MODELING, APPROXIMATION, AND TIME OPTIMAL TEMPERATURE CONTROL FOR BINDER REMOVAL FROM CERAMICS

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ABSTRACT. The process of binder removal from green ceramic components—a reaction-gas transport problem in porous media—has been analyzed with a number of mathematical techniques: 1) non-dimensionalization of the governing decomposition-reaction ordinary differential equation (ODE) and of the reaction gas-permeability partial differential equation (PDE); 2) development of a pseudo steady state approximation (PSSA) for the PDE, including error analysis via $L^2$ norm and singular perturbation methods; 3) derivation and analysis of a discrete model approximation; and 4) development of a time optimal control strategy to minimize processing time with temperature and pressure constraints. Theoretical analyses indicate the conditions under which the PSSA and discrete models are viable approximations. Numerical results indicate that under a range of conditions corresponding to practical binder burnout conditions, utilization of the optimal temperature protocol leads to shorter cycle times as compared to typical industrial practice.

1. Introduction. The removal of polymer binder (also called binder burnout or thermolysis) from green body ceramics by heating in a furnace precedes high temperature sintering and must be controlled to avoid damage of the ceramic due to the gas produced in the porous medium. Such reaction-transport problems in porous media have been widely studied. Models have been proposed [3], [8], [10], [22], [24] and mathematical analysis applied (see, for example, [1], [13], [20], [21], [23]).

The reaction-gas permeability model for binder removal is an unsteady state, non-linear, partial differential equation with a non-constant porosity and a non-isothermal source term; these attributes, individually and in combination, are not
often present in many reaction-transport porous media problems. Additionally, as the time for binder removal is often long, development of temperature control strategies (cf. [11]) is paramount to minimize the heating cycle time. Such optimization strategies often lead to constraints, which further complicate the model and method of solution.

Lombardo and coworkers developed a distributed parameter model for the process (see [12], [16], [17], [19] and references therein) and used the pseudo steady state approximation (PSSA) in order to approximate optimal temperature protocols. The motivation for invoking the PSSA was the recognition that heating cycles are often long, spanning tens to hundreds of hours, with slow heating rates and multiple hold periods. Although the accuracy of the PSSA has been widely studied, most previous results are for kinetic analyses with ODEs or for reaction-transport problems with diffusion. The accuracy of the PSSA for gas-permeability problems has been investigated in only a limited fashion [4], [24] and not for situations involving time optimal control.

The paper is organized as follows: In Sec. 2: Theory, we develop in 2.1 a distributed parameter model for binder removal and in 2.2 nondimensionalize it to obtain important time scales. In Sec. 3: Results and Discussion, we introduce some basic facts concerning nonlinear parabolic partial differential equations (PDE) in 3.1 and then develop two approximate models based on the PSSA in 3.2 and a discrete model in 3.3; error analyses in terms of the $L^2$ norm and singular perturbation analysis, which yields a quality function, are then performed as well as numerical experiments to quantity the error between the distributed parameter model and the approximate models. Additionally, a viable optimal temperature protocol is developed in 3.4 that respects constraints on the rate of temperature increase and maximum pressure within the green body; it is applied in one and higher space dimensions. In Sec. 4: Conclusions, we summarize our work and identify potential future research directions.

2. Theory.

2.1. Mathematical model. When heated to a sufficiently high temperature $T$, the binder (which initially resides in the pores of the molded ceramic) decomposes into gaseous products that produce pressure gradients causing the gas with molar density $\rho$ to flow through the body $\Omega$ and eventually exit into the furnace. The body is composed of fixed volume fraction $\epsilon_3$ of ceramic and time $t$ dependent volume fractions of pores $\epsilon$ and polymer $\epsilon_2$ with

$$\epsilon + \epsilon_2 + \epsilon_3 = 1. \quad (1)$$

Additional physical quantities that appear in the model are listed in Table 1. Also used is the scalar permeability function $\kappa$ given by

$$\kappa(t) = \frac{\epsilon(t)^3}{kS^2(1 - \epsilon(t))^2}. \quad (2)$$

The model (which is an adaptation of the porous media model derived from conservation of mass and Darcy’s law) assumes a specified temperature protocol $T$ defined over the physically relevant time interval and is given by the system of
Table 1. Model Parameters

| Name  | Value          | Description               |
|-------|----------------|---------------------------|
| $T_0$ | 300.0 K        | initial temperature       |
| $P_0$ | $1.0 \times 10^5$ Pa | ambient gas pressure    |
| $R$   | 8.314 J/mol-K | ideal gas constant        |
| $M$   | $4.4 \times 10^{-2}$ kg/mol | molecular weight of gas |
| $E$   | $2.22 \times 10^5$ J/mol | activation energy       |
| $A$   | $1.67 \times 10^{16}$ /s | pre-exponential factor   |
| $\mu$ | $2.5 \times 10^{-5}$ Pa-s | viscosity of gas         |
| $S$   | $6 \times 10^6$/m | specific surface          |
| $k$   | 5              | tortuosity                |
| $\epsilon_{20}$ | 0.4 | initial binder volume fraction |
| $\epsilon_3$ | 0.5 | ceramic volume fraction   |
| $\rho_2$ | $1.0 \times 10^3$ kg/m$^3$ | polymer density      |
| $L$   | 0.001–0.1 m   | green body length         |

differential equations

\[
(\epsilon_2)_t = -A \exp\left(\frac{-E}{RT(t)}\right) \epsilon_2, \\
(\epsilon\rho)_t = \nabla \cdot \left( \frac{\mu RT(t)}{\epsilon} \nabla \rho \right) + \frac{\rho_2}{M} \exp\left(\frac{-E}{RT(t)}\right) \epsilon_2 \]  

supplemented by the boundary condition

\[ RT(t)\rho\bigg|_{\partial \Omega} = P_0 \]  

(specifying that gas pressure at the boundary is the furnace pressure) and initial data

\[ \epsilon_2(0) = \epsilon_{20}, \quad \epsilon(0) = 1 - \epsilon_3 - \epsilon_{20}, \quad \rho\bigg|_{t=0} = \rho_0 := \frac{P_0}{RT_0} \]  

(specifying the initial binder volume fraction, porosity, and the initial molar gas density). It may be made more realistic by incorporating Knudsen diffusion to refine Darcy’s law, heat transfer, the full equations of gas dynamics and so on; but, short of validation via physical experiments, the present model serves to illustrate the efficacy of approximations and the construction of optimization protocols that would be appropriate for a predictive model.

Reduction to one space dimension is used for most of our approximation theory, error analysis, and numerical experiments. It corresponds to the simplest ideal geometry: an infinite plate with finite thickness with all burnout gas outflow through its faces. In reality, many manufactured ceramic components have high aspect ratios, often exceeding 10 : 1, where significant burnout gas outflow is in their short direction. Body material is assumed to be homogeneous; in particular, $A$, $k$, $M$, $S$, $\mu$, and $\rho_2$ are positive constants. For the time-optimal control theory developed here, space dimension does not play a significant role, and thus it is applied to higher dimensional bodies as well.

A coordinate system is chosen so that the axis of symmetry lies along the $x$-axis in a usual $(x, y, z)$ Cartesian coordinate system. The body covers an interval of length $L$ in the $x$-direction and the origin of the coordinate system is chosen at the
midpoint of this interval. Under these assumptions, the model equations reduce to

\[ (\epsilon_2)_t = -A \exp\left(\frac{-E}{RT}\right)\epsilon_2, \]

\[ (\epsilon \rho)_t = \left(\frac{\kappa \rho}{\mu}(RT \rho)_x\right)_x + \frac{\rho_2}{M}A \exp\left(\frac{-E}{RT}\right)\epsilon_2 \]  \hspace{1cm} (5)

with boundary condition

\[ RT(t) \rho(\pm \frac{L}{2}, t) = P_0 \]  \hspace{1cm} (6)

and initial data

\[ \rho(x, 0) = \rho_0 \]

together with \( 0 < \epsilon_20 < 1 \), a given initial binder volume fraction.

The model equations may be transformed in various ways, some of which are particularly advantageous for specific purposes. One useful rearrangement is the separated form

\[ \epsilon_t = A \exp\left(\frac{-E}{RT}\right)(1 - \epsilon_3 - \epsilon), \]

\[ \epsilon \rho_t = \frac{\kappa(\epsilon)RT}{\mu}(\rho \rho_x)_x + \left(\frac{\rho_2}{M} - \rho\right)A \exp\left(\frac{-E}{RT}\right)(1 - \epsilon_3 - \epsilon); \]  \hspace{1cm} (7)

another is the porosity-density form

\[ \epsilon_t = A \exp\left(\frac{-E}{RT}\right)(1 - \epsilon_3 - \epsilon), \]

\[ u_t = \frac{q(\epsilon)RT}{\mu}(uu_x)_x + \frac{\rho_2}{M}A \exp\left(\frac{-E}{RT}\right)(1 - \epsilon_3 - \epsilon), \]  \hspace{1cm} (8)

where

\[ u := \epsilon \rho, \quad q(\epsilon) = \frac{\epsilon}{kS^2(1 - \epsilon)^2}. \]

In all cases the temperature \( T \) is a control variable; it must be specified as a function of time for the model to have a unique solution.

2.2. Nondimensionalization. Dimensionless versions of the model equations are useful especially in perturbation analysis where the relative sizes of parameters (which become dimensionless groups of physical parameters) are desired.

For characteristic time \( \tau \), length \( \ell \), density \( \delta \), and temperature \( T_0 \) define new dimensionless variables

\[ s = t/\tau, \quad \xi = x/\ell, \quad \eta = \rho/\delta, \quad \Gamma(s) = \frac{T(t)}{T_0}. \]  \hspace{1cm} (9)

In dimensionless time \( s \), the volume fraction \( \epsilon_2 \) is redefined to be

\[ \alpha(s) = \epsilon_2(s\tau) \]

In addition, define the dimensionless function \( q \) by

\[ q(y) = \frac{y}{(1 - y)^2} \]  \hspace{1cm} (10)

and the dimensionless group

\[ \gamma = \frac{E}{RT_0} \]
to recast the dynamical system in the general dimensionless form

$$\alpha_s = -\tau A \exp\left(-\frac{\gamma}{\Gamma(s)}\right)\alpha,$$

$$\epsilon_{\eta}(s) = \frac{\tau RT_0 \delta}{kS^2 \mu \ell^2} \Gamma(s) q(\epsilon)(\epsilon_{\eta}(s))\xi + \frac{\tau \rho_2}{M \delta} \exp\left(-\frac{\gamma}{\Gamma(s)}\right)\alpha. \quad (11)$$

The dimensionless corresponding boundary conditions (on the half-body) are

$$\epsilon_{\eta}(0, s) = 0, \quad (\epsilon_{\eta}(\frac{L}{2\ell}, s) = \frac{P_0}{RT_0 \delta} \frac{\epsilon(\tau s)}{\Gamma(s)},$$

and on the full body

$$\epsilon_{\eta}(\pm \frac{1}{2\ell}, s) = \frac{P_0}{RT_0 \delta} \frac{\epsilon(\tau s)}{\Gamma(s)}.$$

The initial conditions, which are compatible with the boundary conditions, are

$$\alpha(0) = \epsilon_{20}, \quad (\epsilon_{\eta}(\xi, 0) = \frac{\rho_0}{\delta}(1 - \epsilon_3 - \epsilon_{20}).$$

There are at least two important time scales: the kinetic

$$\hat{t} = \frac{1}{A} \quad (12)$$

and transport time scale

$$t = \frac{\mu kS^2 L^2}{4P_0}. \quad (13)$$

In this paper, the transport time scale ($s = t/t$) is used. With

$$\ell = \frac{L}{2}, \quad \delta = \frac{P_0}{RT_0},$$

the evolution equations are recast into the form

$$\alpha_s = -At \exp\left(-\frac{\gamma}{\Gamma(s)}\right)\alpha,$$

$$\epsilon_{\eta}(s) = \Gamma(s) q(\epsilon)(\epsilon_{\eta}(s))\xi + c \exp\left(-\frac{\gamma}{\Gamma(s)}\right)\alpha, \quad (14)$$

where $At$, the ratio of the kinetic and transport time scale, and

$$c := \frac{At \rho_2}{M \rho_0},$$

are dimensionless groups.

