-hand side of this equation and collecting the resultant terms of orders $n_M^{1/2}$ and n_M^0 separately, we have

$$\frac{\partial \pi}{\partial \gamma} - n_M^{1/2}\left(\frac{d\varphi}{d\gamma}\right)\frac{\partial \pi}{\partial \xi}$$

$$= n_M^0\left[2\alpha(1-\varphi)\frac{\partial}{\partial \xi}(\xi\pi) + \frac{1}{2}\alpha(1-\varphi)^2\frac{\partial^2 \pi}{\partial \xi^2}\right]$$

$$-n_M^{1/2}\left[\alpha(1-\varphi)^2\frac{\partial \pi}{\partial \xi}\right]$$

$$+\alpha n_M^{-1/2}\left[-\frac{\partial^2}{\partial \xi^2}(\xi\pi) - \frac{\partial}{\partial \xi}(\xi^2\pi) + \varphi\frac{\partial^2}{\partial \xi^2}(\xi\pi) + \frac{1}{2}n_M^{-1/2}\frac{\partial^2}{\partial \xi^2}(\xi^2\pi)\right] \tag{C.17}$$

Comparing both sides of the above expression gives rise to

$$\frac{d\varphi}{d\gamma} = \alpha(1-\varphi)^2 \tag{C.18}$$

and

$$\frac{\partial \pi}{\partial \gamma} = 2\alpha(1-\varphi)\frac{\partial}{\partial \xi}(\xi\pi) + \frac{1}{2}\alpha(1-\varphi)^2\frac{\partial^2 \pi}{\partial \xi^2} \tag{C.19}$$

Of these two equations, the former is the macroscopic equation governing the overall behavior of the process, and the latter is a linear Fokker-Plank equation governing the fluctuations of the process around the macroscopic values and whose coefficients depend on t through φ, i.e., φ(t).

Appendix D - Formation of Carbon Molecular Sieves: Derivation of the Mean and Variance for the Pure-Birth Process with a Non-Linear Intensity of Transition Based on a Single Random Variable

For convenience, Eq. (C.5) for random variable N(t) is rewritten below

$$N(t) = n_M \varphi(t) + n_M^{1/2} \Xi(t) \tag{D.1}$$

As defined earlier, the mean, E[N(t)] or m(t), is the expected value, or first moment, of the distribution of random variable, N(t); thus, from the above equation, we obtain

$$\begin{aligned} E[N(t)] &= E[n_M \varphi(t) + n_M^{1/2} \Xi(t)] \\ &= n_M E[\varphi(t)] + n_M^{1/2} E[\Xi(t)] \end{aligned}$$

or

$$m(t) = n_M \varphi(t) + n_M^{1/2} E[\Xi(t)] \tag{D.2}$$

Similarly, the variance, Var[N(t)] or $\sigma^2(t)$, which is the second moment of the distribution of N(t) about the mean, E[N(t)], is obtained as

$$\begin{aligned} Var[N(t)] &= Var[n_M \varphi(t) + n_M^{1/2} \Xi(t)] \\ &= n_M^2 Var[\varphi(t)] + n_M Var[\Xi(t)] \end{aligned}$$

or

$$\sigma^2(t) = n_M Var[\Xi(t)]$$

In light of Eq. (B.18), this equation can be rewritten as

$$\sigma^2(t) = n_M \left(E[\Xi^2(t)] - \{E[\Xi(t)]\}^2 \right) \tag{D.3}$$

where $E[\Xi(t)]$ and $E[\Xi^2(t)]$ are the first and second moments of the random variable, $\Xi(t)$. Clearly, the functions, $\varphi(t)$, $E[\Xi(t)]$, and $E[\Xi^2(t)]$, need be evaluated prior to obtaining the expressions for m(t) and $\sigma^2(t)$; their derivation is detailed in what follows.

At the outset of the process, i.e., at t = 0, N(0) = 0; moreover, no fluctuations arise around 0, which implies that $\Xi(0) = 0$. Hence, from Eq. (D.1),

$$\varphi(0) = 0 \tag{D.4}$$

The macroscopic equation governing the overall behavior of the process is given by Eq. (C.18) as

$$\frac{d\varphi}{d\gamma} = \alpha(1-\varphi)^2$$

Because $n_M t = \gamma$, this equation can be rewritten as

$$\frac{d\varphi}{dt} = \alpha n_M (1-\varphi)^2$$

Integration of this equation, Eq. (C.18), gives

$$\varphi(t) = 1 - \frac{1}{(\alpha n_M)t + c}$$

In view of Eq. (D.4), the constant, c, in the above expression is 1; thus,

$$\varphi(t) = \frac{(\alpha n_M)t}{(\alpha n_M)t + 1} \tag{D.5}$$

As indicated in Appendix B, for any arbitrary functions f and g which take integers, the following expression holds[71]

$$\sum_{n=0}^{n_M-1}[g(n)\mathbb{E}\,f(n)] = \sum_{n=1}^{n_M}[f(n)\mathbb{E}^{-1}g(n)] \tag{D.6}$$

When $g(-1) = f(n_M + 1) = 0$, this equation becomes

$$\sum_{n=0}^{n_M}[g(n)\mathbb{E}\,f(n)] = \sum_{n=0}^{n_M}[f(n)\mathbb{E}^{-1}g(n)] \tag{D.7}$$

If functions f and g take real numbers, the central-difference approximation gives

$$\frac{\partial}{\partial x}f(x) \approx \frac{f(x+\Delta x) - f(x)}{\Delta x} \tag{D.8}$$

and

$$\frac{\partial^2}{\partial x^2}f(x) \approx \frac{f(x+\Delta x) - 2f(x) + f(x-\Delta x)}{(\Delta x)^2} \tag{D.9}$$

Hence,

$$\sum_x \left[g(x) \frac{\partial}{\partial x} f(x) \right] \approx \sum_x \left\{ g(x) \left[\frac{f(x+\Delta x) - f(x)}{\Delta x} \right] \right\}$$

or

$$\sum_x \left[g(x) \frac{\partial}{\partial x} f(x) \right] \approx \frac{1}{\Delta x} \left\{ \sum_x \left[g(x) f(x+\Delta x) \right] - \sum_x \left[g(x) f(x) \right] \right\} \tag{D.10}$$

By extending the property of the one-step operator, Eq. (B-7), to the domain of the real numbers, the right-hand side of the above expression can be transformed to

$$\begin{aligned} & \sum_x \left[g(x) \frac{\partial}{\partial x} f(x) \right] \\ & \approx \frac{1}{\Delta x} \left\{ \sum_x \left[g(x) f(x+\Delta x) \right] - \sum_x \left[g(x) f(x) \right] \right\} \\ & = \frac{1}{\Delta x} \left\{ \sum_x \left[g(x) \mathbb{E} f(x) \right] - \sum_x \left[g(x) f(x) \right] \right\} \end{aligned}$$

or

$$\begin{aligned} & \sum_x \left[g(x) \frac{\partial}{\partial x} f(x) \right] \\ & = \frac{1}{\Delta x} \left\{ \sum_x \left[f(x) \mathbb{E}^{-1} g(x) \right] - \sum_x \left[g(x) f(x) \right] \right\} \\ & = \frac{1}{\Delta x} \left\{ \sum_x \left[f(x) g(x-\Delta x) \right] - \sum_x \left[f(x) g(x) \right] \right\} \end{aligned}$$

or

$$\begin{aligned} & \sum_x \left[g(x) \frac{\partial}{\partial x} f(x) \right] \\ & = \sum_x \left\{ f(x) \left[\frac{g(x-\Delta x) - g(x)}{\Delta x} \right] \right\} \\ & = -\sum_x \left\{ f(x) \left[\frac{g(x) - g(x-\Delta x)}{\Delta x} \right] \right\} \end{aligned} \tag{D.11}$$

In light of Eq. (D.8), this expression reduces to

$$\sum_x \left[g(x) \frac{\partial}{\partial x} f(x) \right] = -\sum_x \left[f(x) \frac{\partial}{\partial x} g(x) \right] \tag{D.12}$$

Similarly,

$$\sum_x \left[g(x) \frac{\partial^2}{\partial x^2} f(x) \right]$$

$$\approx \sum_x \left\{ g(x) \left[\frac{f(x+\Delta x) - 2f(x) + f(x-\Delta x)}{(\Delta x)^2} \right] \right\}$$

$$\approx \frac{1}{(\Delta x)^2} \left\{ \sum_x \left[g(x) f(x+\Delta x) \right] - 2 \sum_x \left[g(x) f(x) \right] + \sum_x \left[g(x) f(x-\Delta x) \right] \right\} \tag{D.13}$$

