

A reaction-diffusion-growth framework for anaerobic granule formation and stability in high-rate
wastewater reactors

by

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Abstract

High-rate anaerobic wastewater reactors rely on dense microbial granules to retain biomass and sustain elevated volumetric conversion rates. Within these aggregates, microorganisms are embedded in a porous matrix where substrate transport occurs primarily through diffusion. As a result, the substrate concentration experienced by microbial populations varies spatially within the granule, and the reaction rates observed at the reactor scale differ from the intrinsic microbial kinetics governing metabolism.

This work develops a reaction-diffusion-growth framework for analyzing microbial activity, pathway selectivity, and structural stability in granular anaerobic systems. A spherical reaction-diffusion model with Monod kinetics and external film transport was solved numerically to evaluate intragranular substrate distributions and effectiveness factors. The analysis demonstrates that diffusion limitations can bias kinetic parameters inferred from reactor measurements and modify the apparent activity and selectivity of competing metabolic pathways. Dimensionless analysis identifies the reaction-diffusion parameter and the mass-transfer Biot number as the primary variables governing transport regimes within granular biomass. Coupling the transport model with a biomass growth-detachment balance reveals stability boundaries linking granule size and hydrodynamic conditions. These results demonstrate that granular anaerobic reactors can be interpreted as transport-limited reacting particles in which apparent microbial kinetics, pathway selectivity, and structural stability emerge from the coupled reaction-diffusion-growth system governing substrate transport and microbial metabolism within the aggregate.

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1 Introduction

1.1 High-Rate Anaerobic Wastewater Reactors and Granular Biomass

Anaerobic wastewater reactors are widely used in industrial and municipal treatment systems because they enable efficient removal of organic contaminants while simultaneously producing renewable biogas. Their ability to operate at high loading rates with low energy input makes them a key technology for sustainable wastewater treatment and resource recovery in carbon-neutral process systems. High-rate anaerobic reactors rely on dense microbial aggregates to sustain elevated volumetric conversion rates under continuous flow conditions[1–3]. The fundamental engineering question is the relationship between intrinsic microbial growth kinetics with these aggregates and the apparent reaction rates measured at the reactor scale. Resolution of this question requires formulation from first principles of mass conservation applied to a representative granular control volume, with explicit linkage between transport resistance and observed behavior. To better understand this, the definition of the granular aggregate as a reacting porous medium subject to coupled transport and growth processes is required, with supporting evidence drawn from the granulation theory, aggregate microstructure studies, diffusion measurements and reactor scale modeling literature[1–11].

Consider a single anaerobic granule of radius R suspended within a bulk liquid phase. The granule is modeled as a spherical porous domain containing immobilized microbial biomass distributed throughout the internal volume, with radial coordinate r measured from the granule center [1,3,6]. The control volume is defined as a differential spherical shell of thickness dr at position r , with substrate transport occurring by diffusion through the aqueous phase within the granule matrix [6]. Biomass is treated as immobilized relative to the matrix over the substrate diffusion time scale, with structural evolution occurring over longer time scales associated with growth, detachment, and selection pressure [1,3,6]. This geometric and time scale separation motivates a reaction-diffusion-growth formulation that preserves conservation structure while enabling quantitative interpretation of apparent kinetics in granular systems [6,12].

Granulation theories and unifying conceptual reviews identify selection pressure, shear, extracellular polymeric substances (EPS), and cation effects as drivers of aggregate compaction

and retention [1,3,4,13]. Granule size distribution, settling behavior, and stability can be defined as outcomes of coupled growth and removal processes rather than purely biological descriptors [1,3,14]. Calcification and inorganic deposition introduce additional structural modification pathways that affect pore space, diffusional accessibility, and biomass activity in calcium rich wastewaters [15,16]. These mechanisms motivate treatment of biomass as a spatially distributed reacting phase whose effective activity depends on transport accessibility, with stability determined by the balance between internal growth and surface loss [1,6,17–19].

1.2 Granule Formation & Stability

Biomass within the granule is treated as retained within the porous matrix, with negligible internal convection or diffusion over the substrate diffusion time scale. This interior immobilization assumption is a closure that becomes reasonable when biomass structural rearrangement is slow relative to substrate transport and local kinetic response [1,20]. The local biomass balance is then written as growth minus decay, with local growth coupled to local substrate concentration through Monod kinetics[20,21]. The local biomass balance is shown in equation 1 where b represents endogenous decay [20,21].

$$\frac{\partial X}{\partial t} = \mu(S)X - bX \quad [\text{eqn. 1}]$$

Under conditions of sustained reactor operation with stable granule size, net biomass production within the granule must be balanced by biomass loss through surface detachment and erosion [17,18]. This requirement links growth kinetics and transport limitation to stability through a boundary loss mechanism influenced by hydrodynamics and selection pressure. Again, consider R defined in section 1.1 containing immobilized biomass distributed within a porous matrix. Biomass within the granule is treated as immobilized in the matrix over the substrate diffusion time scale. This assumption leads to a situation where any effective biomass loss is represented as a boundary flux at the granule surface rather than a volumetric transport term [6]. Biomass conservation with the granule is expressed in equation 2 where $\mu S(X)$ represents local growth, bX represents endogenous decay, and J_X represents net biomass transport.

$$\frac{\partial X}{\partial t} = \mu(S)X - bX - \nabla \cdot j_X \quad [\text{eqn. 2}]$$

The interior biomass transport term is set to zero, which is a constitutive closure that enforces immobilized biomass in the interior domain. This closure is reasonable when biomass diffusion and internal convective migration are negligible relative to growth and decay. Any residual redistribution effects will be treated later through bounded sensitivity on an effective biomass field $X(r)$ rather than through an internal biomass flux model [6]. Granule radius remains constant only if net biomass production with the volume equals biomass loss at the surface. The total biomass (M) within the granule is represented in equation 3.

$$M = \int_0^R X(r) 4\pi r^2 dr \quad [\text{eqn. 3}]$$

The time rate of change of total biomass is then shown in equation 4 where J_{det} is the biomass detachment flux at the surface.

$$M = \int_0^R (\mu(S)X - bX) 4\pi r^2 dr - J_{det} 4\pi R^2 \quad [\text{eqn. 4}]$$

The surface loss term is a boundary closure that represents net erosion, detachment, and fragmentation effects as a single outward flux at $r = R$. This closure is reasonable when detachment is dominated by surface processes and the interior biomass remains retained. The detachment flux coefficient introduced below will be treated later as a bounded parameter informed by hydrodynamic regime and reactor operating conditions [1,11,18]. A steady granule implies that equation 5 is true.

$$\frac{dM}{dt} = 0 \quad [\text{eqn. 5}]$$

Equation 5 implies equation 6.

$$\int_0^R (\mu(S)X - bX) 4\pi r^2 dr = J_{det} 4\pi R^2 \quad [\text{eqn. 6}]$$

The surface detachment is then driven by hydrodynamic forcing at the granule boundary. We can impose a linear constitutive closure relating detachment flux to hydrodynamic shear stress in equation 7.

$$J_{det} = k_d \tau \quad [\text{eqn. 7}]$$

This expression is a constitutive closure that collapses complex surface mechanisms into a linear proportionality between detachment flux and shear stress. This closure is reasonable when the surface removal rate increases monotonically with applied shear and when detachment remains controlled by boundary stresses rather than by interior failure. The proportionality constant k_d will be treated later as a tunable variable within bounded ranges that preserve physical units and stability regimes inferred from shear dependent granulation studies [17,18,22,23]. Steady granule size implies that volumetric biomass production must be balanced by surface detachment flux, consistent with multiscale granulation models in which growth and detachment reach dynamic equilibrium [23]. Shear stress depends on flow regime and relative velocity between fluid and granule surface [22]. A scaling pathway is introduced to connect hydrodynamic velocity to shear stress without asserting a universal quality. The shear stress can then be represented in equation 8 where C_τ is an order one coefficient that depends on flow regime and U is a characteristic relative velocity consistent with classical transport scaling relations [22].

$$\tau \approx C_\tau \rho U^2 \quad [\text{eqn. 8}]$$

The velocity U may be taken as a superficial up flow velocity scale or a local slip velocity scale depending on the reactor configuration. This scaling is reasonable for inertial dominated boundary forcing and becomes a bounded approximation under laminar or transitional regimes. The coefficient C_τ will be treated later as bounded by regime dependent estimates derived from hydrodynamic characterization and CFD evidence rather than as an empirical fit [24–27].