In addition the system requires either half or full body boundary conditions

$$\epsilon_{\eta}(0, s) = 0, \quad (\epsilon_{\eta}(1, s) = \frac{\epsilon(s)}{\Gamma(s)}$$

or

$$\epsilon_{\eta}(\pm 1, s) = \frac{\epsilon(s)}{\Gamma(s)}$$

and initial data

$$\alpha(0) = \epsilon_{20}, \quad \epsilon(0)_{\eta}(\xi, 0) = 1 - \epsilon_{20} - \epsilon_3.$$

In the physical regime of most interest, $At \rho_2/(M \rho_0)$ is large (on the order of $10^{18}$), which suggests the source term in the PDE is large. But, the size of the
exponential factor at the characteristic temperature $T_0$ is on the order of $10^{-39}$. Thus, the source term taken as a whole is small.

The abstract PDE corresponding to the transport scale is

$$u_s = A(s)\Phi(u)\xi + B(s), \quad u(\pm 1, s) = b(s), \quad u(\xi, 0) = b(0),$$

where $\Phi$ is a twice continuously differentiable function such that $\Phi(0) = 0$ and $\Phi' > 0$ for positive real values,

$$A(s) = \Gamma(s)q(\epsilon), \quad B(s) = c\exp\left(-\frac{\gamma}{\Gamma(s)}\right)\alpha, \quad b(s) = \frac{\epsilon(s)}{\Gamma(s)}.$$

Note that

$$b'(s) = \frac{\epsilon'}{\Gamma} - \frac{\epsilon'}{\Gamma}\frac{\Gamma'}{\Gamma},$$

$$B(s) = ce^{\gamma/\Gamma}(1 - \epsilon) - \frac{\epsilon'}{\Gamma}\Gamma'\Gamma.$$

These formulas after some manipulation imply a useful proposition: If $\Gamma(0)$ is positive and $\Gamma'(s) \geq 0$, then

$$B(s) \geq \frac{\rho_2}{M\rho_0}b'(s).$$

If in addition $\rho_2/(M\rho_0) \geq 1$, then $B(s) > b'(s)$.

3. Results and discussion.

3.1. Definitions and basic facts. The PDE in the binder burnout model belongs to the well studied class of nonlinear PDEs of parabolic type (see the important book [25] and for an introductory text [14]) that enjoy many useful properties. Moreover, it is a version of the porous medium equation. A more general form of the PDE in model (8) is

$$u_t = A(x,t)(\Phi'(u)u_x)_x + B(x,t) + C(x,t)u,$$

where $A$ is positive, $B$ and $C$ are not negative, all three are as smooth as desired, and $\Phi$ is a smooth function on the real line such that $\Phi(0) = 0$ and $\Phi'(y) > 0$ for all $y > 0$. In the binder burnout model, $\Phi(u) = u^2/2$, $C = 0$, and $A$ and $B$ are positive and not space dependent.

Solutions exist and are unique. Proofs are not given here; instead, we rely on [25] (especially Sec. 3.1.1) where all the necessary ideas are presented and discussed. The key assumption of uniform parabolicity (written here for the scalar case) is that there are positive constants $c_1$ and $c_2$ such that

$$c_1\xi^2 \leq A(x,t)\Phi'(u)\xi^2 \leq c_2\xi^2$$

for all real numbers $\xi$. For this condition to hold, $A$ and $\Phi'$ must be positive. But, the assumption $\Phi'(y) > 0$ for all $y > 0$ is not sufficiently strong as $u$ might attain a negative or zero value.

A basic problem encountered for the PDE (18) is easily seen by expanding the spatial derivative of $\Phi$ to produce the PDE

$$u_t = A(x,t)(\Phi'(u)u_{xx} + \Phi''(u)(u_x)^2) + B(x,t) + C(x,t)u.$$

Its desired parabolic nature is lost when $\Phi'(u) = 0$ as the PDE drops from being second order in $x$ to a first-order PDE. This fact has led to a rich mathematical
theory and the discovery of new dynamical phenomena that are of interest in some applications. This theory is not needed for the binder burnout application because only positive solutions are physically relevant; to wit gas density is not negative and the porosity $\epsilon$ is assumed to be positive. Mathematically, the desired positivity is obtained from the physically relevant boundary and initial data. In fact, the relevant data are given by a positive function $b$ so that

$$u(\pm \frac{L}{2}, t) = b(t), \quad u(x, 0) = b(0).$$

This initial data thus satisfies the boundary condition and $b(0) > 0$. As explained more precisely in [25], in this case classical theory can be applied by modifying the PDE outside the domain of interest. The idea is to leave the function $A(x, t)\Phi'(u)$ as is for $u$ in some appropriate range, say $\lambda < u(x, t) < 1/\lambda$ for some $\lambda > 0$ chosen so that $\lambda < b(0) < 1/\lambda$; and, outside this range modify the function so that it remains smooth and is bounded above zero. The existence of a unique classical solution that stays in the specified range can then be proved. Of course, this solution is the desired (positive) solution of the original problem.

Once a temperature protocol $T$ is specified the volume fraction $\epsilon$ is determined via the model ODE as in Eq. (8). The key point, which plays a significant role in this paper, is that the model PDE for the gas density may be viewed separately with $T$ and $\epsilon$ considered to be given functions of time.

In the binder burnout application $\epsilon$ is not negative and for all (positive absolute) temperature protocols, the porosity increases toward the constant solution given by $\epsilon(t) \equiv 1 - \epsilon_3$, that is the (positive) state with no binder in the pores. Equivalently, the binder volume fraction decreases toward zero. For simplicity and with attention to physical applications where the initial configuration of binder does not fill the pores completely, we assume that $\epsilon > 0$ in the physically relevant regime.

Names for various parts of the physical domain and its boundary are convenient to make precise mathematical statements. Let $t_*$ be a positive real number such that the temporal variable restricted to the open interval $(0, t_*)$ accounts for all the physically relevant duration. Define $\mathcal{J}$ to be the interval $(-L/2, L/2)$, $\Omega$ the domain $\mathcal{J} \times (0, t_*)$, and $\Sigma$ the parabolic boundary

$$\Sigma := (\mathcal{J} \times \{0\}) \cup ([0, t_*) \times \{-\frac{L}{2}\}) \cup ([0, t_*) \times \{\frac{L}{2}\})$$

with

$$\mathcal{K} := \mathcal{J} \times \{t_*\}$$

the remaining part of the boundary. The PDE is required to hold on $\Omega$. Also, as usual, $\bar{\Omega}$ denotes the closure of $\Omega$. Since $t_*$ is finite, $\bar{\Omega}$ is a compact set.

Much of parabolic PDE theory is devoted to proving general forms of the maximum principle and applying these fundamental results. In short, the expectation is that a solution of a parabolic PDE with zero source function does not attain its maximum or minimum in $\Omega$ unless the solution is constant. Very general results have been proved and many of them now appear in graduate textbooks on PDEs. The full power of the theory is not needed here; rather, a special case of a useful more elementary result suffices:

**General comparison theorem.** Let $F : \mathbb{R}^5 \to \mathbb{R}$ be a continuously differentiable function and define the differential operator $\mathcal{D}$ on the space of twice continuously
differentiable functions defined on \( \Omega \) by
\[
D(u)(x,t) = F(x,t,u,u_x,u_{xx}) - u_t.
\]
(To use Leibniz notation, let the fifth argument of \( F \) be called \( r \); it corresponds to the position of \( u_{xx} \).) Also define the differential operator \( \mathcal{F} \) by
\[
\mathcal{F}(u) = F_r(x,t,u,u_x,u_{xx}).
\]
If (1) \( f \) is a continuous function on \( \bar{\Omega} \), \( u \), \( \hat{w} \), and \( \hat{W} \) are continuous functions on \( \bar{\Omega} \) and twice continuously differentiable in \( \Omega \),
(2) for all \((x,t)\) in \( \Omega \)
\[
D(u)(x,t) = f(x,t),
\]
(3) for all \((x,t)\) in \( \Omega \)
\[
D(\hat{W})(x,t) \leq f(x,t) \leq D(\hat{w})(x,t),
\]
(4) for each \( \theta \) in the interval \([0, 1]\) and all \((x,t)\) in \( \Omega \)
\[
\mathcal{F}(\theta \hat{w} + (1-\theta)u)(x,t) > 0, \quad \mathcal{F}(\theta \hat{W} + (1-\theta)u)(x,t) > 0,
\]
and (5) for all \((x,t)\) in \( \Sigma \)
\[
\hat{w}(x,t) \leq u(x,t) \leq \hat{W}(x,t),
\]
then for all \((x,t)\) in \( \Omega \)
\[
\hat{w}(x,t) \leq u(x,t) \leq \hat{W}(x,t).
\]

**Proof.** The theorem is formulated and a complete proof is given in [14]. \( \square \)

The general comparison theorem is used to prove the positivity of some solutions of the parabolic boundary value problem (18)–(19). These results imply gas density in the binder burnout model is positive—as it should be—and bounded below by its time-dependent boundary value.

**Theorem 3.1.** If \( C \) vanishes, \( b \) and \( B \) are positive functions, and \( B(x,t) > b'(t) \) for all \((x,t)\) in \( \bar{\Omega} \), then
\[
u(x,t) \geq b(t)
\]
on \( \bar{\Omega} \).

**Proof.** Define an infinitely smooth function \( \Psi \) on the real line such that \( \Psi(0) = 0 \), \( \Psi' \) is positive, and \( \Psi \) is equal to \( \Phi \) on the interval \((\min_{0 \leq t \leq t^*} b(t))/2, \infty]\). Also define operators on the space of twice continuously differentiable functions on \( \Omega \) given by
\[
D(v) := A(\Psi'(v)v_{xx} + \Psi''(v)(v_x)^2) - v_t, \quad \mathcal{F}(v) = A\Psi'(v).
\]
Suppose that \( u \) is a solution of PDE (18) with \( C = 0 \), \( \Phi \) replaced by \( \Psi \), and no change in boundary and initial data so that
\[
D(u) = -B.
\]
Define functions \( \hat{W} \) and \( \hat{w} \) on \( \bar{\Omega} \) by \( \hat{W}(x,t) = \min_{0 \leq t \leq t^*} b(t) \) and \( \hat{w}(x,t) = b(t) \). Hypotheses (1) and (2) are satisfied with \( f = -B \). Moreover,
\[
D(\hat{W}) = 0, \quad D(\hat{w}) = -b'(t)
\]
and, because \( B \) is positive and \( B(x,t) > b'(t) \), hypothesis (3) holds. The differential operator \( \mathcal{F} \) is zero order (that is, it does not apply differentiation) and positive
for every function \( v \) in its domain by construction of \( \Psi \) and the positivity of \( \mathcal{A} \); this implies hypothesis (4). Finally, to verify hypothesis (5) note that the solution \( u \) satisfies the boundary condition \( u(x,t) = b(t) \) on the parabolic boundary \( \Sigma \). According to the general comparison theorem \( u(x,t) \geq b(t) \) on \( \bar{\Omega} \) for the modified PDE. Clearly this function \( u \) is a solution of the original PDE because its values are always larger than half the minimum of \( b \) and \( \Psi \) agrees with \( \Phi \) at these values. \( \Box \)

The last result is stronger than a straightforward application of the classical maximum principle to the semilinear equation

\[
\tilde{u}_t = \Psi'(u)A(x,t)\tilde{u}_{xx} + \Psi'(u)B(x,t)
\]

where \( u \) is the solution of PDE (18) with \( C = 0 \) and \( \tilde{u} = \Psi(u) \). In this case, the implication is that the minimum of \( u \) over \( \bar{\Omega} \) is assumed somewhere on the parabolic boundary.