By virtue of Eq. (D.7), we obtain

$$\sum_x \left[g(x) \frac{\partial^2}{\partial x^2} f(x) \right]$$

$$= \frac{1}{(\Delta x)^2} \left\{ \sum_x \left[g(x) \mathbb{E} f(x) \right] - 2 \sum_x \left[g(x) f(x) \right] + \sum_x \left[g(x) \mathbb{E}^{-1} f(x) \right] \right\}$$

$$= \frac{1}{(\Delta x)^2} \left\{ \sum_x \left[f(x) \mathbb{E}^{-1} g(x) \right] - 2 \sum_x \left[g(x) f(x) \right] + \sum_x \left[f(x) \mathbb{E} g(x) \right] \right\}$$

or

$$\sum_x \left[g(x) \frac{\partial^2}{\partial x^2} f(x) \right]$$

$$= \frac{1}{(\Delta x)^2} \left\{ \sum_x \left[f(x) g(x-\Delta x) \right] - 2 \sum_x \left[f(x) g(x) \right] + \sum_x \left[f(x) g(x+\Delta x) \right] \right\}$$

$$= \sum_x \left\{ f(x) \left[\frac{g(x+\Delta x) - 2g(x) + g(x-\Delta x)}{(\Delta x)^2} \right] \right\}$$

or in view of Eq. (D.9),

$$\sum_x \left[g(x) \frac{\partial^2}{\partial x^2} f(x) \right] = \sum_x \left[f(x) \frac{\partial^2}{\partial x^2} g(x) \right] \tag{D.14}$$

The linear Fokker-Plank equation governing the fluctuations of the process around the macroscopic values is given by Eq. (C.19) as

$$\frac{\partial \pi}{\partial \gamma} = 2\alpha (1-\varphi) \frac{\partial}{\partial \xi} (\xi \pi) + \frac{1}{2} \alpha (1-\varphi)^2 \frac{\partial^2 \pi}{\partial \xi^2} \tag{D.15}$$

Because $n_M t = \gamma$, this equation can be rewritten as

$$\frac{\partial \pi}{\partial t} = 2\alpha n_M (1-\varphi)\frac{\partial}{\partial \xi}(\xi\pi) + \frac{1}{2}\alpha n_M (1-\varphi)^2 \frac{\partial^2 \pi}{\partial \xi^2} \tag{D.16}$$

Multiplying both sides of the above equation by ξ and summing over all values of ξ yield

$$\sum_\xi \xi \frac{\partial}{\partial t}\pi = [2\alpha n_M (1-\varphi)]\left[\sum_\xi \xi \frac{\partial}{\partial \xi}(\xi\pi)\right] + \frac{1}{2}[\alpha n_M (1-\varphi)^2]\left[\sum_\xi \xi \frac{\partial^2}{\partial \xi^2}\pi\right] \tag{D.17}$$

By virtue of Eqs. (B-12) and (B-14), the right-hand side of this expression can be transformed to

$$\sum_\xi \xi \frac{\partial}{\partial t}\pi = [2\alpha n_M (1-\varphi)]\left[-\sum_\xi \xi\pi \frac{\partial}{\partial \xi}\xi\right] + \frac{1}{2}[\alpha n_M (1-\varphi)^2]\left[\sum_\xi \pi \frac{\partial^2}{\partial \xi^2}\xi\right]$$

or

$$\sum_\xi \xi \frac{\partial}{\partial t}\pi = -[2\alpha n_M (1-\varphi)]\left[\sum_\xi \xi\pi\right] \tag{D.18}$$

The first moment of random variable $\Xi(t)$, i.e., $E[\Xi(t)]$, is defined as

$$E[\Xi(t)] = \sum_\xi \xi\pi(\xi;t)$$

or

$$E[\Xi(t)] = \sum_\xi \xi\pi \tag{D.19}$$

and thus,

$$\frac{d}{dt}E[\Xi(t)] = \sum_\xi \xi \frac{\partial}{\partial t}\pi \tag{D.20}$$

In light of the above two equations, Eq. (D.18) reduces to

$$\frac{d}{dt}E[\Xi(t)] = -[2\alpha n_M (1-\varphi)]\,E[\Xi(t)] \tag{D.21}$$

Inserting Eq. (D.5) for $\varphi(t)$ into this equation and integrating the resulting expression yield

$$E[\Xi(t)] = \frac{c'}{\left[(\alpha n_M)t + 1\right]^2} \tag{D.22}$$

From the initial conditions for the transformed probability distribution, $\pi(\xi;t)$,

$$\pi(\xi;0) = \begin{cases} 1 & \text{if} \quad \xi = 0 \\ \\ 0 & \text{elsewhere} \end{cases} \tag{D.23}$$

and the definition of $E[\Xi(t)]$, as given by Eq. (B-19), we have

$$E[\Xi(0)] = 0, \tag{D.24}$$

thereby indicating that

$$c' = 0 \tag{D.25}$$

Hence,

$$E[\Xi(t)] = 0 \tag{D.26}$$

As discerned from this equation, the mean of random variable $\Xi(t)$ signifying the fluctuations of the process around their mean values is null.

Similarly, multiplying both sides of Eq. (D.16) by ξ^2 and summing over all values of ξ yield

$$\sum_{\xi} \xi^2 \frac{\partial}{\partial t}\pi = [2\alpha n_M (1-\varphi)]\left[\sum_{\xi} \xi^2 \frac{\partial}{\partial \xi}(\xi\pi)\right] + \frac{1}{2}[\alpha n_M (1-\varphi)^2]\left[\sum_{\xi} \xi^2 \frac{\partial^2}{\partial \xi^2}\pi\right] \tag{D.27}$$

By virtue of Eqs. (D.12) and (D.14), the right-hand side of the above expression can be transformed to

$$\sum_{\xi} \xi^2 \frac{\partial}{\partial t}\pi = [2\alpha n_M (1-\varphi)]\left[-\sum_{\xi} \xi\pi \frac{\partial}{\partial \xi}\xi^2\right] + \frac{1}{2}[\alpha n_M (1-\varphi)^2]\left[\sum_{\xi} \pi \frac{\partial^2}{\partial \xi^2}\xi^2\right]$$

or

$$\sum_{\xi} \xi^2 \frac{\partial}{\partial t}\pi = -4[\alpha n_M (1-\varphi)]\left[\sum_{\xi} \xi^2\pi\right] + [\alpha n_M (1-\varphi)^2]\left[\sum_{\xi} \pi\right] \tag{D.28}$$

For the transformed probability distribution, $\pi(\xi;t)$, the following property must hold

$$\sum_{\xi} \pi(\xi;t) = 1$$

or

$$\sum_{\xi} \pi = 1 \tag{D.29}$$

Thus, Eq. (D.28) can be rewritten as

$$\sum_{\xi} \xi^2 \frac{\partial}{\partial t}\pi = -4[\alpha n_M (1-\varphi)]\left[\sum_{\xi} \xi^2\pi\right] + [\alpha n_M (1-\varphi)^2] \tag{D.30}$$

The second moment of random variable $\Xi(t)$, i.e., $E[\Xi^2(t)]$, is defined as

$$E[\Xi^2(t)] = \sum_{\xi} \xi^2 \pi(\xi;t)$$

or

$$E[\Xi^2(t)] = \sum_{\xi} \xi^2 \pi \tag{D.31}$$

and thus,

$$\frac{d}{dt} E[\Xi^2(t)] = \sum_{\xi} \xi^2 \frac{\partial}{\partial t} \pi \tag{D.32}$$

In view of the above two equations, Eq. (B-30) reduces to

$$\frac{d}{dt} E[\Xi^2(t)] = -4[\alpha n_M (1-\varphi)]\, E[\Xi^2(t)] + [\alpha n_M (1-\varphi)^2] \tag{D.33}$$

Inserting Eq. (D.5) for $\varphi(t)$ into this equation and integrating the resulting expression yield

$$E[\Xi^2(t)] = \frac{1}{3\left[(\alpha n_M)t+1\right]^4} + \frac{c''}{\left[(\alpha n_M)t+1\right]^4} \tag{D.34}$$

From the aforementioned initial conditions for the transformed probability distribution, $\pi(\xi;t)$, as given by Eq. (D.23), and the expression of $E[\Xi^2(t)]$ as defined by Eq. (D.31), we have

$$E[\Xi^2(0)] = 0, \tag{D.35}$$

thereby indicating that

$$c'' = -\frac{1}{3} \tag{D.36}$$

Hence,

$$E[\Xi^2(t)] = \frac{1}{3\left[(\alpha n_M)t+1\right]} \left\{ 1 - \frac{1}{\left[(\alpha n_M)t+1\right]^3} \right\} \tag{D.37}$$

The mean, E[N(t)] or m(t), is obtained by substituting Eqs. (D.5) and (D.26) into (D.2) as

$$m(t) = n_M \left[\frac{(\alpha n_M)t}{(\alpha n_M)t+1} \right]$$

or

$$m(t) = n_M \left(\frac{\alpha' t}{\alpha' t+1} \right) \tag{D.38}$$

where $\alpha' = (\alpha n_M)$; this is Eq. (3.4) in the text. Similarly, the variance, Var[N(t)] or $\sigma^2(t)$, is obtained by inserting Eqs. (D.26) and (D.37) into Eq. (D.3) as

$$\sigma^2(t) = n_M \left(\frac{1}{3\left[(\alpha n_M)t + 1\right]} \left\{ 1 - \frac{1}{\left[(\alpha n_M)t + 1\right]^3} \right\} \right)$$

or

$$\sigma^2(t) = \frac{n_M}{3(\alpha' t + 1)} \left[1 - \frac{1}{(\alpha' t + 1)^3} \right] \tag{D.39}$$

This is Eq. (3.6) in the text.