Biomass growth within the interior depends on substrate availability. The substrate concentration profile is governed by the steady state diffusion reaction equation derived later in this introduction. Substrate penetration at depth (δ_a) defines the region within which substrate concentration remains sufficient to sustain net growth. Outside this region substrate concentration falls below the kinetic range required for positive $\mu(S) - B$, which results in a metabolically inactive core. This active zone concept is consistent with observed heterogeneous microbial activity in aggregates and measured microenvironment gradients [6,28,29]. Define $r = R - \delta_a$ as the boundary between active and inactive biomass. Only the region $r < R - \delta_a$, R contributes significantly to net biomass production. Then the total net growth term can be reduced to equation 9.

$$\int_{R-\delta_a}^R (\mu(S)X - bX)4\pi r^2 dr \quad [\text{eqn. 9}]$$

This reduction is an asymptotic closure that treats growth as negligible in the diffusion limited core relative to the diffusion penetrated shell. This closure is reasonable when substrate concentration in the core remains low due to diffusion resistance and consumption near surface. The active zone boundary will be determined later though a numerical solution of the coupled diffusion reaction problem rather than empirical fitting [6,21]. δ_a is determined by the balance between diffusion and reaction. For first order or locally linearized mono kinetics, the penetration depth scaling can be expressed as equation 10 where k_{eff} represents an effective first order uptake rate obtained by local linearization of the volumetric consumption term around an operating substrate range and local biomass level [21,22].

$$\delta_a \approx \sqrt{\frac{D_e}{k_{eff}}} \quad [\text{eqn. 10}]$$

This scaling is an asymptotic interpretation used to classify regimes and guide sensitivity. The full concentration profile and active zone thickness will be computed later from the governing boundary value problem, with D_e bounded using published diffusional property measurements and k_{eff} bounded using intrinsic kinetics and biomass ranges derived from the reference material [5,6,12,19,30].

Equation 11 comes from substituting the reduced active region into the steady state biomass balance.

$$\int_{R-\delta_a}^R (\mu(S)X - bX)4\pi r^2 dr = k_d \tau 4\pi R^2 \quad [\text{eqn. 11}]$$

This relation demonstrates that granule radius R satisfies an implicit constraint linking intrinsic kinetic parameters μ_{max} , K_s , Y , D_e , b , and shear dependent surface loss through $k_d C_\tau \rho U^2$. For small granules with $R \ll \delta_a$, most of the volume remains diffusion penetrated and net growth can exceed surface loss[6,17,20]. For large granules with $R \gg \delta_a$, inactive core volume increases and surface loss can exceed net growth. A stable radius emerges when volumetric growth integrated over the diffusion penetrated shell equals hydrodynamically forced surface loss. This motivates stability interpretation in which granule size and size distribution reflect a

constrained transport reaction detachment equilibrium rather than descriptive biology [1,2]. Granule size distribution in high-rate anaerobic reactors is therefore a transport-reaction-detachment equilibrium problem [11,23,31].

1.3 Limitations of Descriptive Granulation Studies

The reaction term is expressed in intrinsic kinetic form through a growth associated substrate utilization rate. Equation 12 and 13 are for a single limiting substrate with Monod growth where μ_{max} , is the maximum specific growth rate, K_s is half saturation constant, Y is the yield coefficient and $X(r)$ is the local biomass concentration [20,21].

$$r_s(S, X) = -\frac{1}{Y}\mu(S)X \quad [\text{eqn. 12}]$$

$$\mu(S) = \mu_{max} \frac{S}{K_s + S} \quad [\text{eqn. 13}]$$

This intrinsic expression represents well mixed kinetics at the microscale. This representation becomes inconsistent with reactor scale apparent kinetics when spatial gradients exist inside aggregates, which is experimentally demonstrated by parameter estimation bias under diffusion limitation and by trophic group dependence on interspecies transfer constraints [12,32]. These inconsistencies motivate explicit separation between intrinsic kinetics and observed rates through transport resolved formulation rather than direct assignment of intrinsic parameters to reactor scale balances [6,12].

Apparent kinetic parameters inferred from bulk measurements therefore embed transport limitation effects, which is supported by evidence that mass transfer limitation biases hydrogen half saturation constant estimation and influences trophic group contributions during volatile fatty acid (VFA) degradation [5,12,32]. Temperature dependent difference between dispersed and granular sludge conversion further support diffusion length effects on apparent rate [5]. Long chain fatty acid adsorption and inhibition introduce additional constraints that alter local substrate field and reaction accessibility, reinforcing the need to treat apparent kinetics as transport conditioned rather than purely intrinsic [5,7,33]. Calcification and inorganic deposition introduce additional structural modification pathways that affect pore space, diffusional accessibility, and biomass

activity in calcium rich wastewaters [15,16]. These limitations motivate formal treatment of aggregates as transport limited reacting systems rather than as homogenous biomass compartments.

Structured anaerobic digestion models provide reactor scale state variable frameworks that require calibration and modification for substrate specificity and hydraulics representation, which motivates explicit mapping between granule scale transport limitations and reactor scale lumped kinetics [8–10,20,21,34]. Multiple industrial modeling studies demonstrate that model performance depends on hydraulic representation and parameter sensitivity, reinforcing the need for physically constrained rate interpretation rather than unconstrained fitting [9,10]. Tracer based hydrodynamic studies and RTD analyses in anaerobic systems demonstrate the non-ideal flow influences the local transport environment experienced by granules [24,26,27]. CFD studies support spatial variation in shear and mixing, reinforcing that boundary conditions are reactor dependent rather than material dependent. These considerations motivate inclusion of hydrodynamic context as a part of the governing framework instead of an auxiliary observation.

1.4 Granular Biomass as a Transport Limited Reacting System

Mass conservation for a limited substrate is written on the differential spherical shell described in section 1.1 as an accumulation equal diffusive inflow minus the diffusive outflow minus consumption by reaction. The diffusive flux is represented by Fick's law, with an effective diffusivity D_e that accounts for tortuosity, porosity, and restricted transport within the granule matrix as done with porous media [6,20–22]. Under steady state conditions for the substrate field, the accumulation term is treated as zero and the balance reduces to a second order ordinary differential equation in r . The spherical symmetry condition imposes that $dS/dr = 0$ at $r = 0$, which enforces a finite flux at the granule center [6,20,21]. The steady state intragranular substrate can be expressed as equation 14 where $S(r)$ is the local substrate concentration and $r_s(S, X)$ is the volumetric consumption rate [6].

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 D_e \frac{dS}{dr} \right) - r_s(S, X) = 0 \quad [\text{eqn. 14}]$$

The diffusive term establishes the internal transport constraint. The reactor term establishes consumption coupled to biomass growth kinetics. The coupled structure requires boundary conditions that represent external transport from bulk liquid to the granule surface [6,21].

As stated in section 1.1, the granule exists in a flowing bulk liquid which has a substrate concentration S_b . Transport from bulk liquid to the granule surface occurs through an external concentration boundary layer of thickness δ . The boundary condition is formulated by equating the diffusive flux within the granule at $r = R$ to an external film mass transfer flux. The steady state intragranular substrate balance is then represented in equation 15 where $S_s = S(r)$ and k_L is the external mass transfer coefficient.

$$J = k_L(S_b - S_s) \quad [\text{eqn. 15}]$$

The flux continuity at the surface then gives equation 16.

$$-D_e \left. \frac{dS}{dr} \right|_{r=R} = k_L(S_b - S_s) \quad [\text{eqn. 16}]$$

The coupling of equation 15 and 16 establishes that the apparent rate depends on both internal diffusion and external film resistance, even when intrinsic kinetics are fixed. The external transport coefficient is linked to hydrodynamics through dimensionless correlations like the Sherwood number (Sh) which is displayed in equation 17, where $d_p = 2R$ and D_b is the bulk diffusivity [6,22].

$$Sh = \frac{k_L d_p}{D_b} \quad [\text{eqn. 17}]$$

In the context of hydrodynamics, the Sherwood number is determined through Reynolds and Schmidt dependence. Reactor scale hydrodynamics, non-ideal flow, and residence time distribution influence the local transport environment experienced by granules, as demonstrated by tracer based studies in anaerobic systems [24,27]. As stated prior, CFD studies on anaerobic reactor systems reinforce that external boundary conditions are reactor dependent [25]. Flow pattern condition and influent equalization approaches influence the hydrodynamic environment that sets the boundary layer thickness and therefore the surface concentration driving intragranular diffusion [19,34]. These considerations motivate the inclusion of external transport closure as part of the granule scale governing framework, rather than a post hoc correction.