The general comparison theorem implies an upper bound for this \( u \):

**Theorem 3.2.** There are positive constants \( c_1, c_3, \) and \( c_4 \) and a nonnegative constant \( c_2 \) (which are effectively computable) such that

\[
\hat{w}(t) := c_1 + c_2 \int_0^t B(x,\tau) \, d\tau \leq u(x,t) \leq c_3 + c_4 \int_0^t B(x,\tau) =: \hat{W}(t).
\]

**Proof.** For the solution \( u \) of the PDE with the stated initial and boundary data, use the general comparison theorem with

\[
F(x,t,u,u_x,u_{xx}) = \mathcal{A}(x,t)(\Psi'(u)u_x^2 + \Psi'(u)u_{xx}), \quad f = -B
\]

and \( \hat{w} \) defined previously with positive constants \( c_1 \) and \( c_2 \) to be determined. Note that

\[
F_r(x,t,u,u_x,u_{xx}) = \mathcal{A}(x,t)\Phi'(u)
\]

is positive for all admissible \( x, t \) and all positive \( u \). As in the comparison principle, let \( \theta \) be in the closed unit interval. Since \( c_1 > 0, c_2 \geq 0, \) and \( B \) is positive, so is \( \hat{w} \). It follows that

\[
F(\theta u + (1 - \theta) \hat{w})(x,t) > 0.
\]

Using the same argument for \( c_3 > 0, c_4 > 0, \) and the previously defined \( \hat{W} \),

\[
F(\theta u + (1 - \theta) \hat{W})(x,t) > 0.
\]

Thus, hypotheses (1), (2), and (4) are satisfied. For (3), impose the conditions

\[
c_2 \leq 1, \quad c_4 \geq 1,
\]

note that \( \hat{w} \) does not depend on \( x \), and

\[
\mathcal{D}(\hat{w}) = -c_2 B(t), \quad \mathcal{D}(\hat{W}) = -c_4 B(t).
\]

Hypothesis (5) is satisfied whenever

\[
c_1 + c_2 \int_0^t B(\tau) \, d\tau \leq b(t) \leq c_3 + c_4 \int_0^t B(\tau) \, d\tau.
\]

(23)
The required inequalities hold (for example) with
\( b_{\min} := \min_{[0,t^*]} b, \quad b_{\max} := \max_{[0,t^*]} b, \quad B_{\max} := \max_{[0,t^*]} B, \)
\[ c_1 = \frac{b_{\min}}{2}, \quad c_2 = \min\left\{\frac{b_{\min}}{2t^*B_{\max}}, 1\right\} \]
\[ c_3 = b_{\max}, \quad c_4 = 1. \]  
(24)

Two other results are important for the binder burnout problem: The first, called radial symmetry in [25], is true in much more generality than needed here where this symmetry is in the \( x \)-direction.

Radial symmetry. For the scalar case, solutions of the PDE (18) with \( C = 0, B \) even in its first argument, and even initial data are even.

Proof. Outline: The desired symmetry is easily proved under the assumption that solutions satisfying perhaps more general boundary conditions are unique. In fact, when \( x \mapsto u(x,0) \) is an even function, the model is invariant under the replacement of \( x \) by \(-x\). This result follows from the uniqueness of solutions (see Proposition 5.15 in [25]).

The second result, called radial monotonicity in [25] and modified here for the case at hand, is useful for theory and computation.

Radial monotonicity. For the scalar case, suppose that \( C = 0, B \) is positive and even in its first argument, the initial data is even, and \( \Psi ' \) and \( \Psi '' \) are positive for positive arguments. If (for the boundary data) \( b'(t) < 0 \) on some interval \( 0 \leq t \leq t^* \), then \( u_x(x,t) < 0 \) for \( 0 \leq x \leq 1 \). Moreover, by evenness \( u_x(x,t) > 0 \) for \(-1 \leq x \leq 0 \) and the maximum value of \( x \mapsto u(x,t) \) occurs at \( x = 0 \).

Proof. The argument given here is based on a clever idea in [9] used to prove radial monotonicity for the Patlak–Keller–Segel equation, which has the porous medium equation as a special case.

Return to the PDE (18) and define \( \tilde{w} \), a scalar function of a scalar variable, by
\[ \tilde{w}(t) = \sup_{0 \leq d_1 \leq d_2 \leq 1} u(d_2,t) - u(d_1,t). \]
By choosing \( d_1 = d_2 \), for example, the definition of this function implies \( \tilde{w}(t) \geq 0 \) for all \( t > 0 \). Also, because \( u \) is initially constant, \( \tilde{w}(0) = 0 \). The goal is to prove that \( \tilde{w}(t) = 0 \) for \( t > 0 \). This result ensures that \( x \mapsto u(x,t) \) does not increase on the interval \( 0 \leq x \leq 1 \) and suffices to prove the desired result for the even positive solution \( u \).

Suppose that \( \tilde{w}(t_1) > 0 \) for \( 0 < t_1 < t^* \) and seek a contradiction. In general, \( \tilde{w}(t) \) cannot exceed \( \max_x u(x,t) \). By the monotonicity lemma or simply by continuity and compactness, \( u \) and therefore \( \tilde{w} \) are bounded above for \( 0 \leq t \leq t^* \). Choose \( \lambda > 0 \) sufficiently large so that
\[ \tilde{w}(t_1) > e^{-\lambda(t_*-t_1)} \tilde{w}(t_*) \]
and let \( v \) be the function defined by
\[ v(t) = \tilde{w}(t)e^{-\lambda t}. \]
Because \( \upsilon \) is continuous, \( \upsilon(0) = 0 \), and \( \upsilon(t_1) > \upsilon(t_*) \). This function has a positive (interior) maximum at some \( t_2 \) such that \( 0 < t_2 < t_* \), in particular
\[
\bar{\omega}(t_2) > 0. \tag{25}
\]

For an arbitrary \( t \geq 0 \), the function \( \Psi \) given by
\[
\Psi(x, y) = u(x, t) - u(y, t)
\]
is continuous on the compact set \([0, 1] \times [0, 1]\). Thus, it attains its maximum on the compact subset \( \{(x, y) : x \leq y\} \). For \( t = t_2 \), this fact implies there are \( x = \hat{c} \) and \( x = \hat{d} \) with \( \hat{c} < \hat{d} \) such that
\[
\bar{\omega}(t_2) = u(\hat{d}, t_2) - u(\hat{c}, t_2).
\]

Claim: \( u(\hat{c}, t_2) \) is a local minimum and \( u(\hat{d}, t_2) \) is a local maximum of \( x \mapsto u(x, t_2) \) on the interval \([0, 1]\). Moreover, \( u_x(\hat{c}, t_2) = u_x(\hat{d}, t_2) = 0 \), \( u_{xx}(\hat{c}, t_2) \geq 0 \), and \( u_{xx}(\hat{d}, t_2) \leq 0 \). In case \( \hat{d} \) and \( \hat{c} \) are interior points and the claim were not true, an appropriately chosen small perturbation of \( \hat{c} \) would make \( u \) smaller or a perturbation of \( \hat{d} \) would make \( u \) larger to produce a larger value of \( \bar{\omega}(t_2) \) so the maximum value would not be achieved at the pair \( \hat{c} \) and \( \hat{d} \). If \( \hat{c} = 0 \), evenness of \( x \mapsto u(x, t_2) \) implies that \( u(\hat{c}, t_2) \) is a local minimum.

The remaining case is \( \hat{d} = 1 \), which would correspond to a local end point maximum. By the hypothesis on the boundary function \( b \), \( u(t_1, t) \leq 0 \) on the temporal interval of interest. Also, \( \mathcal{B} \) is positive. Under the assumption that the underlying PDE is valid at the boundary, which can be arranged with appropriate extensions and smoothness assumptions, \( \mathcal{A}(t)\Phi(u)_{xx} \leq 0 \) at this boundary. Because \( \mathcal{A} \) is positive, this implies \( \Phi(u)_{xx} \leq 0 \) and in turn that
\[
\Phi''(u)(u_x)^2 + \Phi'(u)u_{xx} \leq 0.
\]

Using the positivity hypotheses on \( \Phi \) this inequality implies
\[
u_{xx}(1, t) \leq 0.
\]

In case \( u_{xx}(1, t) = 0 \) the first derivative \( u_x(1, t) \) must also vanish.

At \( x = 1 \) and an arbitrary \( t > 0 \) where the one sided partial derivative of \( u_x(1, t) \) exists,
\[
u_x(1, t) = \lim_{h \to 0^+} \frac{u(1 - h, t) - u(1, t)}{-h} = \lim_{h \to 0^+} \frac{u(1 - h, t) - b(t)}{-h}.
\]

By the previous positivity result (\( u(x, t) \geq b(t) \)), the numerator of the difference quotient is positive; therefore
\[
u_x(1, t) \leq 0.
\]

In case \( u_x(1, t_2) = 0 \), the claim is true. Otherwise, \( u_x(1, t_2) < 0 \) and for all \( x \) sufficiently close to but not equal to the boundary point \( (x = 1) \), \( u_x(x, t_2) > u_1(1, t_2) \).

But this implies the choice of \( \hat{c} \) and \( \hat{d} \) does not produce the value \( \bar{\omega}(t_2) \). This completes the proof of the claim. An immediate corollary of the claim is that \( u_x(\hat{c}, t_2) = u_x(\hat{d}, t_2) = 0 \), \( u_{xx}(\hat{c}, t_2) \geq 0 \), and \( u_{xx}(\hat{d}, t_2) \leq 0 \).

The function \( Q \) given by
\[
Q(t) = (u(\hat{d}, t) - u(\hat{c}, t))e^{-\lambda t}
\]
is differentiable. Since, by the definition of \( \tilde{w} \) and the choice of \( \hat{d} \) and \( \hat{c} \), \( u(\hat{d}, t) - u(\hat{c}, t) \leq \tilde{w}(t) \), the function \( Q \) has a maximum at \( t_2 \). Therefore

\[
Q'(t_2) = 0
\]

and, by expanding the derivative,

\[
u_t(\hat{d}, t_2) - u_t(\hat{c}, t_2) = \lambda(u(\hat{d}, t) - u(\hat{c}, t)).
\]

(26)

Using the PDE,

\[
u_t(\hat{d}, t_2) - u_t(\hat{c}, t_2) = A(t)(\Phi'(v(\hat{d}, t_2))u_{xx}(\hat{d}, t_2) + \Phi''(u(\hat{d}, t_2))(u_x(\hat{d}, t_2))^2
- \Phi'(u(\hat{c}, t_2))u_{xx}(\hat{c}, t_2) - \Phi''(u(\hat{c}, t_2))(u_x(\hat{c}, t_2))^2)
\]

\[\leq 0.\]

But, \( \lambda > 0 \) and \( \tilde{w}(t_2) > 0 \) imply

\[\lambda(u(\hat{d}, t) - u(\hat{c}, t)) > 0\]

in contradiction to Eq. (26). The hypothesis that \( \tilde{w}(t_1) > 0 \) must not be valid; therefore \( \tilde{w} = 0 \), as desired.

3.2. The PSSA. Using the abstract form of the transport dimensionless form (16) of the model system, assume—in accordance with physical reality—that the evolution is over a finite time scale \( 0 \leq s \leq s^* \) and let \( J \) denote the spatial domain

\[ J := \{ \xi : -1 \leq \xi \leq 1 \}. \]

Under physically realistic assumptions for the binder burnout model the solution of the PDE \( u(x, s) \geq b(s) \) and \( b(s) > 0 \), (see Eq. (21)), the model solution is even, and its maximum occurs on the center line \( \xi = 0 \).

The PSSA \( v \) for system (16) is the solution of the ODE

\[ A(s)\Phi(v(\xi, s))_{xx} + B(s) = 0 \]

(27)

that satisfies the system boundary conditions. In fact,

\[
\Phi(v(\xi, s)) = \frac{B(s)}{2A(s)} (1 - \xi^2) + \Phi(b(s)).
\]

(28)

Under the assumption, enforced here, that \( \Phi' \) is positive on the positive real line, \( \Phi \) can be inverted to obtain an explicit expression for \( v \).

The PSSA problem: Determine a (useful) upper bound for the error \( |u - v| \) that does not depend on the solution \( u \).

The time-dependent model PDE does not have steady states. But, as noticed in a rather long history related to various applications, the PSSA can provide a close approximation to the model solution \( u \). In early work [4], evidence was provided to show that the PSSA was a viable approximation for the binder burnout application. But, the reason(s) for this were not known. Several results in the literature present arguments for the viability of the PSSA for various applications (see, for example, [1], [7], [20], [21], [23]). There does not seem to be a general result that covers all cases of interest. Indeed, due to the variability of special features of model equations, perhaps a general result should not be expected. Where possible, elementary explanations taking advantage of special features are preferable as they often provide insight that would not otherwise be evident.

The advantage of the PSSA from an engineering perspective is simplicity and the possibility to avoid testing and using a PDE solver to approximate solutions of the nonlinear PDE model. Also, the PSSA offers a way to understand the nature...
of actual solutions. For example, for the model at hand, the function $\xi \mapsto v(\xi, s)$ is strictly concave with maximum at $\xi = 0$. Its minimum value $b(s)$ occurs at the boundary of $J$. This insight led to the desire to prove these features for the solution $u$. If viable, the PSSA is a fast and easy way to approximate solutions of the model equations.

From a mathematical perspective, the basic problem is a worthy challenge in the quest to understand the dynamics of nonlinear PDEs. Three results are presented as justification for the utility of the PSSA in some physically relevant regimes for the binder burnout problem. An error bound is determined using singular perturbation theory, which takes the form of a series expansion in powers of the length of the green body. Its derivation provides a geometric explanation, in the spirit of dynamical systems theory, for the PSSA. And, the first nonzero term in the expansion has an explicit expression (called the quality function) that is a useful error approximation in case $L$ is small. A general $L^2$ upper bound for arbitrary $\Phi$ is derived using the energy method, and a sharper $L^2$ bound is proved for the special case where $\Phi$ is given by $\Phi(y) = y^2/2$, which corresponds to the binder burnout application.