Appendix E - Formation of Carbon Molecular Sieves: Derivation of the Probability Density Function and the Cumulative Distribution Function of Waiting Time for the Pure-Birth Process with a Non-Linear Intensity of Transition Based on a Single Random Variable

Let T_n be a random variable representing the waiting time between events for the pure-birth process of interest with the intensity of birth, $\lambda_n(t)$; a realization of T_n is denoted by ν. Given that it is in state n at time t, the system is assumed to remain in this state during time interval $(t, t+\nu)$; at the end of which, i.e., at $(t+\nu)$, a transition occurs and the state of the system changes. The probability that a transition occurs during time interval $(t, t+\nu)$ is specified by the cumulative distribution function, cdf, of T_n with realization ν. This function is denoted by $H_n(\nu)$ and defined as

$$H_n(\nu) = \Pr[T_n \le \nu] \tag{E.1}$$

By definition, $H_n(\nu)$ is within the range from 0 to 1. Moreover, the probability that no transition occurs during time interval $(t, t+\nu)$ given that the system is in state n at time t, $G_n(\nu)$, is[72]

$$G_n(\nu) = \Pr[T_n > \nu] = 1 - H_n(\nu) \tag{E.2}$$

For the succeeding small time interval $[(t+\nu), (t+\nu)+\Delta\nu]$,[74, 122]

$$H_n(\Delta\nu) = [\lambda_n(t+\nu)]\Delta\nu + o(\Delta\nu) \tag{E.3}$$

where $o(\Delta\nu)$ is defined such that

$$\lim_{\Delta\nu \to 0} \frac{o(\Delta\nu)}{\Delta\nu} = 0,$$

Note that the intensity of birth, $\lambda_n(t)$, in Eq. (E.3) is evaluated at the time at which a transition occurs, i.e., at $(t+\nu)$. On the basis of Eq. (E.2), we obtain

$$G_n(\Delta\nu) = \{1 - [\lambda_n(t+\nu)]\Delta\nu\} + o(\Delta\nu) \tag{E.4}$$

The Markovian property implies that disjoint time intervals are independent of one another; therefore,[72]

$$G_n(\nu+\Delta\nu) = G_n(\nu)\,G_n(\Delta\nu) \tag{E.5}$$

Inserting Eq. (E.4) into the above equation results in

$$G_n(\nu+\Delta\nu) = G_n(\nu)\{1-[\lambda_n(t+\nu)]\Delta\nu\} + o(\Delta\nu) \tag{E.6}$$

Expanding and rearranging this expression yield

$$G_n(\nu+\Delta\nu) - G_n(\nu) = -[\lambda_n(t+\nu)]\,G_n(\nu)\Delta\nu + o(\Delta\nu) \tag{E.7}$$

Dividing both sides of this equation by $\Delta\nu$ and taking the limit as $\Delta\nu \to 0$ give rise to

$$\frac{d}{d\nu}G_n(\nu) = -[\lambda_n(t+\nu)]\,G_n(\nu) \tag{E.8}$$

By integrating this ordinary differential equation subject to the initial condition,[72, 74, 122]

$$G_n(0) = 1,$$

we have

$$G_n(\nu) = \exp\left\{-\int_0^{\nu}[\lambda_n(t+\nu')]\,d\nu'\right\} \tag{E.9}$$

Equation (D.2) in conjunction with the above equation leads to

$$H_n(\nu) = 1-\exp\left\{-\int_0^{\nu}[\lambda_n(t+\nu')]\,d\nu'\right\} \tag{E.10}$$

Differentiating both sides of this equation with respect to ν gives

$$\frac{d}{d\nu}H_n(\nu) = [\lambda_n(t+\nu)]\exp\left\{-\int_0^{\nu}[\lambda_n(t+\nu')]\,d\nu'\right\} \tag{E.11}$$

The probability density function, pdf, of T_n given that the system is in state n at time t, $h_n(\nu)$, is defined as

$$h_n(\nu) = \frac{d}{d\nu}H_n(\nu) \tag{E.12}$$

Naturally,

$$H_n(\nu) = \int_0^{\nu} h_n(\nu')\,d\nu' \tag{E.13}$$

In light of Eq. (E.12), Eq. (E.11) can be rewritten as

$$h_n(\nu) = [\lambda_n(t+\nu)] \exp\left\{-\int_0^{\nu} [\lambda_n(t+\nu')]d\nu'\right\} \tag{E.14}$$

The above equation in conjunction with Eq. (E.10) reveal that the pdf of T_n is exponential.[74, 122] Clearly, the parameter of this pdf depends on the form of the intensity of birth, $\lambda_n(t)$. Inserting Eq. (3.2) in the text for $\lambda_n(t)$ into Eq. (E.10) yields

$$H_n(\nu) = 1 - \exp\left\{-\int_0^{\nu} [\alpha(n_M - n)^2]d\nu'\right\} \tag{E.15}$$

Upon integration of this expression, we obtain

$$H_n(\nu) = 1 - \exp\left\{-[\alpha(n_M - n)^2]\nu\right\} \tag{E.16}$$

In light of Eq. (E.12),

$$h_n(\nu) = [\alpha(n_M - n)^2] \exp\{-[\alpha(n_M - n)^2]\nu\} \tag{E.17}$$

These two equations indicate that the pdf of random variable T_n is exponential with parameter $\alpha(n_M - n)^2$, i.e., the intensity of birth, $\lambda_n(t)$, of the pure-birth process of concern, which is dependent only on realization n but independent of time t.

Appendix F - Formation of Carbon Molecular Sieves: Estimation of Waiting Time for the Pure-Birth Process with a Non-Linear Intensity of Transition Based on a Single Random Variable

As indicated in the preceding appendix, the random variable, T_n, with realization ν represents the waiting time between successive events for a birth-death process. Equation (E.1) repeated below defines $H_n(\nu)$, i.e., the cdf of T_n, as

$$H_n(\nu) = \Pr[T_n \le \nu] \tag{F.1}$$

This cdf signifies the probability that the system undergoes a transition during time interval $(t, t+\nu)$ given that it is in state n at time t.

Let U be a random variable defined as

$$U = H_n(T_n) \tag{F.2}$$

Thus, u, which is a realization of U, is

$$u = H_n(\nu) \tag{F.3}$$

By definition, any realization u is within the range from 0 to 1. Naturally, the cdf of U with realization u, i.e., $F_U(u)$, is given by

$$F_U(u) = \Pr[U \le u] \tag{F.4}$$

Substituting Eqs. (E.2) and (E.3) into this equation yields

$$F_U(u) = \Pr[H_n(T_n) \le H_n(\nu)] \tag{F.5}$$

The inverse function of any given function, $y = f(x)$, is defined as $x = f^{-1}(y)$, or $x = f^{-1}[f(x)]$, provided that f(x) is continuous and strictly increasing.[131, 132] In other words, the inverse function, $x = f^{-1}(y)$, reverses what the original function, $y = f(x)$, performs over any value x of its domain, thereby returning x. Note that the inverse function of f(x) is not its reciprocal or multiplicative inverse, which is given by [1/f(x)] or $[f(x)]^{-1}$. Herein, $y = f(x)$ stands for $U = H_n(T_n)$ on the basis of Eq. (F.2); thus, its inverse function is given by

$$T_n = H_n^{-1}(U)$$

Inserting Eq. (F.2) into the above equation yields

$$T_n = H_n^{-1}[H_n(T_n)] \tag{F.6}$$

and therefore,

$$\nu = H_n^{-1}[H_n(\nu)] \tag{F.7}$$

Given that the functions, $H_n(T_n)$ and $H_n(\nu)$, are continuous and strictly increasing, they can be substituted by $H_n^{-1}[H_n(T_n)]$ and $H_n^{-1}[H_n(\nu)]$, respectively, in the inequality within the bracket on the right-hand side of Eq. (F.5) without altering the inequality[111]; hence,

$$F_U(u) = \Pr\left\{H_n^{-1}[H_n(T_n)] \le H_n^{-1}[H_n(\nu)]\right\} \tag{F.8}$$