Standard reactor design equations assume spatially uniform substrate concentration within the reacting volume [21]. Equation 18 displays a typical design equation for a continuous stirred tank reactor (CSTR) at steady state where r_{obs} is evaluated at the bulk concentration S_{out} .

$$F(S_{in} - S_{out}) = Vr_{obs} \quad [\text{eqn. 18}]$$

Equation 19 displays represents a plug flow model.

$$\frac{dS}{d\tau} = r_{obs} \quad [\text{eqn. 19}]$$

These equations are consistent only if r_{obs} equals an intrinsic kinetic expression evaluated at uniform concentration. Granular systems violate this assumption because substrate concentrations varies radially within each aggregate, and because only part of the biomass may be effectively utilized under diffusion limitation [6,20]. The reactor scale balance therefore incorporates an apparent rate that is lower than the intrinsic rate predicted from bulk concentration [6,12].

The actual overall substrate consumption rate of a granule is obtained by integrating the local volumetric rate over the granule volume as seen in equation 20.

$$R_{actual} = \int_0^R r_s(S(r), X(r)) 4\pi r^2 \quad [\text{eqn. 20}]$$

A reference intrinsic rate is defined as the rate that would occur if the entire granule volume were exposed to a uniform concentration equal to the surface concentration S_s as demonstrated in equation 21 with an effectiveness factor as shown in equation 22.

$$R_{intrinsic} = r_s(S_s, X_{avg}) \frac{4}{3} \pi R^3 \quad [\text{eqn. 21}]$$

$$\eta = \frac{R_{actual}}{R_{intrinsic}} \quad [\text{eqn. 22}]$$

The effectiveness factor emerges directly from conservation of mass applied to a porous reacting particle with finite diffusivity [6,20,30,35]. The effectiveness factor provides the required modification to classical reactor design equations through equation 23.

$$r_{obs} = \eta r_{intrinsic} \quad [\text{eqn. 23}]$$

This modification is a necessary consequence of spatial gradients and transport resistance within the granular biomass.

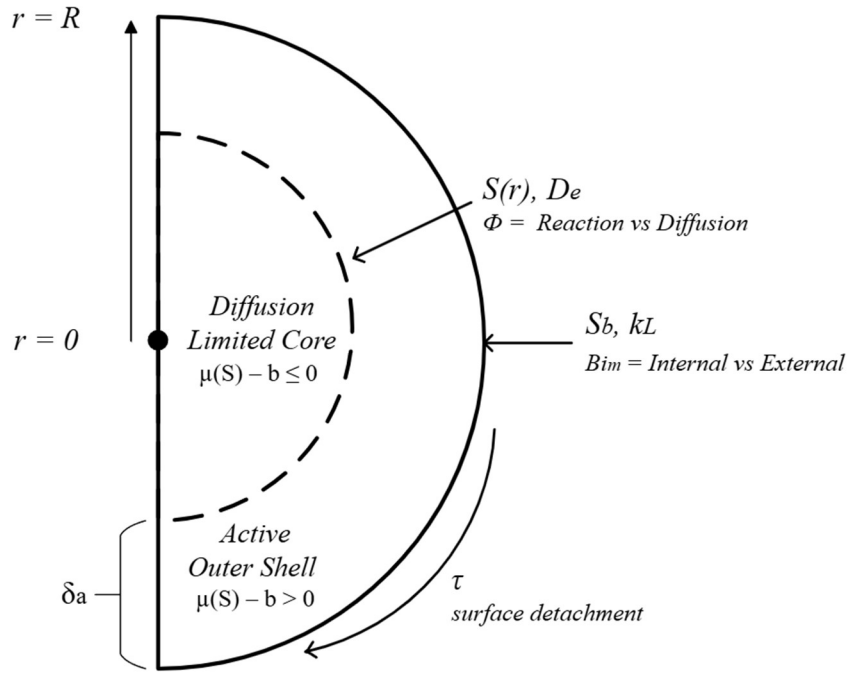
The known elements include intrinsic growth kinetics form and its coupling to substrate utilization through yield relationships [21,34]. Additionally, other known elements include the boundary condition structure which links external film transport to intragranular diffusion through flux continuity and dimensionless correlations like the Sherwood number [6,12,20,22,30]. Unknown elements include effective diffusivity within granular biomass, radial substrate concentration profiles, distribution of active biomass within the aggregate, and the magnitude of effectiveness factor under operating conditions relevant to high-rate anaerobic reactors [6,19]. Additional unknown elements include the degree to which trophic group structure, syntrophic transfer limitations, pH microenvironments, long chain fatty acid adsorption, and inorganic deposition alter effective kinetics and stability [7,12,15,16,32]. The governing engineering problem is the solution of the coupled reaction-diffusion-growth system within a spherical aggregate subject to external mass transfer resistance[6,34].

The goal of this study is to determine how intrinsic microbial kinetics are transformed into apparent reactor scale rate expressions as functions of granule radius, effective diffusivity, external transport coefficients, and kinetic parameters. The same framework defines how kinetic parameter estimation from bulk measurements become biased under transport limitations. Additionally, the framework supports interpretation of trophic group contributions in VFA degradation as transport coupled rather than purely concentration driven. Structured anaerobic digestion models provide reactor scale state variable frameworks that require calibration and modification for substrate specificity and hydraulics representation, which motivates explicit mapping between granule scale transport limitations and reactor scaled lumped kinetics [9,10,20,21,23,29,34,36–38]. Multiple industrial modeling studies demonstrate that model performance is dependent on hydraulic representations and parameter sensitivity, reinforcing the need for physically constrained rate interpretations rather than unconstrained fitting as previously discussed [9–11,31,34,36,39,40].

This report uses published experimental and modeling studies as data sources for parameter ranges and boundary condition definitions that will be used for numerical evaluations. Effective diffusivity values, micro-profile gradients, adsorption parameters, hydrodynamic descriptors and base assumptions will be extracted from published works to bound inputs for the granule scale model. Rate parameters and inhibition forms reported with modified structured models will be used to establish defensible parameter bounds for intrinsic kinetics and sensitivity analyses.

Granule size distribution and structural descriptors will be used to select representative radii for regime evaluation and stability interpretation. Granular anaerobic reactors can therefore be interpreted as transport-limited reacting particles in which apparent kinetics, pathway selectivity, and structural stability emerge from the coupled reaction-diffusion-growth system. The physical interpretation of the coupled reaction-diffusion-growth framework is summarized schematically in Figure 1.1.

Figure 1-1 is a schematic of a spherical anaerobic granule as a transport-limited reacting particle. External mass transfer (k_L , S_b) and internal diffusion (D_e) establish a penetration depth (δ_a) separating an active outer shell ($\mu(S) - b > 0$) from a diffusion-limited core ($\mu(S) - b \leq 0$). Internal and external transport effects are characterized by Φ and Bim , while shear (τ) drives surface detachment [6,12,23]



The remainder of this report builds directly on this framework. Chapter 2 distinguishes intrinsic microbial kinetics from apparent reaction rates in granular systems. Chapter 3 examines how transport limitations influence reaction network behavior and pathway selectivity. Chapter 4 presents the coupled reaction-diffusion formulation and corresponding transport regime maps. Chapter 5 incorporates microbial growth and hydrodynamic detachment to evaluate granule stability. Chapter 6 summarizes the key findings and discusses their implications for reactor operation and design.

2 Intrinsic Microbial Kinetics & Apparent Reaction Rates in Granular Systems

2.1 Intrinsic Kinetic Descriptions for Anaerobic Microbial Consortia

Anaerobic wastewater treatment relies on microbial consortia that convert organic substrates into methane and carbon dioxide through a sequence of metabolically coupled biochemical transformations. Although the microbial ecology of anaerobic digestion involves multiple interacting populations, the aggregate metabolic activity of these communities is commonly represented using intrinsic kinetic relationships that link substrate availability to microbial growth and substrate consumption rates. The most widely applied representation is the Monod growth formulation, which relates the microbial growth rate to the concentration of a limiting substrate [21].