The PSSA so far in this section is considered to be a known function that can be explicitly computed. This is true for the simple one-dimensional geometry already considered. For physically realistic domains in three space dimensions the existence of explicit solutions of Eq. (27) depends on the geometry of the domain on which it is defined and the choice of $\Phi$. Two standard cases are three-dimensional blocks and solid cylinders. To give an illustration of the efficacy of the PSSA, consider binder burnout for the solid cylinder case where the solution of the full model equations is rotationally invariant, a fact that is intuitively clear and provable. Equivalently, in cylindrical coordinates the solution is independent of the angular variable. Transport scaling using half the height of the cylinder as the length scale produces a scaled radius $\text{rad}$; the corresponding domain (using $r$ and $z$ as the scaled coordinates) is given by $0 \leq r \leq \text{rad}$ and $-1 \leq z \leq 1$. By treating $u^2/2$ as the new dependent variable, changing the Laplacian to cylindrical coordinates, applying separation of variables to the resulting linear PDE, and using the modified Bessel function of the first kind $I_0$, the explicit solution is

$$v^2(r, z, s) = \frac{B(s)}{A(s)} (1 - z^2) + b(s)^2 - 32 \frac{B(s)}{A(s)} \sum_{n=0}^{\infty} (-1)^n \cos\left(\frac{(2n+1)\pi}{2} z\right) \frac{I_0\left(\frac{(2n+1)\pi}{2} r\right)}{I_0\left(\frac{(2n+1)\pi}{2} \text{rad}\right)}$$

(compare with a different form of this solution in [16]).

3.2.1. A singular perturbation approach to the PSSA for small length green bodies. Evidence acquired via numerical experiments and reported in this paper (see Figs. 1–3) strongly suggest the PSSA is remarkably good in the regime of the (physical) parameters used in this paper. Why?

By considering the square of the length $L$ of the green body as a small parameter a singular perturbation problem arises whose analysis reveals a clear explanation for the utility of the PSSA in a more general setting than the binder burnout application (see [21] for a related result for a simpler model using a different approach). Singular perturbation has also been used to justify PSSAs in chemical reaction dynamics, for example see [1], [7], [20], and [23]. The ideas are similar, but each application requires adjustments. In the present case the model system is not autonomous.
Thus there is no steady state in the usual sense. But there is an attracting invariant set (an orbit in the one-dimensional setting) that substitutes for a steady state. While the presented analysis is rigorous and applies in more generality than needed for the binder burnout application, our goal is to emphasize geometry in favor of technical lemmas so that the evidence presented for the validity of the PSSA can be appreciated with a minimum of mathematical sophistication.

The geometric scenario consists of several elements: A small parameter is specified (which is the square of the length of the green body in the binder burnout application). The relevant abstract PDE is replaced by an ODE whose solutions converge, in the limit as the absolute value of the small parameter decreases to zero, to those of the PDE evaluated at the point in space where for each fixed time the solution of the PDE has its maximum value. This is the midpoint of the green body for the binder burnout application. This ODE has an attracting orbit. The physically relevant solution of the ODE does not lie on this orbit but it deviates from the attracting orbit by no more than does the corresponding initial positions of these solutions, and this distance again vanishes in the limit as the small parameter vanishes. The time evolution of the PSSA, evaluated at the same spatial value as is the mentioned solution of the PDE, is not a solution of the ODE but lies close to the attracting orbit so that the corresponding distance vanishes with the small parameter. Thus, the distance between the PSSA and the corresponding solution of the PDE vanishes in the same limit as the specified parameter goes to zero. This explains the efficacy of the PSSA, at least in this small parameter regime. In addition, an explicit formula for the first-order term of the asymptotic approximation in the small parameter of the difference between the PSSA and the attracting orbit of the ODE is obtained. Since it provides a useful measure of the quality of the PSSA, we call it the quality function.

Let $A$, $B$, and $b$ be positive continuous scalar functions on the nonnegative reals, and $\Phi$ a twice continuously differentiable scalar function defined on the same domain with $\Phi(0) = 0$ and $\Phi'(y) > 0$ for all $y > 0$ as structure functions of the PDE

$$u_t = A(t)(\Phi(u))_{xx} + B(t),$$  \hspace{1cm} (30)

defined on $-L/2 < x < L/2$ and $t > 0$, with constant initial data $b(0)$ at $t = 0$ and Dirichlet boundary data $u(\pm L/2, t) = b(t)$. Also let $v$ be its PSSA, that is the unique positive solution of

$$A(t)(\Phi'(v)v_x)_x + B(t) = 0$$

with boundary (but not initial) data $b$. In fact,

$$v(x, t) = \Phi^{-1}\left(\frac{B(t)}{2A(t)}\frac{L^2}{4} - x^2\right) + \Phi(b(t)).$$  \hspace{1cm} (31)

Note that PDE (30) is a special case of PDE (18); therefore, as proved using the minimum principle and the given data, the solution $u$ of PDE (30) is positive.

For the binder burnout application, $\Phi(y) = y^2/2$ and

$$u_t = A(t)(\frac{y^2}{2})_{xx} + B(t).$$

Consider the method of lines applied to PDE (30) with the spatial domain discretized by exactly three nodes $-L/2$, $0$, and $L/2$. Taking into account the boundary
data and defining $Z$ to be the value of the solution $u$ at the center node,

$$\dot{Z} = \frac{8A(t)}{L^2}\Phi'(Z)(b(t) - Z) + \mathcal{B}(t) + O\left(\frac{L^2}{2}\right).$$

Thus, the family of solutions of the ODE

$$\dot{Z} = \frac{8A(t)}{L^2}\Phi'(Z)(b(t)) - Z) + \mathcal{B}(t) \tag{32}$$

parameterized by $L$ converges to the solution of the PDE evaluated at the center node (in standard function spaces) as $L$ goes to zero. In this limit the PDE degenerates to the ODE.

The PSSA of PDE (30) evaluated at the center node is

$$V(t) = \Phi^{-1}\left(\frac{B(t)}{2A(t)}\frac{L^2}{4} + \Phi(b(t))\right). \tag{33}$$

Treat $L^2$ as a small parameter and view ODE (32) as a system in the usual manner to obtain the planar system

$$\dot{\tau} = 1,$$

$$L^2\dot{Z} = \frac{8A(\tau)}{L^2}\Phi'(Z)(b(\tau) - Z) + L^2\mathcal{B}(\tau), \tag{34}$$

with the same independent variable $t$. Treating $L^2$ as a small parameter, this system is singular. The following (geometric) singular perturbation procedure is standard; it is outlined here for the convenience of the reader.

Change the independent variable (the slow time $t$) to the fast time $s$ via

$$t = L^2s$$

to obtain the fast time system

$$\frac{d\Xi}{ds} = L^2,$$

$$\frac{d\Upsilon}{ds} = 8\mathfrak{A}(\Xi)\Phi'(\Upsilon)(b(\Xi) - \Upsilon) + L^2\mathfrak{B}(\Xi), \tag{35}$$

where $\Xi(s) := \tau(L^2s)$ and the other (fraktur) functions are defined similarly.

Put $L^2 = 0$ in system (35) to obtain the reduced system

$$\frac{d\Xi}{ds} = 0,$$

$$\frac{d\Upsilon}{ds} = 8\mathfrak{A}(\Xi)\Phi'(\Upsilon)|\Xi - \Upsilon|. \tag{36}$$

In the positive quadrant of the phase plane, which is assigned Cartesian coordinates $(\Xi, \Upsilon)$, every vertical half-line is invariant and on each of these lines there is exactly one rest point. At the lower boundary of this quadrant, the horizontal axis consists entirely of semi-hyperbolic rest points that have unstable manifolds in the corresponding half-lines. The family of half-lines is parameterized by $\Xi$ and the corresponding rest points are $\Upsilon = b(\Xi)$. Since $\mathfrak{A}$ and $\Phi'$ are positive, and the linearized system restricted to the half-line is

$$\frac{d\Psi}{ds} = -8\mathfrak{A}(\Xi)\Phi'(b(\Xi))\Psi,$$

this rest point is a hyperbolic sink. Thus the curve of rest points given by

$$\Xi \mapsto (\Xi, b(\Xi))$$
is a normally hyperbolic invariant manifold. Fenichel theory, with appropriate attention to technical details not pursued here, implies that this object persists for sufficiently small values of $L^2$ (see, [5], [6], and [2]). It may be identified in coordinates by taking advantage of its invariance, which is the next step in the analysis.

Perhaps the identification of the perturbed normally hyperbolic invariant manifold is best considered in abstract form where computations are transparent. For this, consider the slow time system

$$\frac{dX}{ds} = \epsilon f(X, Y, \epsilon),$$

$$\frac{dY}{ds} = g(X, Y, \epsilon)$$

(37)

with small parameter $\epsilon$. It has a normally hyperbolic invariant manifold at $\epsilon = 0$ in case there is a (smooth) function $h$ such that

$$Y = h(X), \quad g(X, h(X), 0) = 0, \quad g_Y(X, h(X), 0) \neq 0,$$

where the subscript denotes a partial derivative. Persistence implies the perturbed system has a normally hyperbolic invariant manifold that may be represented as a power series in the small parameter up to some order determined by the minimum smoothness of the functions $f$ and $g$ with leading constant term $h(X)$. Suppose the system is sufficiently smooth so that

$$Y = h(X) + \epsilon k(X) + O(\epsilon^2).$$

On this slow manifold, the flow is given by

$$\frac{dX}{ds} = \epsilon f(X, h(X) + \epsilon k(X) + O(\epsilon^2), \epsilon)$$

$$= \epsilon f(X, h(X), 0) + O(\epsilon^2).$$

At every point on the invariant manifold the dot product of a normal vector and the tangent vector to the flow must vanish. In the simple two-dimensional (ambient) space considered here a normal is

$$(h'(X) + \epsilon k'(X) + O(\epsilon^2), -1)$$

and, using $g(X, h(X), 0) = 0$ in the expansion

$$g(X, h(X) + \epsilon k(X) + O(\epsilon^2), \epsilon) = \epsilon(g_Y(X, h(X), 0)k(X) + g_e(X, h(X), 0)) + O(\epsilon^2),$$

the tangent to the flow $(\frac{dX}{ds}, \frac{dY}{ds})$ is

$$(\epsilon f(X, h(X), 0) + O(\epsilon^2), \epsilon(g_Y(X, h(X), 0)k(X) + g_e(X, h(X), 0)) + O(\epsilon^2).$$

Equating at first order in $\epsilon$ and solving for $k$ yields

$$k(X) = \frac{h'(X)f(X, h(X), 0) - g_e(X, h(X), 0)}{g_Y(X, h(X), 0)}$$

and the desired normally hyperbolic invariant manifold is parameterized by

$$X \mapsto \left(X, h(X) + \epsilon \frac{h'(X)f(X, h(X), 0) - g_e(X, h(X), 0)}{g_Y(X, h(X), 0)} + O(\epsilon^2) \right).$$

(38)

For the fast time system (35),

$$f \equiv 1,$$

$X$ corresponds to $\mathfrak{F}$, $Y$ to $\mathfrak{U}$, $g$ to

$$(\mathfrak{F}, \mathfrak{U}, L^2) \mapsto 8\mathfrak{K}(\mathfrak{F})\Phi'(\mathfrak{U})(b(\mathfrak{F}) - \mathfrak{U}) + L^2\mathfrak{B}(\mathfrak{F}),$$
and \( h \) to
\[
(\Xi, \Upsilon, L^2) \mapsto b(\Xi).
\]
Substitution into the curve (38) provides the perturbed attracting invariant manifold
\[
(\Xi, \Upsilon, L^2) \mapsto (\Xi, b(\Xi) - \frac{b'(\Xi)}{8A(\Xi)} L^2 + O(L^4)).
\] (39)
Translated back to the original fast-time variables, the one-dimensional invariant manifold (which therefore must be a solution of system (34)), is parameterized by
\[
(\tau, u) \mapsto (\tau, b(\tau) - \frac{b'(\tau)}{2A(\tau)\Phi'(b(\tau))} L^2 + O(L^4)).
\] (40)
The attracting solution (40) has initial value
\[
\tau(0) = 0, \quad u(0) = b(0) - \frac{b'(0)}{8A(0)\Phi'(b(0))} L^2 + O(L^4).
\]
Thus it differs from the solution of the model that has \( u(0) = b(0) \) by a quantity that is \( O(L^2) \). For small \( L \) the model solution stays close to the attracting solution.