In light of Eqs. (F.6) and (F.7), this equation reduces to

$$F_U(u) = \Pr[T_n \le \nu] \tag{F.9}$$

Note that the right-hand side of this expression is $H_n(\nu)$ as defined by Eq. (F.1); thus,

$$F_U(u) = H_n(\nu) \tag{F.10}$$

Because of Eq. (F.3),

$$F_U(u) = u \tag{F.11}$$

This is the expression for the cdf of U with realization u; by definition, its pdf is

$$f_U(u) = \frac{d}{du} F_U(u)$$

Substituting Eq. (F.11) into the right-hand side of this equation gives

$$f_U(u) = \frac{d}{du}(u)$$

or

$$f_U(u) = 1 \tag{F.12}$$

This equation in conjunction with Eq. (F.11) imply that U is the uniform random variable on interval (0, 1).[111] As a result, a realization of T_n, i.e., ν, can be estimated by sampling a realization of U, i.e., u, on interval (0, 1), and solving Eq. (F.3) for ν as[74]

$$\nu = H_n^{-1}(u) \tag{F.13}$$

Figure F.1 illustrates this scheme to estimate waiting time ν. For the pure-birth process of interest, Eq. (F.3) is

$$u = 1 - \exp\left\{-[\alpha(n_M - n)^2]\nu\right\} \tag{F.14}$$

Clearly, the right-hand side of this expression is $H_n(\nu)$ as given by Eq. (E.16). By solving the above equation for ν, we obtain

$$\nu = \frac{-1}{[\alpha(n_M - n)^2]}\ell n(1-u) \tag{F.15}$$

This is Eq. (3.20) in the text. Note that ν is dependent on realization n but independent of time t.

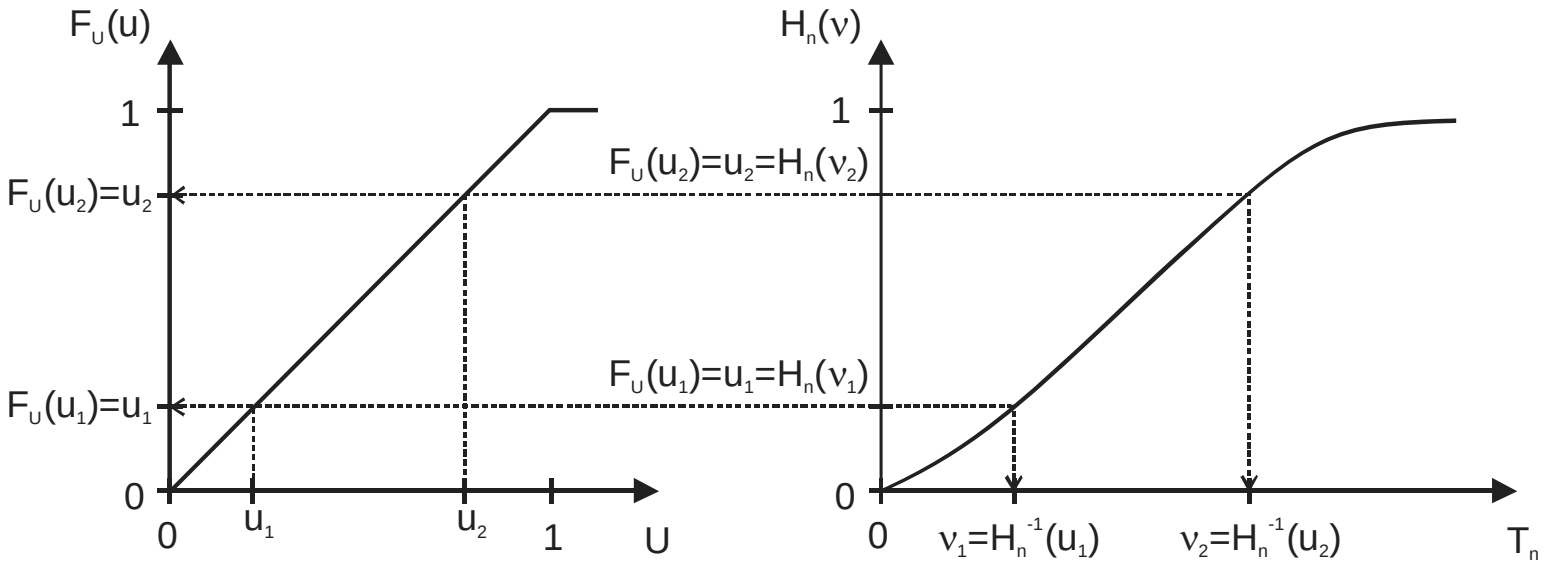

Figure F.1. Schematic for estimating realization ν of the random variable, T_n, representing the waiting time on the basis of realization u of the uniform random variable, U, on interval (0,1).

Appendix G - Formation of Carbon Molecular Sieves: Computer Codes for Performing Monte Carlo Simulation of the Pure-Birth Process with a Non-Linear Intensity of Transition Based on a Single Random Variable via the Event-Driven and Time-Driven Approaches

Two computer codes have been written in Microsoft Visual Basic for simulating the pure-birth process of interest through the Monte Carlo method via the event-driven and time-driven approaches on two separate spreadsheets of Microsoft Excel for Windows. The resultant codes for the event-driven approach as well as for the time-driven approach are listed in Tables G.1 and G.2, respectively.

Table G.1. Computer Code in Microsoft Visual Basic for Performing Monte Carlo Simulation of the Pure-Birth Process via the Event-Driven Approach.

```
Sub EventDriven()
'MONTE CARLO SIMULATION VIA EVENT-DRIVEN APPROACH
'CMS FORMATION AS A PURE-BIRTH PROCESS WITH A NON-LINEAR
'INTENSITY FUNCTION BASED ON A SINGLE RANDOM VARIABLE

Randomize

Dim OutputData As Integer

   OutputData = 19

   Range("B" + CStr(OutputData)).Select

Range(Selection, Selection.End(xlToRight).End(xlDown)).ClearContents

Range("B" + CStr(OutputData)).Select


'Constants

   alfa = Range("c3").Value
   nM = Range("c4").Value
   n0 = Range("c5").Value
   t0 = Range("c6").Value
   tf = Range("c7").Value
   dtheta = Range("c8").Value
   Zf = Range("c9").Value
```

```
For Z = 1 To Zf

    OutputData = 19
    Range("B" + CStr(OutputData)).Select


    t = t0                  ' Initial value of clock time
    theta = t0              ' Initial value of data-recording time
    n = n0                  ' Initial value of random variable N(t)


    Do While t <= tf


        u = Rnd(1)                          ' Uniform random number

        lambda = alfa * (nM - n) ^ 2        ' Intensity function


        If lambda > 0 Then

          nu = (-1 / lambda) * Log(1 - u)   ' Random waiting time

        Else

          Exit Do

        End If

        t = t + nu
```

```
Do While (theta < t)

    ' Column of data-recording time
    Range("B" + CStr(OutputData)).Value = theta

    ' Column of realizations of N(t)
    Range("C" + CStr(OutputData)).Value = n

    ' Column of sum of realizations
    Range("D" + CStr(OutputData)).Value = Range("D" + CStr(OutputData)).Value +
Range("C" + CStr(OutputData)).Value

    ' Column of means
    Range("E" + CStr(OutputData)).Value = Range("D" + CStr(OutputData)).Value / Zf

   ' Column of sum of squares of realizations
    Range("F" + CStr(OutputData)).Value = (Range("F" + CStr(OutputData)).Value) +
(Range("C" + CStr(OutputData)).Value) ^ 2

    ' Column of variances
    Range("G" + CStr(OutputData)).Value = (1 / (Zf - 1)) * (Range("F" +
CStr(OutputData)).Value - (1 / Zf) * (Range("D" + CStr(OutputData)).Value) ^ 2)

    ' Column of means plus standard deviations
    Range("H" + CStr(OutputData)).Value = Range("E" + CStr(OutputData)).Value +
Sqr(Range("G" + CStr(OutputData)).Value)


  ' Column of means minus standard deviations
```

```
            Range("I" + CStr(OutputData)).Value = Range("E" + CStr(OutputData)).Value -
Sqr(Range("G" + CStr(OutputData)).Value)

            OutputData = OutputData + 1

            If theta <= tf Then

               theta = theta + dtheta

            Else

               Exit Do

            End If

         Loop


         n = (n + 1)

      Loop


Next Z

End Sub
```