The intrinsic microbial growth rate is expressed in equation 24

$$\mu(S) = \mu_{\max} \frac{S}{K_s + S} \quad [\text{eqn. 24}]$$

which corresponds to the intrinsic kinetic expression derived in Appendix A (Eq. A.12). In this formulation, $\mu_{\max}$ represents the maximum specific growth rate and K_s represents the half-saturation constant. This equation describes the biochemical capability of the microbial population under conditions where substrate concentration is spatially uniform. When substrate concentrations greatly exceed K_s , the growth rate approaches the maximum value $\mu_{\max}$, whereas at low substrate concentrations the growth rate becomes approximately proportional to substrate availability. This formulation therefore represents the intrinsic kinetic behavior of microbial metabolism independent of transport constraints [21].

In suspended microbial systems, substrate concentrations surrounding individual cells remain relatively uniform due to mixing, and intrinsic kinetic expressions can therefore be evaluated using bulk substrate concentrations. Granular anaerobic systems differ fundamentally because biomass is organized into dense microbial aggregates that can reach millimeter-scale diameters. Within these aggregates, microorganisms are embedded in a porous matrix through

which substrates must diffuse before reaching metabolically active cells. Consequently, the substrate concentration experienced by microorganisms becomes a spatially varying field rather than a uniform value equal to the bulk concentration [6,20].

Experimental investigations of microbial aggregates demonstrate that significant concentration gradients can develop within granular biomass. Microelectrode measurements and substrate micro-profile studies have shown that metabolic activity within methanogenic aggregates is spatially heterogeneous, with higher activity near the aggregate surface and reduced activity within the interior regions of the granule [28,29]. Diffusion measurements further indicate that the effective diffusivity within granular sludge is lower than that of the surrounding liquid phase due to tortuosity and structural resistance within the biomass matrix [19]. These observations support the interpretation of granular biomass as a porous reacting medium in which transport processes control the accessibility of substrate to microbial cells.

Microscopic investigations of anaerobic aggregates further reveal that the internal architecture of granular sludge often contains distinct microbial clusters and layers associated with different metabolic activities. Observations of aggregates grown in expanded granular sludge bed reactors show spatial segregation of microbial populations, including zones dominated by acetoclastic methanogens and regions containing syntrophic bacteria and hydrogenotrophic methanogens, indicating that microbial organization within granules reflects transport-limited growth conditions within the aggregate structure [41].

To represent this behavior mechanistically, the microbial aggregate is modeled as a spherical porous particle in which substrate transport occurs by diffusion while microbial consumption occurs throughout the biomass matrix. The spatial substrate distribution within the granule is governed by the steady reaction–diffusion equation. For the present model, the governing equation is given in equation 25, with the full derivation in Appendix A.

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 D_e \frac{dS}{dr} \right) - \frac{\mu_{\max} X_0}{Y} \frac{S}{K_s + S} = 0 \quad [\text{eqn. 25}]$$

where D_e represents the effective intragranular diffusivity, X_0 represents the biomass concentration within the aggregate, and Y represents the biomass yield coefficient. This equation expresses the balance between diffusive substrate transport and microbial consumption within the porous biomass matrix. The full derivation of this transport–reaction formulation is provided in

Appendix A.

Two boundary conditions define the solution of this reaction–diffusion system. At the center of the spherical granule, symmetry requires that the radial substrate gradient vanish, which corresponds to the symmetry condition given in equation 26, with the full derivation provided in Appendix A.

$$\frac{dS}{dr} \big|_{r=0} = 0 \quad [\text{eqn. 26}]$$

At the granule surface, continuity of flux between the external liquid phase and the granule interior produces the external mass-transfer boundary condition which corresponds to the surface transport condition given in equation 27, with the full derivation provided in Appendix A.

$$-D_e \frac{dS}{dr} \big|_{r=R} = k_L (S_b - S_s) \quad [\text{eqn. 27}]$$

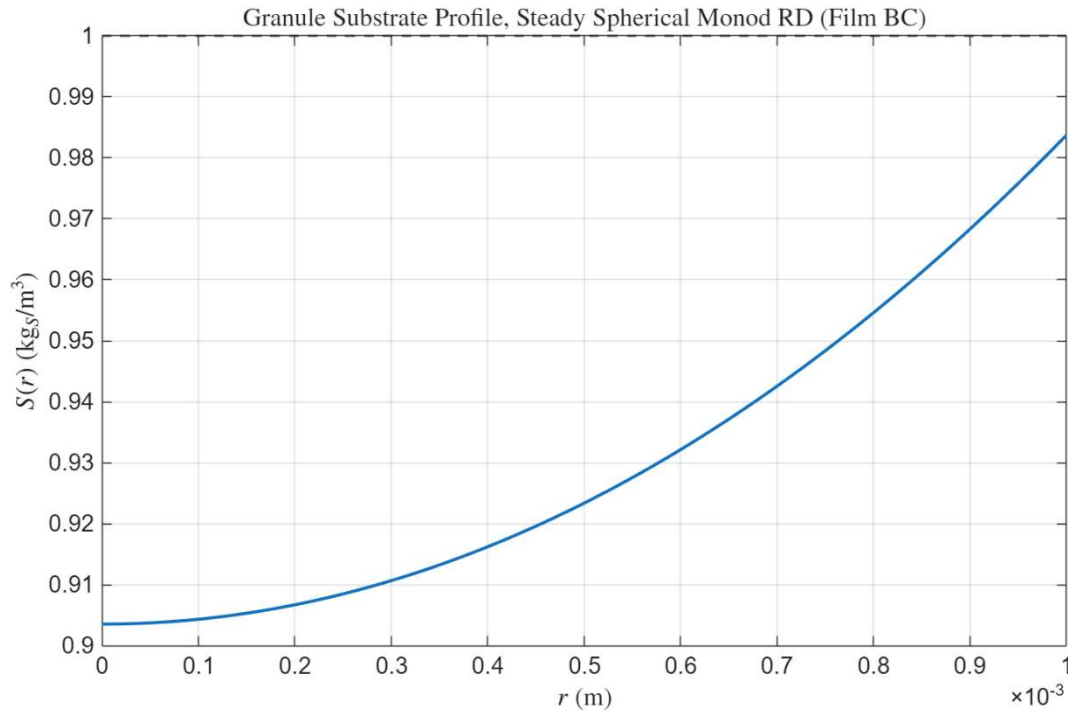
This boundary condition establishes the coupling between reactor hydrodynamics and intragranular transport behavior by linking external mass transfer to internal diffusion within the biomass [6,22].

The nonlinear boundary-value problem defined by these equations determines the substrate concentration field within the microbial aggregate. The steady substrate distribution used in this work was obtained by numerically solving the governing transport–reaction equations described in Appendix A using the Newton-iteration solver presented in Appendix B.

Figure 2-1 illustrates the computed steady-state substrate concentration profile within a representative anaerobic granule obtained from the numerical solution of the reaction–diffusion model. The radial coordinate represents the distance from the center of the aggregate, while the concentration curve represents the local substrate concentration experienced by the microbial population. The monotonic decrease in substrate concentration from the granule surface toward the interior reflects the competition between diffusive transport and microbial consumption within the biomass matrix. As substrate is consumed in the outer layers of the aggregate, diffusion must replenish substrate from the bulk liquid, producing a gradient that confines active metabolism primarily to the outer regions of the granule. This behavior arises because substrate must diffuse through the biomass matrix to replenish the substrate consumed by microbial metabolism. Even

under moderate reaction rates, the balance between diffusion and microbial consumption produces measurable concentration gradients within the aggregate.

Figure 2-1 Granule substrate profile, steady spherical Monod reaction–diffusion with external film boundary condition.



The presence of these gradients has important implications for interpreting reactor behavior. Microorganisms located near the granule surface experience substrate concentrations close to the bulk liquid concentration and therefore operate near intrinsic kinetic conditions. In contrast, microorganisms located deeper within the granule encounter progressively lower substrate concentrations as diffusion resistance increases. As a result, microbial activity becomes spatially heterogeneous within the aggregate, with metabolic activity concentrated near the outer regions of the biomass.

The intrinsic kinetic formulation therefore represents only the biochemical potential of the microbial community. The effective reaction behavior of granular biomass emerges from the interaction between intrinsic microbial kinetics and the transport processes that govern substrate accessibility within the aggregate. Subsequent sections examine how these transport processes

transform intrinsic microbial kinetics into the apparent reaction rates observed at the reactor scale in granular anaerobic systems.