Because a non-constant PSSA is not a solution of the corresponding dynamical system, there is no reason why it should be attracted to the invariant manifold. But, since
\[
V = b(\tau) + \frac{B(\tau)}{8A(\tau)\Phi'(b(\tau))} L^2 + O(L^4),
\] (41)
its distance to the attracting orbit (given by Eq. (40)) as a function of \( \tau \) does not exceed
\[
\frac{|b'(\tau)|}{8A(\tau)\Phi'(b(\tau))} L^2 + O(L^4),
\] (42)
again a quantity of order \( L^2 \) (on every finite time-interval). This completes the derivation of the evidence for the efficacy of the PSSA as outlined in the introduction to this section.

As also mentioned, a useful asymptotic approximation of the distance between the PSSA and the corresponding solution of PDE (30) with compatible boundary and initial data is the absolute value of the leading term of the expansion (42); that is, the quality function \( qf \),
\[
qf(\tau) = \frac{|b'(\tau)|}{8A(\tau)\Phi'(b(\tau))} L^2.
\] (43)
Numerical evidence for the utility of this function is presented in Fig. 3 and explained in Sec. 3.2.4.

Of course, taking \( \tau(0) = 0 \), the temporal parameter \( \tau \) is equal to the original \( t \). In fact, for the physical parameters and variables, the functions \( A \) and \( b \) (which have the dimensions of gas density) are
\[
A(t) = \frac{\kappa(\epsilon(t))RT(t)}{\epsilon(t)^2 \mu}, \quad b(t) = \frac{\rho_0(\epsilon(t))}{RT(t)}
\]
and the quality function is
\[
qf(t) = \frac{\mu k S^2 (1 - \epsilon(t))^2}{8Re(t)T(t)} \left( \frac{\epsilon'(t)}{\epsilon(t)} - \frac{T'(t)}{T(t)} \right) L^2.
\] (44)
The quality function is thus proportional to the transport and kinetic quantities appearing in the model as well as on the temperature protocol. An alternative expression for this function will be used in the discussion of time-optimal control:

\[ q_\ell (t) = \frac{\mu k S^2 (1 - \epsilon(t))^2}{8 R \epsilon(t) T(t) \epsilon(t) \rho(t)} ((\epsilon \rho)'(t) - \epsilon(t) \rho(t) \frac{P'(t)}{P(t)}) L^2. \tag{45} \]

Using these functions, the exponential pre-factor \(A\), and

\[ B(t) = \frac{\rho_2 A}{M} e^{-E/(RT(t))} (1 - \epsilon_3 - \epsilon(t)), \]

the PSSA evaluated at the center \( x = 0 \) for the binder burnout model is

\[ V(t) = \sqrt{\frac{B(t)}{A(t)} (L^2 / 4) + b(t)^2}. \tag{46} \]

3.2.2. A general \( L^2 \) PSSA error bound. An abstract \( L^2 \) error bound for the PSSA approximation for the solution of the parabolic boundary value problem for PDE (16) is proved. The purpose is to demonstrate that upper bounds can be obtained in this generality. Of course, sharper bounds are possible for special cases of the function \( \Phi \). A better bound for the porous media case—used in the binder burnout model—is obtained in Sec. 3.2.3.

Consider functions defined on \( J = [-1, 1] \) with finite \( L^2 \) norm; that is,

\[ \|f\|_2 := \sqrt{\int_{-1}^{1} f^2 d\xi} < \infty. \]

For each \( s \), treat \( b(s) \) as a constant function in \( L^2(\Omega) \). By Minkowski’s inequality,

\[ \|u - v\|_2 \leq \|u - b(s)\|_2 + \|v - b(s)\|_2. \tag{47} \]

Because \( \|v - b(s)\|_2 \) does not depend on \( u \) and can in principle be computed explicitly, an error bound is determined by providing a bound for \( \|u - b(s)\|_2 \) that does not depend on \( u \). Of course, the error estimate does depend on the temporal variable \( s \). In fact, under the assumptions that \( A \) is positive, \( \Phi' \) and \( \Phi'' \) are positive on the positive real line, and \( b \) is positive, the desired estimate is

\[ \|u - b(s)\|_2 \leq \sqrt{2} \int_0^s \exp \left( - \frac{1}{4} \int_\sigma^s A(\tau) \Phi'(b(\tau)) d\tau \right) |B(\sigma) - b'(\sigma)| d\sigma. \tag{48} \]

A derivation of inequality (48) proceeds in the standard manner for energy inequalities. The PDE for \( \tilde{z} \) given by

\[ \tilde{z}(\xi, s) = u(\xi, s) - b(s) \]

is

\[ \tilde{z}_s = A(s) \Phi(\tilde{z} + b(s)) \xi + B(s) - b'(s) \]

with zero boundary and initial data. Multiply by \( \tilde{z} \) and integrate. Apply integration by parts and Hölder’s inequality to obtain the inequality

\[ \frac{1}{2} \frac{d}{ds} \int_{-1}^{1} \tilde{z}^2 d\xi \leq A(s) \left( \tilde{z} \Phi' (\tilde{z} + b(s)) \tilde{z}_\xi \right|_{-1}^{1} - \int_{-1}^{1} \Phi' (\tilde{z} + b(s)) (\tilde{z}_\xi)^2 d\xi \]

\[ + |B(s) - b'(s)| \|1\|_2\|\tilde{z}\|_2. \]
Use the zero boundary data to remove the boundary terms of the integration by parts. Also, by the positivity of $\Phi''$,

$$\Phi'(b(s)) \leq \Phi'(\hat{z} + b(s)).$$

Thus,

$$\|\hat{z}\|_2 \frac{d}{ds} \|\hat{z}\|_2 \leq -A(s)\Phi'(b(s))\|\hat{z}\|_2^2 + \sqrt{2}|B(s) - b'(s)|\|\hat{z}\|_2.$$

By an application of Poincaré’s inequality and division by the nonnegative quantity $\|\hat{z}\|_2$, compute the ODE inequality

$$\frac{d}{ds} \|\hat{z}\|_2 \leq -\frac{1}{4} A(s)\Phi'(b(s))\|\hat{z}\|_2 + \sqrt{2}|B(s) - b'(s)|.$$

The claimed bound is obtained by solving the linear ODE inequality with zero initial condition. This completes the derivation.

3.2.3. Direct $L^2$ estimate for porous medium case. For the special case corresponding to the binder burnout model and the standard porous medium equation, where $\Phi(y) = y^2/2$, an $L^2$ norm bound is proved for the difference

$$\tilde{y} = u - v$$

between the solution $u$ and PSSA $v$ for PDE (16).

Note that $\tilde{y}$ satisfies the PDE

$$\tilde{y}_s = A(s)\Phi(u)\xi + B(s) - v_s$$

and $\tilde{y}$ vanishes at the boundary. Proceed as usual with multiplication by $\tilde{y}$, integration over the spatial domain, and an integration by parts to obtain

$$\frac{1}{2} \frac{d}{ds} \|\tilde{y}\|_2^2 = -A(s) \int_{-1}^{1} \Phi'(u) u \xi \tilde{y} \xi \, d\xi + B(s) \int_{-1}^{1} \tilde{y} \, d\xi - \int_{-1}^{1} v_s \tilde{y} \, d\xi$$

$$= -A(s) \int_{-1}^{1} \Phi'(u)(\tilde{y})^2 - A(s) \int_{-1}^{1} \Phi'(u) v \xi \tilde{y} \xi \, d\xi$$

$$+ B(s) \int_{-1}^{1} \tilde{y} \, d\xi - \int_{-1}^{1} v_s \tilde{y} \, d\xi.$$

The special form of $\Phi$ is used at this point to write $\Phi'(u) = v + \tilde{y}$ in the second term so that

$$\frac{1}{2} \frac{d}{ds} \|\tilde{y}\|_2^2 = -A(s) \int_{-1}^{1} \Phi'(u)(\tilde{y})^2 - A(s) \int_{-1}^{1} vv \xi \tilde{y} \xi \, d\xi$$

$$- A(s) \int_{-1}^{1} \tilde{y} v \xi \tilde{y} \xi \, d\xi + B(s) \int_{-1}^{1} \tilde{y} \, d\xi - \int_{-1}^{1} v_s \tilde{y} \, d\xi.$$

Integrate by parts in the new second term and use the zero boundary data for $\tilde{y}$ to write

$$\frac{1}{2} \frac{d}{ds} \|\tilde{y}\|_2^2 = -A(s) \int_{-1}^{1} \Phi'(u)(\tilde{y})^2 + \int_{-1}^{1} A(s)\Phi(v)\xi \xi \tilde{y} \xi \, d\xi + \int_{-1}^{1} B(s) \tilde{y} \, d\xi$$

$$- A(s) \int_{-1}^{1} v \xi \tilde{y} \xi \, d\xi - \int_{-1}^{1} v_s \tilde{y} \, d\xi$$

$$= -A(s) \int_{-1}^{1} \Phi'(u)(\tilde{y})^2 - A(s) \int_{-1}^{1} v \xi \tilde{y} \xi \, d\xi - \int_{-1}^{1} v_s \tilde{y} \, d\xi.$$
Apply another integration by parts in the new second term to derive the equality
\[
\frac{1}{2} \frac{d}{ds} \|\tilde{\gamma}\|_2^2 = -A(s) \int_{-1}^1 u(\tilde{\gamma}_{\xi})^2 + \frac{1}{2} A(s) \int_{-1}^1 v_{\xi} \tilde{\gamma}_\xi^2 d\xi - \int_{-1}^1 v_{\xi} \tilde{\gamma} d\xi.
\] (49)

In view of the positivity of \(A\), positive lower bound \(b(s)\) for \(u(\xi, s)\), zero boundary data for \(\tilde{\gamma}\), and Poincaré’s inequality,
\[
\frac{1}{2} \frac{d}{ds} \|\tilde{\gamma}\|_2^2 \leq -A(s) \frac{b(s)}{4} \|\tilde{\gamma}\|_2^2 + \frac{1}{2} A(s) \int_{-1}^1 v_{\xi} \tilde{\gamma}_\xi^2 d\xi - \int_{-1}^1 v_{\xi} \tilde{\gamma} d\xi.
\]

From the explicit formula for \(v\),
\[
\|v\|_\infty := \max_{-1 \leq x \leq 1} v(x, s) = \sqrt{\frac{\mathcal{B}(s)}{\mathcal{A}(s)}} + b(s)^2
\] (50)
and
\[
-v_{\xi} = \frac{\mathcal{B}(s)/\mathcal{A}(s) + v_s^2}{v} \geq \frac{\mathcal{B}(s)}{\mathcal{A}(s)} \|v\|_\infty^2;
\] (51)
therefore,
\[
\frac{1}{2} \frac{d}{ds} \|\tilde{\gamma}\|_2^2 \leq -(A(s) \frac{b(s)}{4} + \frac{1}{2} \|v\|_\infty) \|\tilde{\gamma}\|_2^2 - \int_{-1}^1 v_{\xi} \tilde{\gamma} d\xi.
\] (52)

By an application of Hölder’s inequality,
\[
\frac{1}{2} \frac{d}{ds} \|\tilde{\gamma}\|_2^2 \leq -(A(s) \frac{b(s)}{4} + \frac{1}{2} \|v\|_\infty) \|\tilde{\gamma}\|_2^2 + \|v_s\|_2 \|\tilde{\gamma}\|_2.
\] (53)

With
\[
\tilde{\gamma} := \|\tilde{\gamma}\|_2
\]
and \(umv(\xi) := u(\xi, 0) - v(\xi, 0)\), the error is a solution of the differential inequality
initial value problem
\[
\tilde{\gamma} \leq -(A(s) \frac{b(s)}{4} + \frac{1}{2} \|v\|_\infty) \tilde{\gamma}^2 + \|v_s\|_2 \tilde{\gamma}, \quad \tilde{\gamma}(0) = \|umv\|_2,
\] (54)
where all coefficients and the initial data are independent of the solution \(u\). For each \(s\), either \(\tilde{\gamma}(s) = 0\) or
\[
\tilde{\gamma} \leq -(A(s) \frac{b(s)}{4} + \frac{1}{2} \|v\|_\infty) \tilde{\gamma} + \|v_s\|_2, \quad \tilde{\gamma}(0) = \|umv\|_2.
\] (55)

Because zero is the smallest possible error, a solution of the differential inequality provides an upper bound:
\[
\tilde{\gamma}(s) \leq \tilde{\gamma}(0) \exp \left( - \int_0^s \left( A(\tau) \frac{b(\tau)}{4} + \frac{1}{2} \|v(\tau)\|_\infty \right) d\tau \right)
+ \int_0^s \exp \left( - \int_\sigma^s \left( A(\tau) \frac{b(\tau)}{4} + \frac{1}{2} \|v(\tau)\|_\infty \right) d\tau \right) \|v_s\|_2 d\sigma.
\] (56)

For practical computation, the solution of the corresponding ODE given by equality in the inequality (55) is the desired upper bound.
3.2.4. Binder burnout PSSA error. To check the PSSA error for the binder burnout application, consider (as a standard example) the physical parameters listed in
Table 1 and the temperature protocol $T$ given by a linear temperature rise starting at 300 K with constant heating rate $\beta = 5.6 \times 10^{-4}$ K/s (a convenient legacy value used for comparison with other numerical work); it is

$$ T(t) = \beta t + 300. \quad (57) $$

Numerical approximations of solutions of the PDE model are made using a MacCormack solver written in FORTRAN 95 and compared for accuracy via experiments with COMSOL and Mathematica solvers. The standard test case is forward in time integration until the binder volume fraction reaches 0.01.