Table G.2. Computer Code in Microsoft Visual Basic for Performing Monte Carlo Simulation of the Pure-Birth Process via the Time-Driven Approach.

```
Sub TimeDriven()
'MONTE CARLO SIMULATION VIA TIME-DRIVEN APPROACH
'CMS FORMATION AS A PURE-BIRTH PROCESS WITH A NON-LINEAR
'INTENSITY FUNCTION BASED ON A SINGLE RANDOM VARIABLE

Randomize

Dim OutputData As Integer

   OutputData = 18

   Range("B" + CStr(OutputData)).Select

   Range(Selection, Selection.End(xlToRight).End(xlDown)).ClearContents

   Range("B" + CStr(OutputData)).Select

   OutputData = 18
   Range("B" + CStr(OutputData)).Select

   ' Constants

   alpha = Range("c3").Value
   nM = Range("c4").Value
   n0 = Range("c5").Value
   t0 = Range("c6").Value
   tf = Range("c7").Value
```

```
    dt = Range("c8").Value
    Zf = Range("c9").Value


For Z = 1 To Zf

    OutputData = 18

    'Range("B" + CStr(OutputData)).Select

    t = t0                      ' Initial value of clock time
    n = n0                      ' Initial value of random variable N(t)

       Do Until t >= tf

      ' Column of time
       Range("B" + CStr(OutputData)).Value = t

       ' Column of realizations of random variable N(t)
       Range("C" + CStr(OutputData)).Value = n

        ' Column of sum of realizations
       Range("D" + CStr(OutputData)).Value = Range("D" + CStr(OutputData)).Value +
Range("C" + CStr(OutputData)).Value

       ' Column of means
       Range("E" + CStr(OutputData)).Value = Range("D" + CStr(OutputData)).Value / Zf

       ' Column of sum of squares of realizations
       Range("F" + CStr(OutputData)).Value = (Range("F" + CStr(OutputData)).Value) +
(Range("C" + CStr(OutputData)).Value) ^ 2
```

```
    ' Column of variances
    Range("G" + CStr(OutputData)).Value = (1 / (Zf - 1)) * (Range("F" +
CStr(OutputData)).Value - (1 / Zf) * (Range("D" + CStr(OutputData)).Value) ^ 2)

    ' Column of means plus standard deviations
    Range("H" + CStr(OutputData)).Value = Range("E" + CStr(OutputData)).Value +
Sqr(Range("G" + CStr(OutputData)).Value)

    ' Column of means minus standard deviations
    Range("I" + CStr(OutputData)).Value = Range("E" + CStr(OutputData)).Value -
Sqr(Range("G" + CStr(OutputData)).Value)


    OutputData = OutputData + 1


    t = t + dt


    u = Rnd(1)                                  ' Uniform random number


    lambdadt = alpha * (nM - n) ^ 2 * dt        ' Probability of occurrence for the birth event
```

```
        If u <= lambdadt Then

            n = n + 1

        Else

            n = n

        End If


    Loop

Next Z


End Sub
```

Appendix H - Formation of Carbon Molecular Sieves: Simulation of Experimental Data for the Pure-Birth Process with a Non-Linear Intensity of Transition Based on a Single Random Variable

At the outset, or early stage, of the pore-narrowing, the number of carbon packets depositing onto the pores' mouths is minute. Consequently, the random variable, N(t), with realization n can be assumed to obey a Poisson probability distribution given by[110, 132, 133]

$$\Pr[N(t) = n] = \frac{(\beta t)^n}{n!}\exp[-(\beta t)] \tag{H.1}$$

where the positive parameter, (βt), corresponds to the distribution's mean, $m_P(t)$; thus,

$$m_P(t) = \beta t \tag{H.2}$$

Naturally, this is the equation of a straight line whose slope is β; hence,

$$\beta = \frac{[m_P(t_f) - m_P(t_0)]}{(t_f - t_0)} \tag{H.3}$$

where t_0 and t_f are the initial and final times of an experiment performed at certain temperature. An estimate of β, which is denoted by $\hat{\beta}$, can be computed in view of Eq. (H.3) as

$$\hat{\beta} = \frac{(n_f - n_0)}{(t_f - t_0)} \tag{H.4}$$

where n_0 and n_f are the realizations of N(t) at t_0 and t_f, respectively. In terms of $\hat{\beta}$, Eq. (H.2) can be rewritten as

$$m_P(t) \cong \hat{\beta} t \tag{H.5}$$

At any time t, the random variable, W(t), representing the amount of carbon already deposited on ACs is given by Eq. (3.13) in the text as

$$W(t) = \omega N(t)$$

where ω is the weight of a single packet of carbon; naturally, a realization of W(t) is

$$w = (\omega n) \tag{H.6}$$

Moreover, the mean weight of carbon deposited per unit weight of ACs, $m_W(t)$, is expressed by Eq. (3.14) in the text as

$$m_W(t) = W_M\left(\frac{\alpha' t}{\alpha' t + 1}\right) \tag{H.7}$$

Solving this equation for t gives

$$t = \left(\frac{1}{\alpha'}\right)\frac{\left[\frac{m_W(t)}{W_M}\right]}{\left\{1 - \left[\frac{m_W(t)}{W_M}\right]\right\}} \tag{H.8}$$

At the outset of the pore-narrowing, $m_W(t) << W_M$, and thus, this expression reduces to

$$t = \left(\frac{1}{\alpha'}\right)\left[\frac{m_W(t)}{W_M}\right]$$

By assuming that $m_W(t) \cong w$, this equation can be rewritten as

$$t = \left(\frac{1}{\alpha'}\right)\left[\frac{w}{W_M}\right] \tag{H.9}$$

For illustration, $n_0 = 0$ and $n_f = 100$; thus, from Eq. (H.6), we have

$$w_0 = 0 \tag{H.10}$$

and

$$w_f = (100\,\omega) \tag{H.11}$$

respectively. The values of t_0 and t_f corresponding to w_0 and w_f are obtained from the above two equations in conjunction of Eq. (H.9) as

$$t_0 = 0 \tag{H.12}$$

and

$$t_f = \left(\frac{1}{\alpha'}\right)\left[\frac{100\,\omega}{W_M}\right] \tag{H.13}$$

By assuming that the experiment is performed at 973 K; the values of W_M and α' have been recovered from the experimental data[65] as 0.385 mg C and 0.022 min^{-1}, respectively, in Chapter 3. Moreover, the weight of a single packet is estimated to be $0.63 \cdot 10^{-13}$ mg C; thus, t_f is

computed from the above equation as $7.44 \cdot 10^{-10}$ min. Clearly, this value of t_f verifies that the simulated experiment is being performed at the very outset of the pore-narrowing.

Inserting the values of n_0, n_f, t_0, and t_f into Eq. (H.4) gives $\hat{\beta}$ as $1.36 \cdot 10^{11}$ packets $\cdot$ min^{-1}. With this value of in $\hat{\beta}$, a realization of N(t), i.e., n, at any time t can be simulated by sampling a random number, or deviate, from a Poisson distribution whose mean is given by Eq. (H.5). A set of j Poisson deviates constitutes a set of simulated experimental data at the temperature of interest. Given in Table H.1 is the computer code written in R for generating these deviates.

Table H.1. Computer Code in R for Generating Simulated Experimental Data as Poisson Deviates for the Pure-Birth Process.

```
function(j, betahat, t0, tf){

    # This function generates j Poisson deviates
    # on time interval (t0, tf). The proportionality
    # constant is denoted by betahat.

    timestep<-(tf-t0)/j

    times<-seq(t0, tf, by=timestep)

    means<-betahat*times

    devs<-rpois(j+1,means)

    solution<-cbind(times, devs)

    plot(times,devs)

    solution

}
```

Appendix I - Derivation of the Master Equation of a Pure-Death Process

Suppose that a system comprising a population of particulate or discrete entities in a given space is to be stochastically modeled as a pure-death process. The random variable characterizing this process is denoted by N(t) with realization n; moreover, the intensity of death is denoted by $\mu_n(t)$. Thus, one of the following two events is considered to occur during time interval $(t, t+\Delta t)$. First, the number of entities decreases by one, which is a death event, with conditional probability $\{[\mu_n(t)]\Delta t + o(\Delta t)\}$. Second, the number of entities changes by a number other than one with conditional probability o(Δt), which is defined such that

$$\lim_{\Delta t \to 0} \frac{o(\Delta t)}{\Delta t} = 0 \tag{I.1}$$

Naturally, the conditional probability of no change in the number of entities during this time interval is $(1 - \{[\mu_n(t)]\Delta t + o(\Delta t)\})$.

Let the probability that exactly n entities are present at time t be denoted as $p_n(t) = \Pr[N(t) = n]$, where $n \in (n_0, n_0 - 1, ..., 2, 1, 0)$; n_0 is the initial number of entities in the system. For the two adjacent time intervals, (0, t) and $(t, t+\Delta t)$, the occurrence of exactly n entities being present at time $(t+\Delta t)$ can be realized in the following mutually exclusive ways; see Figure I.1.