2.2 Apparent Reaction Rates in Granular Biomass

The intrinsic microbial kinetic formulation introduced in Section 2.1 describes the biochemical capability of the microbial community as a function of the local substrate concentration. In granular sludge systems, however, microorganisms are embedded within dense spherical aggregates where substrate transport occurs primarily through molecular diffusion within the porous microbial matrix. As a result, the substrate concentration experienced by the microbial population varies spatially within the granule. This spatial variation in substrate availability causes the effective rate of substrate conversion to differ from the intrinsic kinetic rate evaluated using bulk reactor concentrations [6], [20].

The relationship between intrinsic microbial kinetics and the effective substrate utilization rate of the aggregate can be established by integrating the local reaction rate over the granule volume. The total substrate consumption rate of the granule is defined in equation 28, which corresponds to the volumetric integration of the local reaction rate given in Appendix A.

$$R_{obs} = \int_0^R r_S(S(r)) 4\pi r^2 dr \quad [\text{eqn. 28}]$$

This expression represents the net substrate consumption rate produced by the entire microbial aggregate and therefore provides the physically consistent definition of the observed reaction rate for granular biomass. The derivation of this relation follows directly from conservation of mass applied to the spherical control volume used in the reaction–diffusion formulation [6], [20].

For comparison, a reference intrinsic rate may be defined as the rate that would occur if the entire granule were exposed to a uniform substrate concentration equal to the surface concentration S_s . In this hypothetical case, the reaction rate is expressed in equation 29, which corresponds to the intrinsic reaction rate formulation shown in Appendix A.

$$R_{intrinsic} = r_S(S_s, X_{avg}) \frac{4}{3} \pi R^3 \quad [\text{eqn. 29}]$$

This expression represents the substrate conversion rate that would occur in the absence of internal diffusion limitations. The difference between the intrinsic rate and the observed rate therefore quantifies the influence of transport limitations within the aggregate.

A convenient measure of this transport effect is the effectiveness factor is shown in equation 30, which corresponds to the definition derived in Appendix A.

$$\eta = \frac{R_{obs}}{R_{intrinsic}} \quad [\text{eqn. 30}]$$

The effectiveness factor represents the fraction of the intrinsic reaction rate that is realized within the aggregate under the influence of diffusion resistance. Values of $\eta \approx 1$ correspond to kinetically controlled behavior in which substrate concentrations remain nearly uniform throughout the granule. As diffusion limitations increase, substrate penetration into the aggregate interior becomes restricted and the effectiveness factor decreases as a smaller fraction of the biomass remains metabolically active [20,30].

Evaluation of the apparent reaction rate therefore requires knowledge of the spatial substrate concentration profile within the granule. The steady-state concentration distribution used in this work was obtained by solving the nonlinear reaction–diffusion boundary-value problem derived in Appendix A (Eqs. A.5–A.7) using the Newton-based finite-difference solver described in Appendix B. The solver iteratively updates the substrate concentration field until the residual of the discretized governing equations satisfies the specified convergence tolerance.

Figure 2-2 Newton convergence history for steady spherical Monod reaction-diffusion solution (infinity norm of residual versus Newton iteration).

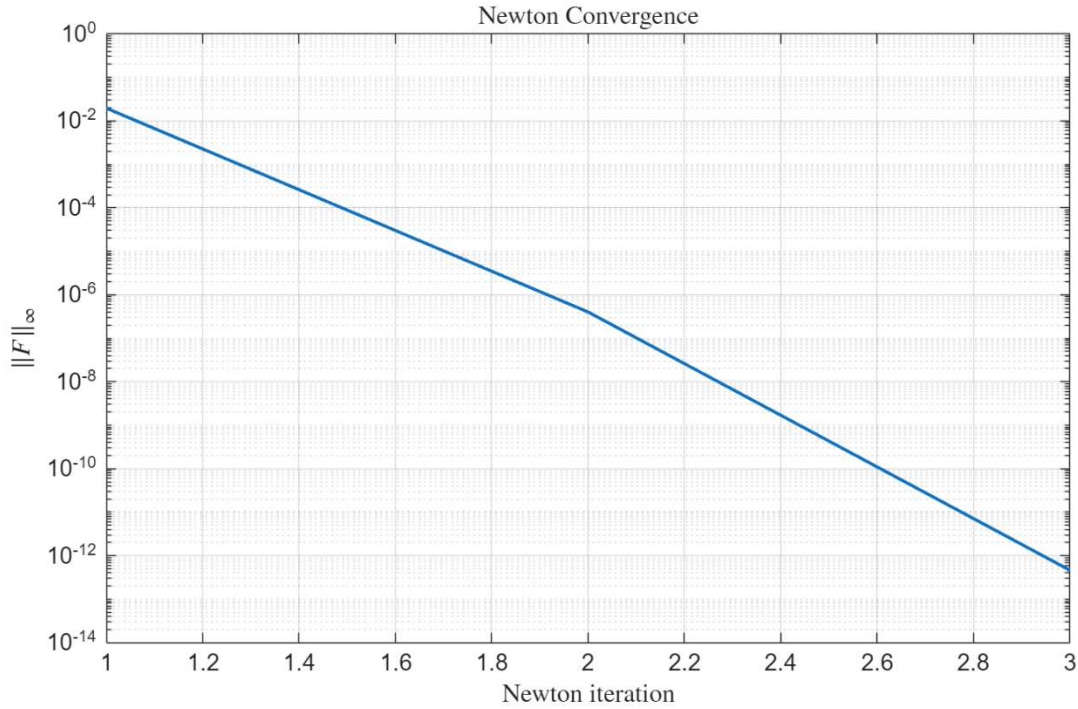


Figure 2-2 presents the convergence history of the numerical solution procedure used to compute the steady reaction–diffusion profile within the granule. The figure shows the infinity norm of the nonlinear residual as a function of Newton iteration number. The residual decreases rapidly over successive iterations, demonstrating stable convergence of the Newton solver for the nonlinear transport–reaction system. Once the solution converges, the resulting substrate concentration field is used to compute the volumetric substrate consumption rate R_{obs} through numerical integration of the reaction term across the radial domain.

The distinction between intrinsic and apparent kinetics is critical for interpreting reactor-scale measurements in granular anaerobic systems. Reactor-scale observations typically measure substrate concentrations and reaction rates in the bulk liquid phase, where the internal substrate distribution within microbial aggregates is not directly observable. When diffusion limitations exist, the apparent reaction rate inferred from bulk measurements reflects the combined influence of microbial metabolism and transport resistance within the biomass.

This transport-conditioning of reaction rates has been observed experimentally in microbial aggregate systems, where diffusion limitations can significantly alter the effective kinetic

parameters inferred from reactor-scale data [6,12]. For example, studies of hydrogen uptake kinetics in methanogenic consortia have demonstrated that diffusion resistance within microbial aggregates can bias the apparent half-saturation constant estimated from experimental measurements[12]. Similar transport effects have been reported for volatile fatty acid conversion in granular sludge systems, where differences between dispersed and aggregated biomass reveal the influence of diffusion length scales on substrate utilization rates [30].

The framework introduced in this section therefore establishes how intrinsic microbial kinetics are transformed into the apparent reaction rates observed in granular anaerobic systems. By integrating the local reaction rate across the granule volume and accounting for spatial concentration gradients produced by diffusion, the apparent reaction rate formulation provides the connection between microscale microbial metabolism and reactor-scale performance. In the following section, this framework is used to examine how transport limitations influence the kinetic parameters obtained from regression of Monod-type models against reactor-scale observations.

2.3 Distinguishing Kinetic Limitation from Transport Limitation

The framework developed in Sections 2.1 and 2.2 demonstrates that the reaction rate observed for granular biomass represents a spatially averaged quantity determined by the coupled effects of intrinsic microbial kinetics and substrate transport within the aggregate. In practice, however, reactor-scale measurements are commonly interpreted using Monod-type kinetic models evaluated at the bulk substrate concentration. This raises an important question for the interpretation of experimental data in granular systems: under what conditions do fitted kinetic parameters represent intrinsic microbial properties, and when are they influenced by transport limitations within the biomass?

To address this question, the reaction–diffusion model derived in Appendix A was used to compute the apparent growth behavior of a spherical microbial aggregate across a range of bulk substrate concentrations. For each bulk concentration S_b , the steady-state substrate distribution $S(r)$ was obtained by solving the reaction–diffusion boundary-value problem defined in Appendix A (Eqs. A.5–A.7). The resulting concentration field was then used to evaluate the observed substrate uptake rate R_{obs} from the volumetric reaction integral defined in Appendix A (Eq. A.6).