The top panel of Fig. 1 depicts pressure versus temperature for $L = 0.01$ m, the length of the green body in the physical regime (which we take to be 0.001–0.1 m). The three curves for the PDE, PSSA, and three station (a discrete model discussed in Sec. 3.3) models are virtually indistinguishable. The relative error in the bottom three panels is computed at the center line as $|\epsilon_{\rho}(0, t) - \text{pssa}(0, t)|/\epsilon_{\rho}(0, t)$ and indicate that the PSSA is valid over the physical range where the model might be employed. The length must be increased to approximately 0.15 m for the PSSA to reach a 0.1 (10%) relative error.

Figure 2 has three panels corresponding from bottom to top to the lengths $L = 0.001, 0.01$, and 0.1 m. Each depicts numerical approximations of two quantities: 1) the $L^2$ norm of the difference between $\epsilon_{\rho}$ from PDE (5) and its corresponding PSSA and 2) the corresponding theoretical bound computed from ODE (55). The PSSA is seen to be accurate in all cases but decreases in accuracy as $L$ increases. The numerically approximated theoretical bound obtained using the energy method is consistently above and near the $L^2$ norm difference. In fact, numerical experiments reported in Fig. 2 suggest that it is a useful bound over the physical range of green body lengths considered here. In contrast, the general error bound derived in Sec. 3.2.2 reduced to the special case where $\Phi(u) = u^2/2$ is much greater, as determined by numerical experiments not shown, than the direct error bound depicted in the figure.

Figure 3 shows a favorable comparison, as $L$ decreases, between the size of the values of the quality function and the corresponding computed difference between the solution of the PDE in the model equations (5) and its PSSA. Using physical variables, as in the model (5), the quality function (44) has the dimensions of gas density. Interpretation of the graphs in Fig. 3 is consistent with convergence of the quality function to the absolute value of the difference between the solution and its PSSA as $L$ decreases to zero. In addition to the geometric insight on PSSA validity provided by the derivation of the quality function, its structure suggests the quality of the PSSA is inversely proportional to the lumped system parameter $kS^2/\mu L^2$, the rate of reaction, and the heating rate; numerical simulations have verified this behavior.

Positive evidence that the PSSA remains useful for physically realistic three-dimensional green bodies for the binder burnout application is provided by the numerical experiment reported via Fig. 4 for a solid cylinder with height 0.03 cm and radius 0.005 cm. Gas pressure computed for our benchmark linear temperature rise test case using one, two, and ten terms of the series representation (29) of the PSSA shows convergence to a PSSA that is not distinguishable at the scale of the figure from the computed model solution. More complex geometry degrades the simplicity of the PSSA as a Poisson equation must be solved to obtain it. But,
Figure 2. Numerically approximated graphs of $L^2$ norms of difference between $\epsilon \rho$ and corresponding PSSA versus temperature in physical units ($[\rho \sqrt{L/2}] = \text{mol/m}^{5/2}$) for the linear temperature rise (57) test case where $\beta = 5.6 \times 10^{-4}$ and green body lengths $L = 0.001, 0.01, 0.1 \text{ m}$ (depicted in order from bottom to top). The $L^2$ error is obtained using finite-difference approximation (MacCormack’s method) of the solution of the model equations (5) and numerical quadrature for the $L^2$ norm, and the theoretical bound is computed likewise from the solution of the ODE (55).

using special dimensional features such as controlling length scales of many applications it remains a useful approximation especially when low overhead numerical computations are desired.

3.3. Discrete model approximation (DMA).

3.3.1. Abstract discrete model. Two usual approaches to obtain models for describing conservation of mass in reaction-transport problems are based on either differential or integral balances in terms of fluxes, velocities, and a source term. Using the divergence theorem, these two approaches lead to equivalent distributed parameter models such as PDE (3). By imposing some natural discretization and employing the same conservation law used to derive the binder burnout PDE, useful semi-discrete models (systems of ODEs) for the same process can be derived. These
Figure 3. Numerically approximated graphs of the absolute value of the quality function and the absolute difference between $u := \epsilon \rho$ and the corresponding PSSA versus temperature (both computed at the centerline) for the linear temperature rise (57) test case where $\beta = 5.6 \times 10^{-4}$ and three green body lengths $L = 0.001, 0.01, 0.1$ m (depicted in order from bottom to top). The solution of the model equations (5) is approximated using MacCormack’s method, and the quality function is computed using (44). Note: To benchmark the values, $\rho_0 = 40$ mol/m$^3$.

may be considered approximations of the continuous model or as viable models themselves subject to validation by physical experiment. They are useful because systems of nonlinear ODEs are generally easier to understand than nonlinear PDEs and are more reliably amenable to numerical methods, including a significant reduction in computational overhead. Of course, a semi-discrete model may be derived by discretizing an evolution type PDE as in the method of lines, but there is value in deriving a similar model directly from physical laws. Additionally, the discrete approach serves as the basis for the singular perturbation analysis in Sec. 3.2.1 and also will be shown to be an accurate representation of binder burnout process under different types of temperature protocols (see Fig. 1), including the time optimal control introduced in Sec. 3.4. One of the strengths of the discrete model is that a
proof of the existence of a time optimal control can be made using standard ODE theory.

For simplicity, suppose that for reasons of symmetry only one spatial dimension is relevant. Space is still viewed in the modeling process as a continuum but only \( m+1 \) uniformly spaced stations at spatial positions \( x_1, x_2, \ldots, x_{m+1} \), where quantities are measured, appear in the model. In this case, \( x_1 \) and \( x_{m+1} \) are on the boundary of the body. The simplest physically relevant case has three stations, one in the interior and two at the boundary.

The amount per volume of the substance being modeled, here the number of moles of gas, at the \( i \)th station is identified with the real number \( w_i \). There are several possible definitions. To take into account all of the substance along the spatial direction in a uniform manner, a reasonable definition is that \( w_i \) is the amount of substance in an interval \( \Omega_i \) with center at \( x_i \) and length the uniform distance \( \Delta x \) between stations. In this case, the total amount at station \( i \) is

\[
\dot{w}_i \Delta x.
\]

The time rate of change of this total amount, \( \dot{w}_i \Delta x \), makes sense (provided of course that this rate of change exists).

For notational convenience, the left and right end points of \( \Omega_i \) are respectively denoted \( x_{i-1/2} \) and \( x_{i+1/2} \). Similar notation is used to denote function values at these points, which are used in the modeling process but should not appear in the model.

Consider the \( i \)th station and the interval \( \Omega_i \). Staying with the assumption that a gas or fluid carries the substance with flow velocity \( v \), the flux vector on the
boundary of \( \Omega_i \) has the form
\[
J = \rho v.
\]
The velocity field might arise from various sources that could be modeled. But, for the binder burnout model and many others, the gas or fluid velocity is assumed to arise from only one source: gradients (or in our discrete view spatial difference quotients) in pressure. To close the system, pressure must be related to the amount of substance by some equation of state
\[
P = h(w),
\]
where \( h \) is an increasing function. Otherwise additional physics (hence a more complicated model) is required.

As a reasonable (but not completely general) statement in cases where closure is possible, suppose also that velocity is a multiple \( g \) of the spatial pressure difference quotient. At the left and right-hand boundaries of \( \Omega_i \) this leads to
\[
J_i^{1/2} := -\rho_i^{1/2} g_i^{1/2} \frac{h(w_i) - h(w_{i-1})}{\Delta x}, \\
J_i^{1+1/2} := -\rho_i^{1+1/2} g_i^{1+1/2} \frac{h(w_{i+1}) - h(w_i)}{\Delta x},
\]
one of several possibilities. Stations further to the right than \( x_{i+1} \) might be involved in generating the field. But as their distances from \( x_i \) increase, the corresponding difference quotients would be expected to decrease and the corresponding terms would make smaller contributions. Thus using the left-hand and right-hand adjacent nodes only is a reasonable first approximation. As in the continuum case, \( g \) might depend on \( x_i, x_{i+1}, t \) and perhaps other variables. The negative—to respect the time rate of change of the total substance—of the net flux is
\[
-(J_i^{1-1/2} + J_i^{1+1/2}) = \rho_i^{1-1/2} g_i^{1-1/2} \frac{h(w_i) - h(w_{i-1})}{\Delta x} \\
+ \rho_i^{1+1/2} g_i^{1+1/2} \frac{h(w_{i+1}) - h(w_i)}{\Delta x}.
\]
The general model equations arising from the discrete version of the divergence of the net flux are
\[
\dot{w}_i = -\frac{J_i^{1-1/2} + J_i^{1+1/2}}{\Delta x} + f_i, \quad i = 1, 2, 3, \ldots, m + 1, 
\]
where \( f_i \) represents the generation of the substance. A simplifying assumption, which is satisfied in the binder burnout model, is that composition of \( g \) with the system variables does not depend on the spatial variable; rather it is a function of time only. In effect, its evaluations do not need a spatial subscript. In this case, for \( i = 1, 2, 3, \ldots, m + 1, \)
\[
\dot{w}_i = g \frac{\rho_i^{1-1/2} (h(w_i) - h(w_{i-1})) + \rho_i^{1+1/2} (h(w_{i+1}) - h(w_i))}{\Delta x^2} + f_i.
\]
In keeping with the assumption that measurements are made at the specified stations only, \( \rho_i^{1-1/2} \) and \( \rho_i^{1+1/2} \) are approximated by averages:
\[
\rho_i^{1-1/2} := \frac{\rho_{i-1} + \rho_i}{2}, \quad \rho_i^{1+1/2} := \frac{\rho_i + \rho_{i+1}}{2}.
\]
Of course, $\rho$ will be related to $w$ in an application. Perhaps $\rho = w$ or more generally it is a multiple of $w$. The discrete model is

$$\dot{w}_i = \frac{g}{2} \left( (\rho_{i-1} + \rho_i) (h(w_{i-1}) - h(w_i)) + (\rho_i + \rho_{i+1}) (h(w_{i+1}) - h(w_i)) \right) \frac{\Delta x^2}{\Delta x^2} + f_i$$

(61)

for $i = 1, 2, 3, \ldots, m + 1$.

3.3.2. Application to binder burnout. For binder burnout (14), the full semi-discrete model retains the ODE for $\alpha = \epsilon_2$ in the continuous model and adds ODEs (61) according to the desired number of stations where the state variable $w$ is taken to be

$$w = \epsilon \rho,$$

where, as before, $\epsilon$ is the volume fraction containing the gas phase and $\rho$ is the molar gas density. Using dimensionless variables as in Sec. 2.2, let the dimensionless state variable corresponding to $w$ be

$$\varpi(\xi, s) := \epsilon(s) \frac{\rho(\ell \xi, \tau s)}{\rho_0} = \frac{w(\ell \xi, \tau s)}{\rho_0}.$$

The equation of state given by the function $h$ in the discrete model (with some algebra) becomes

$$P = h(w) = RT \rho = RT \frac{w}{\epsilon} = \frac{P_0 \Gamma}{\rho_0} \frac{w}{\epsilon} = P_0 \Gamma \frac{\varpi}{\epsilon}. \quad (62)$$

Also, the factor $g$ in the abstract form of the gas velocity

$$v = -g \nabla (h(w))$$

is

$$g = \frac{\kappa(\epsilon)}{\mu},$$

where the function $\kappa$ is defined in Eq. (2). In dimensionless form, this function is replaced by $q$ as in Eq. (10).