(1) With a probability of $\{[\mu_{n+1}(t)]\Delta t + o(\Delta t)\}p_{n+1}(t)$, the number of entities will decrease by one during time interval $(t, t+\Delta t)$, provided that exactly $(n+1)$ entities are present at time t.

(2) With a probability of o(Δt), the number of entities will change by exactly j entities during time interval $(t, t+\Delta t)$, provided that exactly $(n-j)$ entities are present at time t, where $2 \le j \le n_0$.

(3) With a probability of $(1 - \{[\mu_n(t)]\Delta t + o(\Delta t)\})p_n(t)$, the number of entities will remain unchanged during time interval $(t, t+\Delta t)$, provided that n entities are present at time t.

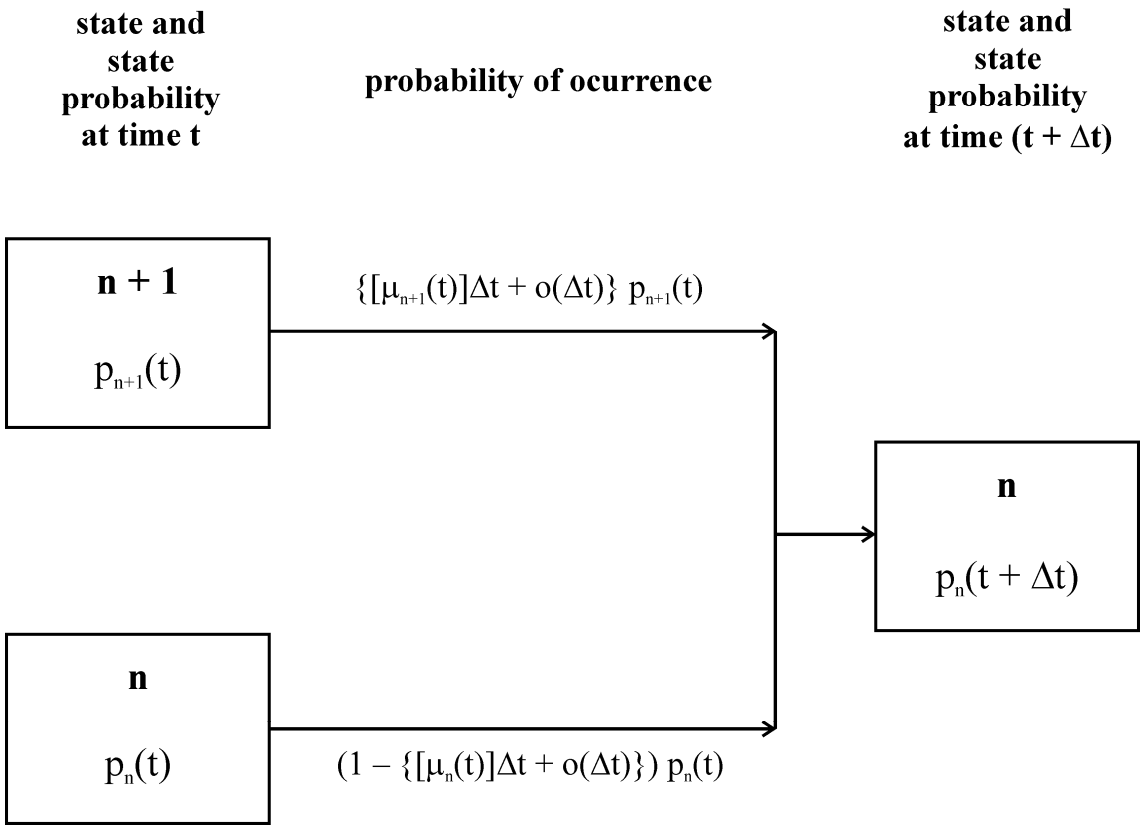

Figure I.1. Probability balance for the pure-death process involving the mutually exclusive events in the time interval, (t, t + Δt).

Summing all these probabilities and consolidating all quantities of o(Δt) yield

$$p_n(t+\Delta t) = \{[\mu_{n+1}(t)]\Delta t\}\, p_{n+1}(t) + \{1-[\mu_n(t)]\Delta t\}\, p_n(t) + o(\Delta t) \tag{I.2}$$

Rearranging this equation, dividing it by Δt, and taking the limit as $\Delta t \to 0$ yield the master equation of the pure-death process as;[73, 134]

$$\frac{d}{dt} p_n(t) = \mu_{n+1}(t)\, p_{n+1}(t) - \mu_n(t)\, p_n(t) \tag{I.3}$$

This in Eq. (4.1) in the text.

Appendix J - Formation of Carbon Molecular Sieves: System-Size Expansion of the Master Equation for the Pure-Death Process with a Non-Linear Intensity of Transition Based on a Single Random Variable

As derived in the preceding appendix, the master equation of the pure-death process, Eq. (I.3), is given by

$$\frac{d}{dt}p_n(t) = \mu_{n+1}(t)p_{n+1}(t) - \mu_n(t)p_n(t), \quad n = n_0, n_0 - 1, \ldots, 2, 1, 0 \tag{J.1}$$

In light of the one-step operator, $\mathbb{E}$, this equation is reduced to

$$\frac{d}{dt}p_n(t) = (\mathbb{E} - 1)\mu_n(t)p_n(t), \quad n = n_0, n_0 - 1, \ldots, 2, 1, 0 \tag{J.2}$$

The intensity of death, $\mu_n(t)$, in this expression is given by Eq. (4.2) in the text as

$$\mu_n(t) = -\frac{dn}{dt} = kn + k'n(n_0 - n)$$

where k and k' are proportionality constants. By expanding and rearranging the right-hand side of this expression, we obtain

$$\mu_n(t) = -\frac{dn}{dt} = (k + k'n_0)n - k'n^2 \tag{J.3}$$

Substituting the above equation into Eq. (J.2) yields

$$\frac{d}{dt}p_n(t) = (\mathbb{E} - 1)[(k + k'n_0)n - k'n^2]p_n(t) \tag{J.4}$$

As elaborated in Appendix C, the random variable, N(t), is expressed as the sum of the macroscopic term, $\Omega\varphi(t)$, and the fluctuation term, $\Omega^{1/2}\Xi(t)$ as

$$N(t) = \Omega\varphi(t) + \Omega^{1/2}\Xi(t)$$

For the pure-death process of interest, the system's size, Ω, in this expression is identified as n_0; thus,

$$N(t) = n_0\varphi(t) + n_0^{1/2}\Xi(t) \tag{J.5}$$

whose realization given by

$$n = n_0\varphi(t) + n_0^{1/2}\xi \tag{J.6}$$

Accordingly, $p_n(t)$ or $p(n;t)$ is transformed into function $\pi(\xi;t)$ as

$$p(n;t) = \pi(\xi;t) \tag{J.7}$$

Differentiating this expression with respect to t gives rise to

$$\frac{d}{dt}p(n;t) = \frac{\partial\pi}{\partial t} - n_0^{1/2}\left(\frac{d\varphi}{dt}\right)\frac{\partial\pi}{\partial\xi} \tag{J.8}$$

where $\pi = \pi(\xi;t)$. In light of the one-step operator, $\mathbb{E}$, we obtain

$$\mathbb{E}\,n = n + 1$$

Substituting Eq. (J.6) for n on the right-hand side of this equation yields

$$\begin{aligned}\mathbb{E}\,n &= [n_0\varphi(t) + n_0^{1/2}\xi] + 1 \\ &= [n_0\varphi(t) + n_0^{1/2}\xi] + [n_0^{1/2}n_0^{-1/2}]\end{aligned}$$

or

$$\mathbb{E}\,n = n_0\varphi(t) + n_0^{1/2}(\xi + n_0^{-1/2})$$

In other words, $\mathbb{E}$ transforms n into $(n+1)$, and therefore, ξ into $(\xi + n_0^{-1/2})$; as a result, from Eq. (J.7),

$$\mathbb{E}\,p(n;t) = \mathbb{E}\,\pi(\xi;t)$$

or

$$p(n+1;t) = \pi(\xi + n_0^{-1/2};t) \tag{J.9}$$

The Taylor expansion of $\pi(\xi + n_0^{-1/2};t)$ about ξ, is obtained as

$$\pi(\xi + n_0^{-1/2};t) = \pi(\xi;t) + n_0^{-1/2}\frac{\partial}{\partial\xi}\pi(\xi;t) + \frac{1}{2!}(n_0^{-1/2})^2\frac{\partial^2}{\partial\xi^2}\pi(\xi;t) + \ldots$$

or

$$\pi(\xi + n_0^{-1/2};t) = \left(1 + n_0^{-1/2}\frac{\partial}{\partial\xi} + \frac{1}{2}n_0^{-1}\frac{\partial^2}{\partial\xi^2} + \ldots\right)\pi(\xi;t) \tag{J.10}$$