The apparent specific growth rate was subsequently determined using the biomass-normalized rate definition derived in Appendix A (Eq. A.10), which relates the observed substrate uptake rate to the effective microbial growth rate.

The relationship between bulk substrate concentration and the apparent growth rate obtained from this procedure is shown in Figure 2-3. The discrete data points represent values obtained from the reaction–diffusion simulations, while the continuous curve represents a nonlinear regression of the simulated data to the Monod form equation 30, which corresponds to the regression formulation described in Appendix B.

$$\mu_{app}(S_b) = \mu_{\max,fit} \frac{S_b}{K_{s,fit} + S_b} \quad [\text{eqn. 30}]$$

Although the apparent reaction rate follows a Monod-type relationship with respect to bulk substrate concentration, the fitted parameters obtained from regression do not necessarily correspond to the intrinsic microbial kinetic constants.

Figure 2-3 Monod regression fit to apparent specific growth rate $\mu_{app}(S_b)$ at $k_L = 1.0 \times 10^{-5}$ m/s.

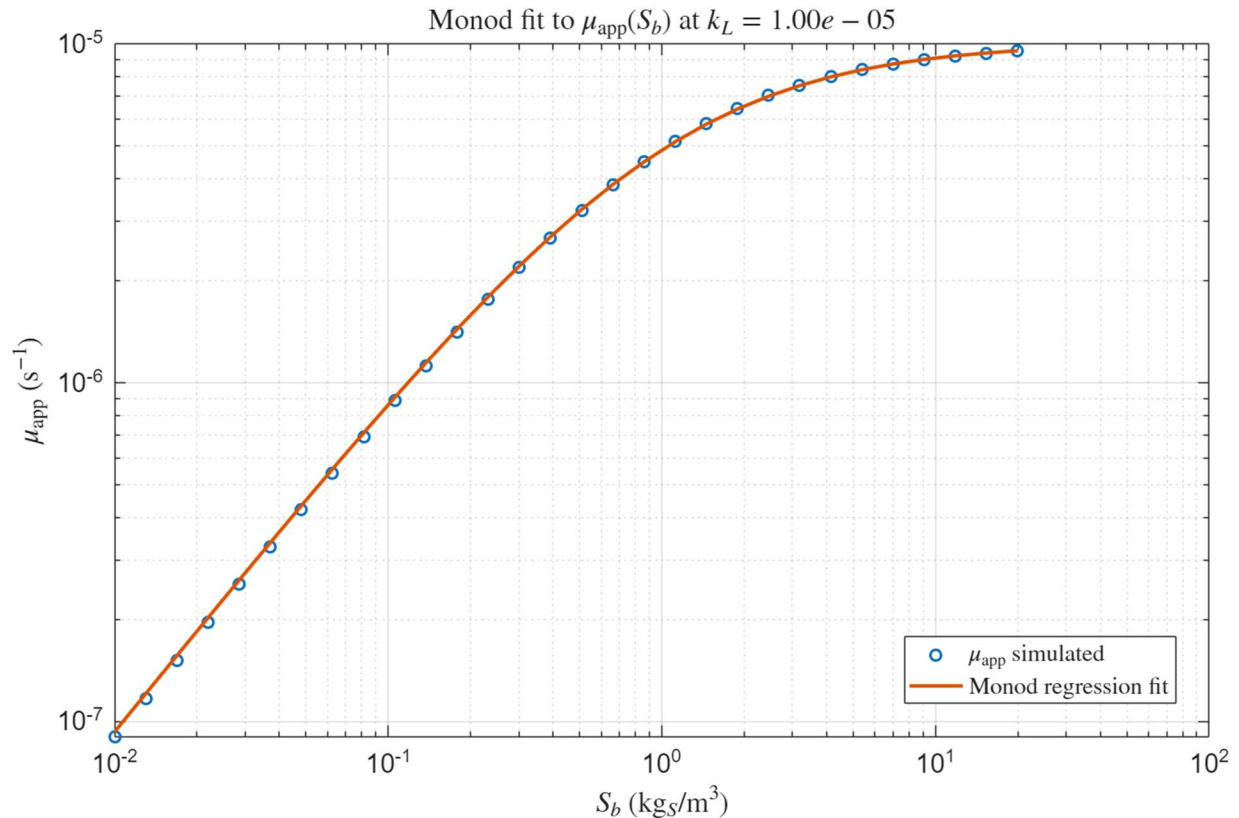
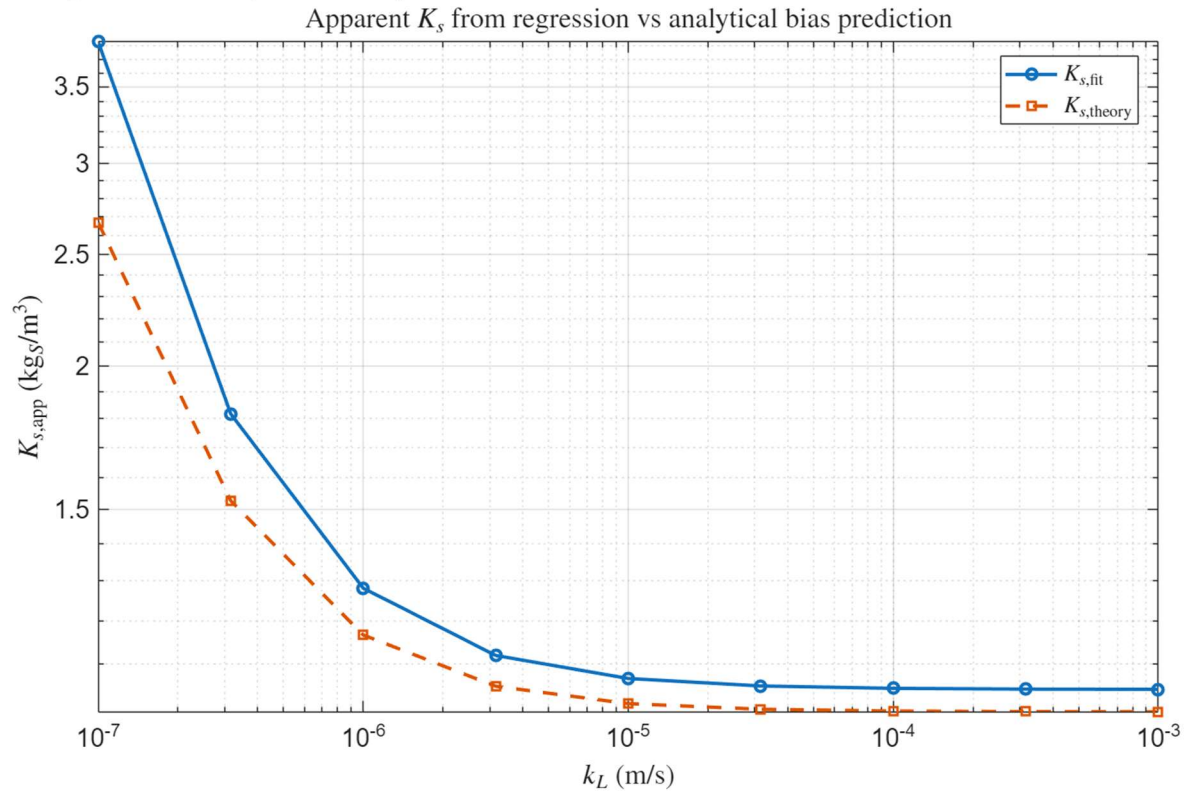


Figure 2-3 shows that the simulated apparent growth rate follows the characteristic Monod dependence on substrate concentration. However, the kinetic parameters obtained from regression depend on the transport conditions imposed at the granule boundary. Because the substrate concentration within the aggregate differs from the bulk liquid concentration, the regression procedure interprets the transport-limited reaction rate as if it were governed solely by intrinsic kinetics [20].

The influence of external transport resistance on the apparent half-saturation constant is illustrated in Figure 2-4. In this analysis, the reaction–diffusion model was evaluated across a range of liquid-film mass transfer coefficients k_L . For each value of k_L , the apparent growth rate data obtained from the numerical model were regressed to the Monod expression above to determine an effective half-saturation constant $K_{s,fit}$. The figure compares the regression results with the analytical bias prediction derived from the transport formulation presented in Appendix B.