The rate of gas production is measured by $f$. It must have units of molar density per time. As the binder burns out the rate of change of its volume fraction, $-\dot{\alpha}$, times binder mass $\rho_2$ (which is assumed to be constant) accounts for the amount of matter per time converted to gas phase. Binder mass is moles times molecular weight. Thus, the rate divided by molecular mass has the correct units and

$$f = \frac{\rho_2 A e^{-\gamma/\Gamma} \alpha}{M}.$$

Pressure is held at the constant ambient furnace pressure $P_0$ at the boundary. Using Eq. (62) and the definition of $\Gamma$ in (9), this condition is

$$\varpi\left(\frac{L}{2\ell}, s\right) = \frac{\epsilon(\tau s)}{\Gamma(s)}, \quad (63)$$

and initial data for $\alpha$ and $\varpi$ are

$$\alpha(0) = \epsilon_{20}, \quad \varpi(\xi, 0) = \frac{\epsilon(0) \rho(\ell \xi, 0)}{\rho_0} = \epsilon(0).$$

A notable special case (which is illustrative, useful, and easy to write) is the three station model where the end stations are at the boundary of the green body, the second station is at its central line, and the spatial increment is $\Delta x = L/2$. 

Redefining \( \varpi \) to be the state at the central line, that is using \( \varpi \) instead of \( \varpi_2 \), this model (in dimensionless form) is

\[
\alpha_s = -\tau A \exp\left(-\frac{\gamma}{\Gamma(s)}\right) \alpha,
\]

\[
\varpi_s = \frac{\tau P_0}{\mu k s^2} \Gamma(s) q(\epsilon(s)) \left(\frac{\epsilon(s)}{\Gamma(s)}\right)^2 - \varpi^2 \left(\frac{L}{2}\right)^2 + \frac{\tau A \rho_2}{M \rho_0} \exp\left(-\frac{\gamma}{\Gamma(s)}\right) \alpha.
\] (64)

The latter ODE is a Riccati equation, albeit one with complicated time-dependent coefficients.

There is at least one remarkable fact: the PSSA obtained from the three-station model is identical to the PSSA for the distributed parameter model when its solution is evaluated at the center line; this lends some validity to the discrete modeling approach.

Further evidence for the utility is displayed in Fig. 1, which shows that the three-station model is virtually indistinguishable from the PDE and PSSA models for the simulation conditions therein. In general, the difference between the center line values of gas density or pressure computed from the three-station and PDE binder burnout models is essentially zero using numerical approximations with up to 128 spatial elements for the PDE method of lines discretization, the test parameters, and linear temperature rise as in Fig. 1 over the physical range of green body lengths 0.001–0.1 m. In fact, significant differences do not appear until the green body length is well outside the physical range (at least 0.5 m). Thus for practical purposes in this parameter regime, the PDE may be replaced up to close approximation by one ODE to take advantage of the efficiency of ODE solvers over PDE solvers and additionally to provide insight into qualitative behavior, parameter dependence, control strategies, etc. Finally, we note that the same discretization procedure, perhaps using large elements, can be applied to 3-d or more complicated geometries using the same approach as in Sec. 3.3.1.

3.4. Time-optimal control. For each temperature protocol the model differential equations may be integrated forward in time until the polymer volume fraction reaches some desired value. The basic problem is to reach this goal in the least possible time while respecting two constraints: the furnace temperature rise rate is bounded and the pressure inside the body is less than some given maximum. A more precise version of this time optimal control problem is discussed. Due to the special form of the model equations, existence and uniqueness is proved up to an existence theorem for a functional nonlinear parabolic PDE. The remaining task is construction of efficient numerical methods to compute the optimal temperature protocol. Several methods to accomplish this are discussed.

3.4.1. Problem statement. The set \( \mathcal{T} \) of admissible controls contains all (absolute) temperature protocols (1) limited in range by some minimum and maximum temperatures, (2) set to a uniform initial temperature in this allowed range at time zero, and (3) the time derivative of each is bounded by a given maximum temperature rise rate. In formulas, there are preassigned numbers \( 0 < T_{\min} \leq T_0 \leq T_{\max} \) and \( \beta_{\max} > 0 \) such that an admissible control is a (piecewise continuous) function \( T' : [0, \infty) \rightarrow [T_{\min}, T_{\max}] \) together with the maximum temperature rise rate constraint

\[
T'(t) \leq \beta_{\max}.
\] (65)
The dynamical system for the states $\alpha$ and $\rho$ with control $T$ is given by

$$
\alpha_t = -A \exp\left(-\frac{E}{RT}\right)\alpha, \\
(\epsilon\rho)_t = \left(\frac{\kappa(\epsilon)\rho}{\mu}(RT\rho)_x + \frac{\rho^2}{M}A \exp\left(-\frac{E}{RT}\right)\alpha\right),
$$

where $\epsilon := 1 - \epsilon_3 - \alpha$. Initial and boundary conditions are

$$
\alpha(0) = \epsilon_{20}, \quad \rho(0) = \rho_0
$$

and

$$
\rho(\pm \frac{L}{2}, t) = \frac{P_0}{RT}.
$$

A maximum allowed pressure $P_{\text{max}}$ in the body during burnout is given. The corresponding constraint is imposed for each $x$ in the spatial domain corresponding to the body and each time $t$ while the process is running:

$$
0 \leq \max_{x \in \Omega} RT(t)\rho(x, t) \leq P_{\text{max}}.
$$

This constraint can be simplified for the simple one dimensional geometry treated here using the result in Section 3.1 that the maximum pressure occurs at the center of the body, that is at $x = 0$. Thus, for the remainder of this section, the constraint is taken to be

$$
0 \leq RT(t)\rho(0, t) \leq P_{\text{max}}.
$$

Also, of course, $P_{\text{max}} > P_0$. A target (positive) binder fraction $\alpha_* < \epsilon_{20}$ is specified and the time of flight is defined by

$$
\min\{t : \alpha(t) = \alpha_*\}.
$$

The problem is to determine among the admissible temperature protocols those (if any) that minimize the time of flight.

Taking into account interpretations of the quantities appearing in the optimization problem, physical intuition suggests a unique solution: Evolve the system using the temperature protocol $T(t) = T_0 + \beta_{\text{max}}t$ until the state and control are on the boundary of the feasible set; that is, until the first time $t = t_1$ when $RT(t_1)\rho(0, t_1) = P_{\text{max}}$, and thereafter choose the control that maintains the process on this boundary until $\alpha$ reaches $\alpha_*$. A basic problem is to show that the model time optimal control problem in fact has a unique solution and to discover its relation to the suggested physical intuition. Once this is accomplished or at least strong evidence is provided in favor of the desired result, the main issue is to demonstrate efficient numerical methods for approximating the optimal temperature protocol and the corresponding minimum burnout time. The solution of both problems can be approached with elementary methods because the ODE in system (66) decouples from the PDE.

3.4.2. **Time optimal control analysis.** To simplify and generalize, transport scale is used in the remainder of this section.

By inspection $\alpha_s < 0$ for all admissible temperature protocols (viewed in the transport scale as choices of $\Gamma = T/T_0$). Consequently for each admissible control, $\alpha$ decreases monotonically with increasing scaled time $s$. In addition, because all admissible controls are uniformly bounded above zero for all $s \geq 0$, $\alpha$ reaches its positive target value (which is chosen less than its initial value) at some positive scaled time that is smaller than a uniform bound.
A basic observation is that binder burnout time is decreased with increasing temperature. To see this is true (using the scaled system), recall that $\gamma > 0$ and examine the function $z \mapsto \tau A \exp(-\gamma/z)$ defined for $z > 0$. It has a positive derivative and hence increases with $z$. Thus for each $s \geq 0$ inspection of the differential equation for $\alpha$ reveals that when $\Gamma$ is increased, $\alpha$ decreases faster. Consequently, the time of flight is minimized by choosing at each time $s$ the (unique) maximum allowed value of $\Gamma(s)$ with respect to the constraints. By inspection of the constraints, in particular in view of the positivity of the dimensionless $\alpha$, $\epsilon = 1 - \epsilon_3 - \alpha$, and $U := \epsilon \rho / \rho_0$ (from the analysis of the model in the physical parameter regime), this largest allowed $\Gamma$ (which is up to scaling the time-optimal control) is determined by solving systems of differential equations with switching among them determined using the maximum allowed rate of temperature increase, pressure, and maximum temperature constraints. Also, the optimal control $\Gamma$ is to be determined as the system evolves. In other words, $\Gamma$ should be considered as a component of the evolving state.

The state space is infinite-dimensional because one of the underlying model equations is a PDE. Given that this PDE has classical solutions (in the physical regime under consideration) the evolution of the state $(\Gamma, \alpha, U)$ may be taken to be in $\mathbb{R}^2 \times C^2([-1,1])$. Constraints depend on the control. With an eye toward numerical approximations via computer code, several functions are useful. Knowing that maximum pressure occurs at $\xi = 0$ a notational and theoretical convenience is supplied by the auxiliary linear function $U_{max} : C^2([-1,1]) \to \mathbb{R}$ defined by

$$U_{max}(f) = f(0).$$

In particular, this function is continuously differentiable (independent of the Banach space on which it is defined). The pressure constraint is imposed via $G : \mathbb{R} \times \mathbb{R} \times C^2([-1,1]) \to \mathbb{R}$ given by

$$G(\Gamma, \alpha, U) = \frac{P_{max}}{P_0} - \frac{\Gamma U_{max}(U)}{1 - \epsilon_3 - \alpha}.$$

The temperature constraint is likewise imposed using $H : \mathbb{R} \times \mathbb{R} \times C^2([-1,1]) \to \mathbb{R}$ defined by

$$H(\Gamma, \alpha, U) = \Gamma_{max} - \Gamma.$$

The feasible region, where for simplicity the minimum allowed $\Gamma$ and the positivity of the state variables are not considered, is the region of state space where $G$ and $H$ are nonnegative. The boundary of the feasible region consists of the hypersurfaces where one of the constraints is zero. Again for simplicity, $\Gamma_{max}$ is considered to be so large that $H$ is positive in the physically relevant regime. Of course, the temperature constraint may be treated (theoretically and numerically) similar to the more important pressure constraint.

With respect to the simplifying assumptions, the interior of the feasible region is the portion of the state space where $G$ is positive and its boundary is the hypersurface on which $G$ vanishes.

In the interior of the feasible region the pressure constraint is inactive. Thus, $\Gamma$ is maintained at its maximum allowed value provided its rise rate is maximal; that is, state evolution proceeds (in what is here called mode 1) via the dynamical
system

\[
\frac{d\Gamma}{ds} = \frac{t\beta_{\text{max}}}{T_0},
\]

\[
\frac{d\alpha}{ds} = -tAe^{-\gamma/\Gamma(s)}\alpha,
\]

\[
\frac{\partial U}{\partial s} = \Gamma(s)q(\epsilon)\Phi(U)_{\xi \xi} + ce^{-\gamma/\Gamma(s)}\alpha
\]

(69)

with previously given boundary data. At the initial point (which lies in the interior of the feasible region) for the optimal control problem, model specified initial data is imposed together with the additional initial condition

\[
\Gamma(0) = 1.
\]

Let \(U_{s}(s)\) be the function given by \(\xi \mapsto U(s, \xi)\). On the boundary of the feasible region, evolution proceeds (in mode 2) governed by the (functional) differential algebraic equation (DAE)

\[
\Gamma = \frac{P_{\text{max}}}{P_0} \frac{\epsilon}{U_{\text{max}}(U_{s}(s))},
\]

\[
\frac{d\alpha}{ds} = -tAe^{-\gamma/\Gamma(s)}\alpha,
\]

\[
\frac{\partial U}{\partial s} = \Gamma(s)q(\epsilon)\Phi(U)_{\xi \xi} + ce^{-\gamma/\Gamma(s)}\alpha,
\]

(70)

which (for this special case) may be integrated by solving the latter two differential equations with \(\Gamma\) replaced by substitution via the functional algebraic equation.

To specify the switching protocol, define \(g: [0, \infty) \rightarrow \mathbb{R}\) by

\[
g(s) = G(\Gamma(s), \alpha(s), U_{\text{max}}(U_{s}(s))),
\]

(71)

where \(\Gamma, \alpha, \) and \(U_{\text{max}}(U_{s})\) are determined by the dynamical system (69), and compute

\[
\frac{d\Gamma}{ds} = \frac{P_{\text{max}}}{P_0} \frac{U_{\text{max}}(U_{s})}{U_{\text{max}}(U_{s})^2} \frac{ds}{ds} - \frac{\epsilon U_{\text{max}}(U_{s})}{U_{\text{max}}(U_{s})^2}
\]

(72)

Switching occurs only at the boundary (which is \(\{(\Gamma, \alpha, U) : G(\Gamma, \alpha, U) = 0\}\)) according to the sign of \(g'\) and the size of \(\Gamma'\). There are several possibilities.

Suppose the system is in mode 1 and evolution proceeds to a point on the pressure boundary. At this point, the tangent vector \(X_1\) of the trajectory points out of the feasible region (that is \(\nabla G \cdot X_1 < 0\)) or is tangent to the boundary \((\nabla G \cdot X_1 = 0)\).