In view of Eqs. (J.7) and (J.9), the above expression can be transformed to

$$p(n+1;t)=\left(1+n_0^{-1/2}\frac{\partial}{\partial\xi}+\frac{1}{2}n_0^{-1}\frac{\partial^2}{\partial\xi^2}+...\right)p(n;t)$$

or

$$\mathbb{E}p(n;t)=\left(1+n_0^{-1/2}\frac{\partial}{\partial\xi}+\frac{1}{2}n_0^{-1}\frac{\partial^2}{\partial\xi^2}+...\right)p(n;t)$$

By comparing both sides of this expression, we have

$$\mathbb{E}=1+n_0^{-1/2}\frac{\partial}{\partial\xi}+\frac{1}{2}n_0^{-1}\frac{\partial^2}{\partial\xi^2}+... \tag{J.11}$$

Substituting this equation in conjunction with Eqs. (J.6), (J.7), and (J.8) into the master equation, Eq. (J.4), leads to

$$\frac{\partial\pi}{\partial t}-n_0^{1/2}\left(\frac{d\varphi}{dt}\right)\frac{\partial\pi}{\partial\xi}$$

$$=n_0\left(n_0^{-1/2}\frac{\partial}{\partial\xi}+\frac{1}{2}n_0^{-1}\frac{\partial^2}{\partial\xi^2}+...\right)[(k+k'n_0)(\varphi+n_0^{-1/2}\xi)-k'n_0(\varphi+n_0^{-1/2}\xi)^2]\pi \tag{J.12}$$

Absorbing the system's size, n_0, into the time variable, t, as

$$n_0 t=\gamma$$

and truncating the terms after the second-order derivative for large n_0 give

$$\frac{\partial\pi}{\partial\gamma}-n_0^{1/2}\left(\frac{d\varphi}{d\gamma}\right)\frac{\partial\pi}{\partial\xi}$$

$$=\left(n_0^{-1/2}\frac{\partial}{\partial\xi}+\frac{1}{2}n_0^{-1}\frac{\partial^2}{\partial\xi^2}\right)[(k+k'n_0)(\varphi+n_0^{-1/2}\xi)-k'n_0(\varphi+n_0^{-1/2}\xi)^2]\pi \tag{J.13}$$

Expanding the right-hand side of this equation and collecting the resultant terms of orders $n_0^{1/2}$ and n_0^0 separately give

$$\frac{\partial\pi}{\partial\gamma}-n_0^{1/2}\left(\frac{d\varphi}{d\gamma}\right)\frac{\partial\pi}{\partial\xi}$$

$$=n_0^0\left\{\left[-(2\varphi-1)k'+\frac{k}{n_0}\right]\frac{\partial}{\partial\xi}(\xi\pi)+\frac{1}{2}\left[-k'\varphi(\varphi-1)+\frac{k}{n_0}\varphi\right]\frac{\partial^2\pi}{\partial\xi^2}\right\}$$

$$-n_0^{1/2}\left\{\left[k'\varphi(\varphi-1)-\frac{k}{n_0}\varphi\right]\frac{\partial\pi}{\partial\xi}\right\}$$

$$+n_0^{-1/2}\left[\left(\frac{1}{2}kn_0^{-1}+\frac{1}{2}k'-k'\varphi\right)\frac{\partial^2}{\partial\xi^2}(\xi\pi)-k'\frac{\partial}{\partial\xi}(\xi^2\pi)-\frac{1}{2}k'n_0^{-1/2}\frac{\partial^2}{\partial\xi^2}(\xi^2\pi)\right] \tag{J.14}$$

Comparing both sides of the above expression gives rise to

$$\frac{d\varphi}{d\gamma}=k'\varphi(\varphi-1)-\frac{k}{n_0}\varphi \tag{J.15}$$

and

$$\frac{\partial\pi}{\partial\gamma}=\left[-(2\varphi-1)k'+\frac{k}{n_0}\right]\frac{\partial}{\partial\xi}(\xi\pi)+\frac{1}{2}\left[-k'\varphi(\varphi-1)+\frac{k}{n_0}\varphi\right]\frac{\partial^2\pi}{\partial\xi^2} \tag{J.16}$$

Of these two equations, the former is the macroscopic equation governing the overall behavior of the process, and the latter is a linear Fokker-Plank equation governing the fluctuations of the process around the macroscopic values and whose coefficients depend on t through φ(t).

Appendix K - Formation of Carbon Molecular Sieves: Derivation of the Mean and Variance of the Pure-Death Process with a Non-Linear Intensity of Transition Based on a Single Random Variable

For convenience, Eq. (A-6) for the random variable, N(t), is rewritten below

$$N(t) = n_0\varphi(t) + n_0^{1/2}\Xi(t) \tag{K.1}$$

From this equation, the mean of N(t), i.e., E[N(t)] or m(t), is obtained as

$$\begin{aligned} E[N(t)] &= E[n_0\varphi(t) + n_0^{1/2}\Xi(t)] \\ &= n_0 E[\varphi(t)] + n_0^{1/2}E[\Xi(t)] \end{aligned}$$

or

$$m(t) = n_0\varphi(t) + n_0^{1/2}E[\Xi(t)] \tag{K.2}$$

Similarly, the variance, Var[N(t)] or $\sigma^2(t)$, is

$$\begin{aligned} Var[N(t)] &= Var[n_0\varphi(t) + n_0^{1/2}\Xi(t)] \\ &= n_0^2 Var[\varphi(t)] + n_0 Var[\Xi(t)] \end{aligned}$$

or

$$\sigma^2(t) = n_0 Var[\Xi(t)] \tag{K.3}$$

As indicated by Eq. (B.18), for any arbitrary random variable N(t), $\sigma^2(t)$ can be related to E[N(t)] as

$$\sigma^2(t) = E[N^2(t)] - \{E[N(t)]\}^2 \tag{K.4}$$

In view of this expression, Eq. (K.3) can be rewritten as

$$\sigma^2(t) = n_0\left(E[\Xi^2(t)] - \{E[\Xi(t)]\}^2\right) \tag{K.5}$$

Because $N(0) = n_0$ and $\Xi(0) = 0$, we have, from Eq. (K.1)

$$\varphi(0) = 1 \tag{K.6}$$

The macroscopic equation governing the overall behavior of the system is given by Eq. (J.15) as

$$\frac{d\varphi}{d\gamma} = k'\varphi(\varphi - 1) - \frac{k}{n_0}\varphi$$

Because $n_0 t = \gamma$, this equation can be rewritten as

$$\frac{d\varphi}{dt} = k' n_0 \varphi(\varphi - 1) - k\varphi \tag{K.7}$$

Upon integration, this expression yields

$$\varphi(t) = \frac{(k + k' n_0)}{c \exp\left[(k + k' n_0)t\right] + k' n_0}$$

In view of Eq. (K.6), the constant, c, in the above expression is k; thus,

$$\varphi(t) = \frac{(k + k' n_0)}{k \exp[(k + k' n_0)t] + k' n_0} \tag{K.8}$$

For convenience, Eqs. (D.12) and (D.14) are rewritten below

$$\sum_x \left[g(x) \frac{\partial}{\partial x} f(x) \right] = -\sum_x \left[f(x) \frac{\partial}{\partial x} g(x) \right] \tag{K.9}$$

and

$$\sum_x \left[g(x) \frac{\partial^2}{\partial x^2} f(x) \right] = \sum_x \left[f(x) \frac{\partial^2}{\partial x^2} g(x) \right] \tag{K.10}$$

The linear Fokker-Plank equation governing the fluctuations of the process around the macroscopic values is given by Eq. (J.16) as

$$\frac{\partial}{\partial \gamma} \pi = \left[-(2\varphi - 1)k' + \frac{k}{n_0} \right] \frac{\partial}{\partial \xi} (\xi \pi) + \frac{1}{2} \left[-k' \varphi(\varphi - 1) + \frac{k}{n_0} \varphi \right] \frac{\partial^2}{\partial \xi^2} \pi \tag{K.11}$$

Because $n_0 t = \gamma$, this equation can be transformed into

$$\frac{\partial}{\partial t} \pi = [-(2\varphi - 1)k' n_0 + k] \frac{\partial}{\partial \xi} (\xi \pi) + \frac{1}{2} [-k' n_0 \varphi(\varphi - 1) + k\varphi] \frac{\partial^2}{\partial \xi^2} \pi \tag{K.12}$$

Multiplying both sides of the above equation by ξ and summing over all values of ξ yield

$$\sum_\xi \xi \frac{\partial}{\partial t} \pi = [-(2\varphi - 1)k' n_0 + k] \left[\sum_\xi \xi \frac{\partial}{\partial \xi} (\xi \pi) \right] + \frac{1}{2} [-k' n_0 \varphi(\varphi - 1) + k\varphi] \left[\sum_\xi \xi \frac{\partial^2}{\partial \xi^2} \pi \right] \tag{K.13}$$