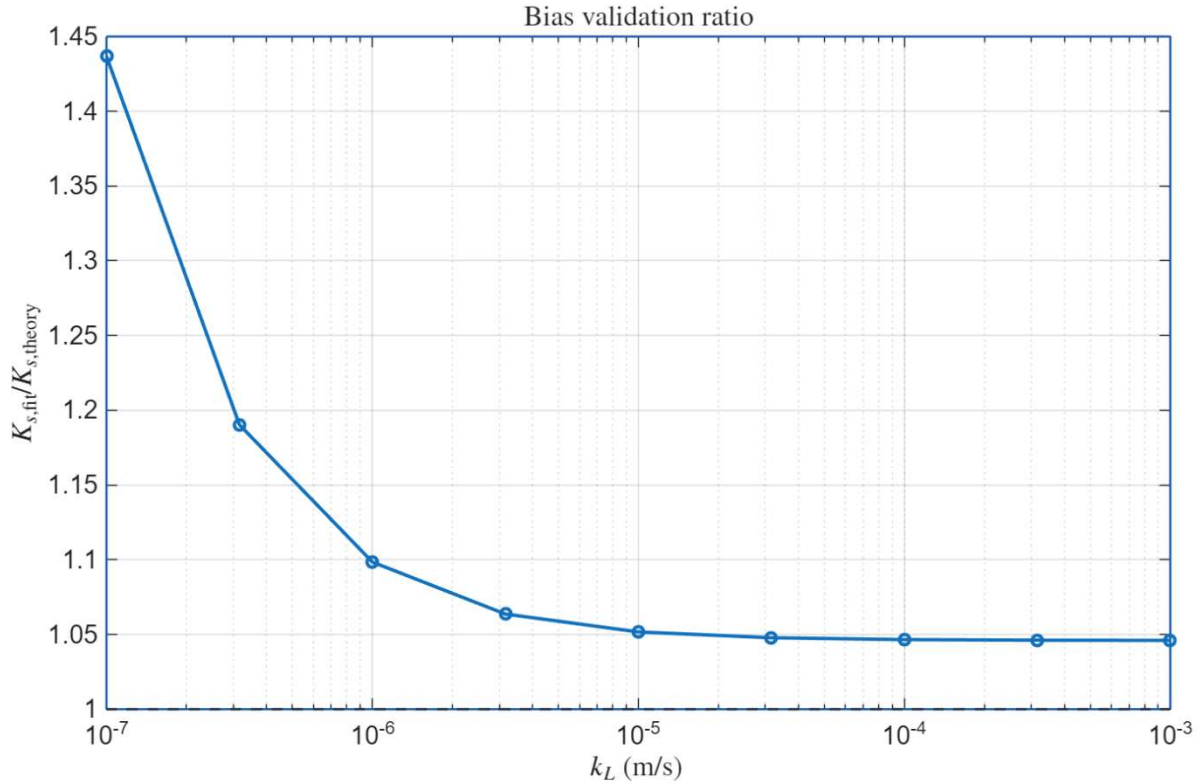
Figure 2-4 Apparent half-saturation constant $K_{s,app}$: nonlinear regression estimate compared to analytical bias prediction as a function of k_L .



The results demonstrate that the apparent half-saturation constant increases substantially as the external mass-transfer coefficient decreases. When mass transfer resistance is strong, the substrate concentration within the granule becomes significantly lower than the bulk concentration. If this transport effect is ignored and the data are interpreted using a standard Monod regression, the system appears more substrate-limited than it actually is at the microbial scale. As a result, the fitted value of the half-saturation constant becomes larger than the intrinsic value. This result demonstrates that kinetic parameters obtained from bulk reactor measurements do not necessarily represent intrinsic microbial properties but may instead reflect transport-conditioned behavior within granular biomass. Experimental investigations of methanogenic biofilms and granular sludge systems confirm that transport limitations can significantly influence the kinetic parameters inferred from reactor measurements. Studies examining hydrogen uptake kinetics in anaerobic biofilms have shown that the apparent half-saturation constant increases with increasing diffusion resistance within the microbial aggregate, demonstrating that kinetic parameters estimated from bulk measurements may reflect mass-transfer limitations rather than intrinsic microbial properties [12].

The accuracy of the analytical bias prediction is evaluated in Figure 2-5, which presents the ratio between the half-saturation constant obtained from nonlinear regression and the theoretical prediction derived from the transport analysis. Across the range of mass-transfer coefficients examined, the regression results closely follow the theoretical relationship predicted by the reaction–diffusion framework.

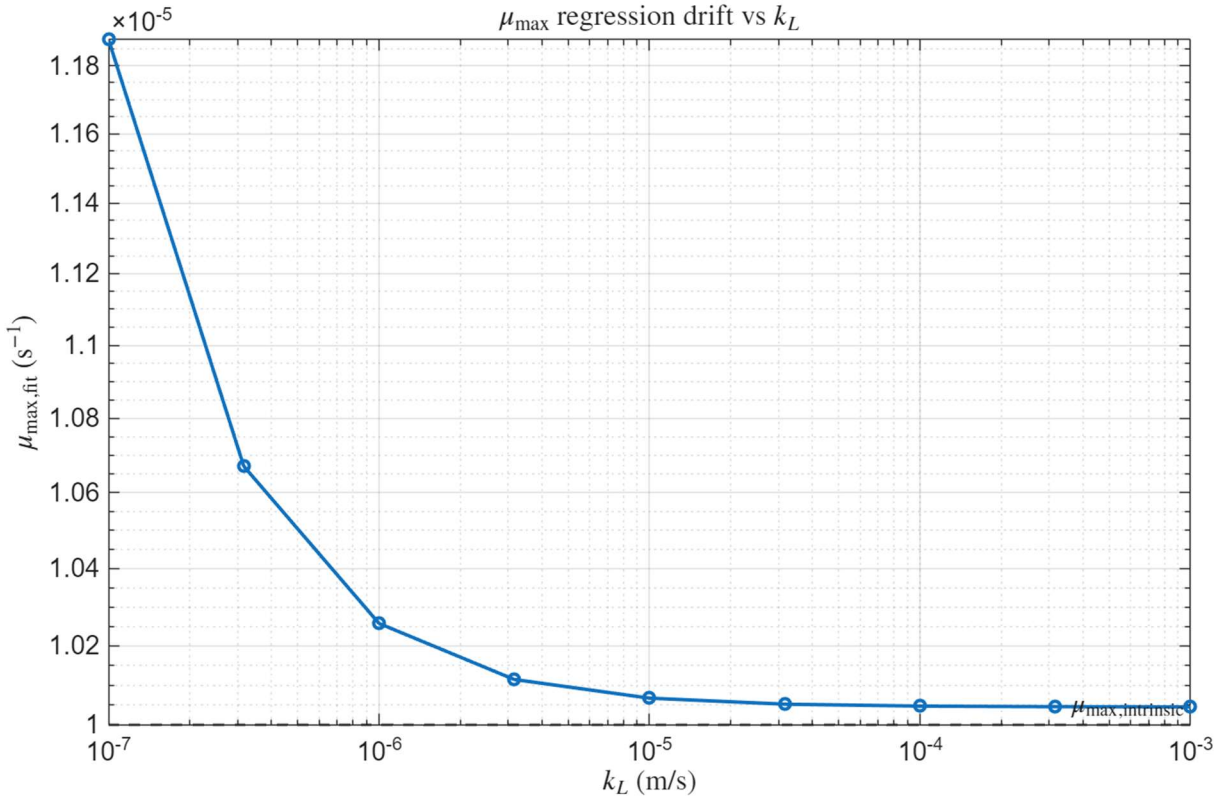
Figure 2-5 Bias validation ratio $K_{s,fit}/K_{s,theory}$ versus external mass transfer coefficient k_L .



The agreement between the numerical simulations and the analytical expression confirms that the apparent kinetic parameter shift is primarily governed by the interaction between intrinsic microbial kinetics and transport resistance within the granular biomass. This result demonstrates that the reaction–diffusion formulation provides a mechanistic explanation for the parameter bias observed in reactor-scale kinetic measurements.

Transport limitations can also influence the apparent value of the maximum specific growth rate obtained from regression. Figure 2-6 shows the variation of the fitted maximum growth rate $\mu_{max,fit}$ as a function of the external mass-transfer coefficient. At very low mass-transfer coefficients, the fitted value of μ_{max} becomes slightly larger than the intrinsic value due to the interaction between nonlinear Monod kinetics and diffusion-limited substrate availability within the aggregate.