In the former case

\[
\nabla G \cdot X_1 = \frac{\Gamma U_{\text{max}}(U_{s})}{\epsilon^2} \frac{ds}{ds} - \frac{U_{\text{max}}(U_{s})}{\epsilon} \frac{dU_{\text{max}}(U_{s})}{ds} - \frac{\Gamma dU_{\text{max}}(U_{s})}{ds} < 0.
\]

(73)

In the latter case, there is a mode 2 trajectory that starts at the point with its tangent vector remaining orthogonal to the gradient of \(G\). There is a formula for the inner product of its tangent vector \(X_2\) corresponding to Eq. (73). It has the same right-hand side except that in the second term \(d\Gamma/ds\) is replaced by the rate of change of \(\Gamma\) with respect to \(s\) along the boundary. Because \(U_{\text{max}}(U_{s})\) and \(\epsilon\) are positive, \(\nabla G \cdot X_2\) would be negative if this rate of change were larger than its mode 1 value, leading to a contradiction. Thus this rate is initially smaller along the boundary and the optimal choice is to proceed with mode 2 integration along the boundary.
When the system is in mode 2, evolution proceeds along the pressure boundary until possibly a point is reached where (the mode 2) \( d\Gamma/ds \) is equal to its mode 1 value. If proceeding along the boundary in mode 2 causes \( d\Gamma/ds \) to increase (that is the temperature rise rate by mode 2 evolution is larger than allowed) and proceeding in mode 1 causes \( g \) to increase, the process must proceed in mode 1 where it will enter the feasible region.

The problematic cases are points on the pressure boundary (\( G \) vanishes) where a degeneracy occurs. In the first instance, evolution proceeds from the feasible region to a point on the pressure boundary where \( X_1 \) is tangent to this boundary. Proceeding further in mode 1 might produce a trajectory on the boundary (that is, a portion of the boundary is an invariant set for this process), the trajectory might exit the feasible region, or it might enter the interior of the feasible region. The first and third alternatives are viable for the optimal control by simply proceeding in mode 1. The second alternative requires proceeding in mode 2 on the boundary as long as \( d\Gamma/ds \) does not exceed its maximum allowed value. If this latter quantity is at its maximum at the boundary point in question and \( d\Gamma/ds \) is increasing, the process cannot continue. Likewise when evolution proceeds along the boundary and a point is reached where \( d\Gamma/ds \) is at its maximum allowed value, there are viable alternatives: proceed from this point in mode 2 when the corresponding extension of the trajectory lies in the feasible region, proceed in mode 1 in case the extension lies on the boundary, or proceed in mode 2 along the boundary when the mode 1 extension lies in the complement of the feasible region and the mode 2 value of \( d\Gamma/ds \) does not increase. Continuation of the process is not possible when the mode 1 trajectory is in the complement and \( d\Gamma/ds \) increases along the mode 2 trajectory. Unfortunately, the cases where the process would not satisfy the constraints if it were to proceed are not simply eliminated by analysis of the system. The desired result might follow from the analysis of higher-order derivatives of \( d\Gamma/ds \) and \( g \), but further degeneracies could occur as higher-order derivatives might vanish. If the undesirable cases could be eliminated the result would be (remarkably) a complete proof that the optimal control exists and a complete description of the optimal control. Numerical evidence suggests that the undesirable cases do not occur for the binder burnout problem, but this is not yet proved.

Existence and uniqueness of the optimal solution for minimum time burnout, under the further assumption that the problematic cases do not occur, would be proved should a technical result become available: The augmented dynamical system with the switching algorithm in force has a unique solution that exists until burnout. The presence of the nonlinear PDE in the dynamical process presents issues whose resolution are beyond the scope of this paper.

Under the assumption that the problematic cases do not occur, complete proofs of the existence and uniqueness of the desired time-optimal solution can be given when the PDE is replaced by the PSSA or the three-station model. Without providing all details, the prescription for obtaining the time optimal control is (with only minor modifications) the same for these approximations. In fact, the arguments are simpler because they take place in a finite-dimensional state space when taking into account that maximum pressure occurs at \( \xi = 0 \) for the PSSA. A proof of existence and uniqueness for the three-station model, for example, uses standard ODE existence theory and known results on preclusion of finite-time blowup.

The objective in switching is to use system (69) whenever possible as it produces the maximum possible temperature. Due to symmetry, recall that \( U(0,s) = 0 \). The
remaining issue is to compute the derivative of $U_{max}$. Fortunately this derivative exists and is easy to compute because this function is linear. The derivative of $U_{max}$ is $U_{max}$ (using the usual identification of the tangent space of a linear space with the linear space itself). Thus, $DU_{max}(U(0,s))U_s = U_s(0,s)$. On the boundary, the algebraic (first equation) in Eq. (71) applies. After substitution using the differential equations,

$$
\begin{align*}
\frac{\partial g}{\partial s}(s) &= \frac{P_{max}tAe^{-\gamma/\Gamma(s)}\alpha(s)}{P_0\epsilon(s)} \\
&\quad - \frac{\Gamma(s)q(\epsilon(s))\Phi'(U(0,s))U_{\xi\xi}(0,s) + \epsilon e^{-\gamma/\Gamma(s)}\alpha(s) + \frac{\epsilon_0}{T_0}U(0,s)}{\epsilon(s)}.
\end{align*}
$$

(74)

This completes the description of the process that produces the time optimal control $\Gamma$ and the shortest burnout time.

Results in this section, for simplicity, are first stated for one space-dimension models. But, the time-optimal control algorithm is independent of the number of space dimensions or the geometry of the green body. Again, the key fact is the decoupling of the ODE and PDE in the model. Burnout rate is determined by the ODE and maximized at each instant of time by the maximum allowed temperature, which is determined by constraints on the temperature rise rate and the gas pressure governed by the PDE. In fact, the inclusion of constraints on pressure gradients, stresses, and so on, as long as this decoupling remains in the model would not in principle change the time optimal control algorithm. The same framework would remain on which new constraints could be attached.

3.4.3. Numerical experiments. Numerical experiments illustrate the time-optimal control strategy discussed in the previous section. A main ingredient in algorithms suitable for computation is the ability to monitor the state at each time step in relation to the pressure boundary where mode switching might occur. Of several possible approaches, a natural choice (used here) is to monitor boundary crossings up to some tolerance. At a crossing from inside to outside the feasible region linear interpolation between the previous and current states is employed to obtain an intermediate state that is on the boundary up to the acceptable tolerance. Forward integration is maintained on the boundary until possibly the temperature rise rate along the boundary exceeds the maximum allowed at which time integration proceeds using the maximum allowed rise rate.

Figure 5 shows that for mid-range physically realistic values of maximum allowed pressure and furnace temperature rise, the PSSA and the three-station model produce time-optimal temperature protocols that agree well for practical use. At least, the latter approximations can be implemented in efficient numerical algorithms that might be used to understand basic features of an intended application prior to simulation using the full PDE model. The regions corresponding to mode 1 (linear temperature rise with $\beta = \beta_{max}$ and $P < P_{max}$) and mode 2 ($\beta < \beta_{max}$ and $P = P_{max}$) and switching between modes are evident.

An additional heuristic reason for the efficacy of the PSSA for time optimal control is apparent by inspection of the alternative form of the quality function (45). In the mode 2 regime, while the pressure is held at its maximum value, the time-derivative of pressure vanishes. This leaves the factor $(\epsilon\rho)'$, which is assumed to also vanish in the construction of the PSSA. It does not vanish in the quality function but is expected to be small. To reinforce this expectation, note that in mode 2
the temperature increases, $\rho = P/(RT)$, and $P = P_{\text{max}}$. Thus, in the expanded derivative $\epsilon'\rho > 0$ and $\epsilon\rho < 0$, which suggests a cancellation.

Figure 6 displays the results of simulated (using the three-station model) time-optimal control protocols for green body body length 0.01 m and maximum allowed pressure 200 000 Pa for a range of maximum temperature rise rates. At 0.15 K per minute the maximum allowed pressure is not reached before burnout set at the binder fraction 0.01. At 0.2 K/min, the pressure boundary is reached, but the trajectory almost immediately records temperature rise rates in excess of the allowed maximum. And, integration until burn out proceeds at this maximum rate. Maximum temperature rise is mandated at 10 K per minute until the pressure boundary is reached, integration proceeds along the boundary until the maximum allowed temperature rise rate is exceeded, and the maximum rise rate continues until burnout.

One feature of note is that mode switching for the PDE and three-station models proceeds in an obvious fashion except that PDE or ODE solvers must allow defining equations to be functional in nature: in particular the maximum value of $U$ is required in the mode 2 time-advance. This is usually of no concern in ODE solvers, but must be considered in the choice (or construction) of a PDE solver. For mode 2 computations using the PSSA, a transcendental equation (obtained by substituting...
Figure 6. Top panel depicts for the three-station model an approximation of the time-optimal temperature protocol for a green body of length 0.01 m for maximum temperature rise rates 0.015, 0.2, 0.5, 10.0 K per minute and maximum allowed gas pressure 200,000 Pa. Bottom panel depicts corresponding pressure versus temperature.

the pressure constraint into the PSSA) must be solved at each time step. A root finder that takes as its initial guess the root computed at the previous time step is viable. In the 1-d case, where we have proved the maximum pressure occurs at the center of the green body, evaluation of the state at this point suffices to compute the pressure. At the present state of knowledge, maximum pressure computation for applications for more complex geometry requires a sweep over the discretization of the entire green body. Determining the locations where maximum pressure occurs in general remains a challenging problem.

For a solid cylinder green body of height 3 cm and radius 0.5 cm, numerical experiments reported in Fig. 7 show agreement between time optimal temperature protocols computed using the full PDE model and corresponding PSSA. Also as expected, in these and other experiments, the maximum gas pressure during heating is seen to occur at the geometric center of the cylindrical green body.

4. Conclusions. Theoretical and numerical tools have been used to analyze and understand the process of binder removal from green ceramic components. The process itself has a number of complicating features not found in many transport problems in porous media: a non-linear transport term that arises from gas permeability as compared to the nearly exclusively-treated diffusional transport in other works and unsteady state behavior in both the (irreversible) reaction kinetics and the porosity, which in turn influences the gas permeability. Additionally, as binder burnout cycles are long, time optimal control affords a mechanism by which the
Figure 7. Top panel depicts a comparison of the time optimal temperature protocols for the solid cylinder of height 3 cm and radius 0.5 cm as computed using the PDE model and ten terms of the series expansion representation (29) of its corresponding PSSA for the case of maximum heating rate 10 K per minute and maximum allowed gas pressure 150,000 Pa, where the maximum is computed at the geometric center of the cylinder. Bottom panel depicts corresponding geometric center gas pressure versus temperature.

Cycle time can be minimized. As in many optimal control problems, constraints then naturally arise, which further add to the complexity.

The governing distributed parameter kinetic ODE and transport PDE have been nondimensionalized so as to obtain useful time constants for theoretical analysis, including error analysis. Two approximate methods, the PSSA and discrete model, have been used to provide further insight into the process. A quality function has been obtained which indicates the transport and kinetic properties and temperature protocols under which the PSSA is accurate. Minimum time heating cycles arise from an optimal control strategy of increasing the temperature at the highest possible rate unless a constraint on pressure in the interior of the green body is exceeded. Both the PSSA and discrete methods are accurate in the physically relevant regime and may be easier to implement in numerical computations as compared to utilizing commercial codes which do not allow easily for solving the functional PDEs that appear in the optimal control strategy.

In this work, the process of binder removal under gas permeability control has been examined, when interconnected porosity initially exists. At higher volume fractions of binder, including complete filling of the pore space such that zero porosity
exists initially, diffusion of the binder decomposition products in the remaining binder may become the controlling mass transport process. Although not treated here, this problem has been addressed (see [3] and [15], and [18] with the references therein), albeit not at the level of mathematical rigor used here. Some results reported in the present work are applicable, however, in case the kinetic ODE remains uncoupled from the diffusion-reaction PDE so that the optimal temperature protocol remains to operate at the highest decomposition rate that satisfies the relevant constraints. Effective modeling of the transition from diffusion to gas permeability control presents a grand challenge (potentially best addressed via percolation theory or cellular automata), which may entail treating these processes in parallel or in series with diffusion followed by gas permeation. Viable modeling of this transition seems to us to depend on the intended applications, a deeper understanding of the physical processes involved, and the results of future experiments. Should such models become available, their validation and predictive potential should be amenable to appropriate applications of existing mathematical tools, computational algorithms, and computer power.

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