By virtue of Eqs. (K.9) and (K.10), the right-hand side of this expression can be transformed to

$$\sum_\xi \xi \frac{\partial}{\partial t} \pi = [-(2\varphi - 1)k' n_0 + k] \left[-\sum_\xi \xi \pi \frac{\partial}{\partial \xi} \xi \right] + \frac{1}{2} [-k' n_0 \varphi(\varphi - 1) + k\varphi] \left[\sum_\xi \pi \frac{\partial^2}{\partial \xi^2} \xi \right]$$

or

$$\sum_{\xi} \xi \frac{\partial}{\partial t} \pi = -[-(2\varphi - 1)k' n_0 + k] \left[\sum_{\xi} \xi \pi \right] \tag{K.14}$$

The first moment of random variable $\Xi(t)$, i.e., $E[\Xi(t)]$, is defined as

$$E[\Xi(t)] = \sum_{\xi} \xi \pi(\xi; t)$$

or

$$E[\Xi(t)] = \sum_{\xi} \xi \pi \tag{K.15}$$

and thus,

$$\frac{d}{dt} E[\Xi(t)] = \sum_{\xi} \xi \frac{\partial}{\partial t} \pi \tag{K.16}$$

In light of the above two equations, Eq. (K.14) reduces to

$$\frac{d}{dt} E[\Xi(t)] = -[-(2\varphi - 1)k' n_0 + k] \, E[\Xi(t)] \tag{K.17}$$

Inserting Eq. (K.8) for $\varphi(t)$ into this equation and integrating the resulting expression yield

$$E[\Xi(t)] = \frac{c' \exp[(k + k' n_0)t]}{\left\{ k \exp[(k + k' n_0)t] + k' n_0 \right\}^2} \tag{K.18}$$

From the initial conditions for the transformed probability distribution, $\pi(\xi;t)$,

$$\pi(\xi; 0) = \begin{cases} 1 & \text{if} \quad \xi = 0 \\ \\ 0 & \text{elsewhere} \end{cases} \tag{K.19}$$

and the definition of $E[\Xi(t)]$, as given by Eq. (K.15), we have

$$E[\Xi(0)] = 0 \tag{K.20}$$

thereby indicating that

$$c' = 0 \tag{K.21}$$

Hence,

$$E[\Xi(t)] = 0 \tag{K.22}$$

Similarly, multiplying both sides of Eq. (K.12) by ξ^2 and summing over all values of ξ yield

$$\sum_{\xi}\xi^2\frac{\partial}{\partial t}\pi=[-(2\varphi-1)k'n_0+k]\left[\sum_{\xi}\xi^2\frac{\partial(\xi\pi)}{\partial\xi}\right]+\frac{1}{2}[-k'n_0\varphi(\varphi-1)+k\varphi]\left[\sum_{\xi}\xi^2\frac{\partial^2}{\partial\xi^2}\pi\right] \tag{K.23}$$

By virtue of Eqs. (K.9) and (K.10), the right-hand side of the above expression can be transformed to

$$\sum_{\xi}\xi^2\frac{\partial}{\partial t}\pi=[-(2\varphi-1)k'n_0+k]\left[-\sum_{\xi}\xi\pi\frac{\partial}{\partial\xi}\xi^2\right]+\frac{1}{2}[-k'n_0\varphi(\varphi-1)+k\varphi]\left[\sum_{\xi}\pi\frac{\partial^2}{\partial\xi^2}\xi^2\right]$$

or

$$\sum_{\xi}\xi^2\frac{\partial}{\partial t}\pi=-2[-(2\varphi-1)k'n_0+k]\left[\sum_{\xi}\xi^2\pi\right]+[-k'n_0\varphi(\varphi-1)+k\varphi]\left[\sum_{\xi}\pi\right] \tag{K.24}$$

For the transformed probability distribution, $\pi(\xi;t)$, the following property must hold

$$\sum_{\xi}\pi(\xi;t)=1$$

or

$$\sum_{\xi}\pi=1 \tag{K.25}$$

Thus, Eq. (K.24) can be rewritten as

$$\sum_{\xi}\xi^2\frac{\partial}{\partial t}\pi=-2[-(2\varphi-1)k'n_0+k]\left[\sum_{\xi}\xi^2\pi\right]+[-k'n_0\varphi(\varphi-1)+k\varphi] \tag{K.26}$$

The second moment of random variable $\Xi(t)$, i.e., $E[\Xi^2(t)]$, is defined as

$$E[\Xi^2(t)]=\sum_{\xi}\xi^2\pi(\xi;t)$$

or

$$E[\Xi^2(t)]=\sum_{\xi}\xi^2\pi \tag{K.27}$$

and thus,

$$\frac{d}{dt}E[\Xi^2(t)]=\sum_{\xi}\xi^2\frac{\partial}{\partial t}\pi \tag{K.28}$$

In view of the above two equations, Eq. (K.26) reduces to

$$\frac{d}{dt}E[\Xi^2(t)]=-2[-(2\varphi-1)k'n_0+k]\,E[\Xi^2(t)]-k'n_0\varphi(\varphi-1)+k\varphi \tag{K.29}$$

Inserting Eq. (K.8) for $\varphi(t)$ into this equation and integrating the resulting expression give rise to

$$
\begin{aligned}
&E[\Xi^2(t)] \\
&= k(k+k'n_0)\frac{\exp[(k+k'n_0)t]}{\{k\exp[(k+k'n_0)t]+k'n_0\}^4} \\
&\cdot\Big\{k^2\exp[2(k+k'n_0)t]-(k'n_0)^2+2k^2k'n_0t\exp[(k+k'n_0)t] \\
&\quad +2k(k'n_0)^2t\exp[(k+k'n_0)t]\Big\} \\
&+\frac{c''\exp[2(k+k'n_0)t]}{\{k\exp[(k+k'n_0)t]+k'n_0\}^4}
\end{aligned}
\tag{K.30}
$$

From the aforementioned initial conditions for the transformed probability distribution, $\pi(\xi;t)$, as given by Eq. (K.19), and the expression of $E[\Xi^2(t)]$ as defined by Eq. (K.27), we have

$$E[\Xi^2(0)]=0, \tag{K.31}$$

thereby indicating that

$$c''=k(k+k'n_0)[(k'n_0)^2-k^2] \tag{K.32}$$

Hence,

$$
\begin{aligned}
&E[\Xi^2(t)] \\
&= k(k+k'n_0)\frac{\exp[(k+k'n_0)t]}{\{k\exp[(k+k'n_0)t]+k'n_0\}^4} \\
&\cdot\Big\{k^2\exp[2(k+k'n_0)t]-(k'n_0)^2+(k+k'n_0)[k'n_0+k(2k'n_0t-1)]\exp[(k+k'n_0)t]\Big\}
\end{aligned}
\tag{K.33}
$$

The mean, E[N(t)] or m(t) is obtained by substituting Eqs. (K.8) and (K.22) into Eq. (K.2) as

$$m(t)=n_0\left\{\frac{(k+k'n_0)}{k\exp[(k+k'n_0)t]+k'n_0}\right\} \tag{K.34}$$

By defining $\alpha=(k+k'n_0)$ and $\beta=k(k+k'n_0)^{-1}$, this expression becomes

$$m(t)=n_0\left\{\frac{1}{1+\beta[\exp(\alpha t)-1]}\right\} \tag{K.35}$$

This is Eq. (4.4) in the text. Similarly, the variance, Var[N(t)] or $\sigma^2(t)$, is obtained by inserting Eqs. (K.22) and (K.33) into Eq. (K.5) as

$$\begin{aligned}&\sigma^2(t)\\&= n_0 \frac{k(k+k'n_0)\exp[(k+k'n_0)t]}{\{k\exp[(k+k'n_0)t]+k'n_0\}^4}\\&\cdot\left\{k^2\exp[2(k+k'n_0)t]-(k'n_0)^2+(k+k'n_0)[k'n_0+k(2k'n_0t-1)]\exp[(k+k'n_0)t]\right\}\end{aligned} \tag{K.36}$$

In terms of α and β, this expression can be transformed into

$$\begin{aligned}\sigma^2(t) = n_0 &\frac{\beta\exp(\alpha t)}{\{1+\beta[\exp(\alpha t)-1]\}^4}\\&\cdot\left(2\beta-1+\exp(\alpha t)\left\{1-2\beta[1+(\beta-1)(\alpha t)]+2\beta^2\sinh(\alpha t)\right\}\right)\end{aligned} \tag{K.37}$$

This is Eq. (4.6) in the text.