Figure 2-6 Maximum specific growth rate $\mu_{\max}$ regression drift as a function of k_L .



As the external mass-transfer coefficient increases, the fitted growth rate converges toward the intrinsic microbial growth rate because the substrate concentration at the granule surface approaches the bulk liquid concentration and diffusion limitations become less significant. Under these conditions, the reaction–diffusion system approaches the kinetically controlled regime in which microbial activity is governed primarily by intrinsic metabolic kinetics.

Together, the results presented in this section demonstrate that kinetic parameters estimated from reactor-scale measurements may reflect both microbial metabolism and transport phenomena within granular biomass. When diffusion or external mass-transfer limitations are present, regression of Monod-type models against bulk substrate concentrations can lead to biased estimates of intrinsic microbial parameters. The reaction–diffusion framework developed in this chapter therefore provides a systematic method for distinguishing between kinetic control and transport limitation in granular anaerobic systems.

This distinction is essential for interpreting experimental data obtained from high-rate anaerobic reactors. Without accounting for the influence of transport processes, reactor-scale

kinetic measurements may incorrectly attribute transport-induced effects to intrinsic microbial metabolism. By explicitly resolving the spatial substrate distribution within microbial aggregates, the reaction–diffusion formulation provides a mechanistic basis for distinguishing intrinsic microbial kinetics from transport-conditioned apparent reaction rates.

The analysis developed in this section established that the reaction rate observed for granular biomass represents a transport-conditioned quantity rather than a direct expression of intrinsic microbial kinetics. Even when the underlying microbial growth law remains unchanged, diffusion limitations and external mass transfer resistance modify the substrate concentration field within the aggregate. As a result, the effective growth behavior inferred from reactor-scale measurements may differ substantially from the intrinsic kinetic properties of the microbial population. The formulation presented thus far considered the case of a single limiting substrate governed by Monod kinetics. In practical anaerobic digestion systems, however, substrate conversion occurs through a network of metabolically coupled microbial reactions. Fermentative microorganisms convert complex organic compounds into intermediate products such as volatile fatty acids and hydrogen, while acetogenic and methanogenic populations subsequently convert these intermediates into methane and carbon dioxide. The metabolic pathways therefore form a reaction network in which the activity of each microbial population depends on the concentrations of intermediate compounds produced by other microbial groups [8], [31]. When such reaction networks operate within granular biomass, the interaction between microbial pathways becomes coupled to the transport processes described previously. Diffusion limitations within the aggregate can alter the spatial distribution of intermediate species, which in turn affects the relative activity of competing microbial reactions. Consequently, the apparent reaction rates observed in granular systems may reflect not only transport-conditioned kinetics for individual reactions but also transport-conditioned selectivity within the microbial reaction network.

The next section extends the reaction–diffusion framework to examine these multispecies interactions. By representing anaerobic conversion pathways as a reduced reaction network embedded within the granular aggregate, the analysis investigates how transport limitations influence the relative activity of competing metabolic reactions and how these effects modify the apparent substrate conversion behavior observed at the reactor scale.

3 Anaerobic Reaction Rate Network Structure in Granular Biomass

3.1 Anaerobic Conversion Pathways and Reaction Network Topology

Anaerobic digestion proceeds through a sequence of microbial transformations in which complex organic substrates are converted into methane and carbon dioxide by metabolically specialized microbial populations. Although the microbial ecology of anaerobic systems is diverse, the dominant metabolic processes can be represented through a reduced reaction network that captures the major substrate conversion pathways responsible for methane production [8,32]. This reduced network representation allows the coupled behavior of microbial populations to be analyzed within the transport framework developed previously.

The anaerobic conversion process is commonly described as a series of functional stages. Complex organic substrates are first hydrolyzed into soluble compounds that can be metabolized by fermentative microorganisms. These fermentative reactions generate intermediate products including volatile fatty acids, alcohols, hydrogen, and carbon dioxide. Subsequent metabolic steps convert these intermediates into methane through the activity of acetogenic and methanogenic microorganisms. Because the products of one microbial population become the substrates for another, the overall process forms a metabolically coupled reaction network rather than a single isolated reaction pathway [8,32]. A simplified representation of this reaction network can be constructed by focusing on the dominant intermediate species involved in methane formation. In this reduced description, volatile fatty acids act as the primary substrate for syntrophic oxidation reactions that produce hydrogen and acetate, while hydrogenotrophic methanogens consume hydrogen to form methane. The microbial populations responsible for these reactions are therefore coupled through the hydrogen concentration field, which acts as an intermediate species linking the metabolic pathways. Mathematical representations of such reduced anaerobic digestion networks are commonly used in structured reactor models and microbial interaction studies [8,38].

To incorporate this reaction network into the transport framework developed earlier, each reaction pathway is represented by a rate expression associated with the microbial population responsible for that metabolic step. The coupled reaction system can then be expressed in compact

form using a stoichiometric matrix formulation, which relates the rate of production or consumption of each species to the vector of reaction rates. The derivation of this reduced reaction network representation is provided in Appendix A.

In this formulation, the bulk species balance may be written as seen in equation 31.

$$\frac{dS_b}{dt} = N\bar{r} \quad [\text{eqn. 31}]$$

where S_b represents the vector of bulk species concentrations, N is the stoichiometric matrix describing the reaction network, and $\bar{r}$ represents the vector of volume-averaged reaction rates defined over the microbial aggregate. The volume-averaged reaction rate for each pathway is obtained by integrating the local reaction rate throughout the granule volume and shown in equation 32,

$$\bar{r}_j = \frac{1}{V} \int_0^R r_j(r) 4\pi r^2 dr \quad [\text{eqn. 32}]$$

which corresponds to the volume-averaged reaction definition derived in Appendix A. This formulation preserves the spatial transport structure of the granular biomass while allowing the reaction network to be represented in a compact form suitable for reactor-scale interpretation.

An important consequence of this reaction network structure is that the rate of methane formation depends on the balance between multiple microbial populations operating simultaneously. Changes in substrate availability or transport conditions may therefore alter the relative activity of the reactions within the network. In particular, the concentration of intermediate species such as hydrogen plays a critical role in regulating syntrophic interactions between microbial populations. Experimental studies have shown that the activity of volatile fatty acid oxidation pathways is strongly influenced by hydrogen concentrations within microbial aggregates, illustrating the importance of intermediate species transport in determining overall metabolic behavior [32].

When these reaction networks operate within granular biomass, their behavior becomes coupled to the transport processes governing substrate and intermediate species diffusion within the aggregate. As described previously, diffusion limitations can create spatial gradients in substrate concentration within the granule. These gradients influence the local reaction rates

associated with each microbial pathway, which in turn modifies the volume-averaged reaction behavior observed at the aggregate scale.

The reaction network representation introduced in this section therefore provides the mechanistic foundation for analyzing multispecies microbial interactions within granular anaerobic systems. By combining the reaction–diffusion framework developed earlier with a reduced metabolic network representation, the model can capture how transport limitations influence both substrate conversion rates and the relative activity of competing metabolic pathways. The following section examines how sequential and parallel reaction pathways within this network interact with transport processes to determine the effective behavior of granular microbial communities.

3.2 Sequential and Parallel Reactions in Granular Systems

The reaction network representation introduced in the previous section provides a framework for describing how microbial populations interact through the exchange of chemical intermediates. Within this network, metabolic pathways can be broadly categorized as either sequential reactions, in which the product of one reaction becomes the substrate for a subsequent reaction, or parallel reactions, in which multiple microbial populations compete for the same substrate but produce different metabolic products. These reaction structures play a central role in determining how microbial activity translates into the overall substrate conversion behavior observed in anaerobic systems [8,32].

Sequential reactions are a defining characteristic of anaerobic digestion. The conversion of complex organic substrates to methane occurs through a cascade of intermediate compounds generated by distinct microbial guilds. In this structure, the effective rate of substrate conversion depends on the ability of each microbial population to process the intermediates produced by upstream reactions. If one step in the sequence proceeds more slowly than the others, the associated intermediate compounds may accumulate within the system. Such accumulation can alter the local chemical environment and influence the activity of other microbial populations within the network [31].

Parallel reactions arise when multiple microbial populations utilize the same substrate but generate different products. In anaerobic fermentation processes, for example, fermentative

microorganisms may convert soluble substrates into different sets of volatile fatty acids, hydrogen, and carbon dioxide. The relative rates of these competing reactions determine how carbon and electrons are distributed among downstream metabolic pathways. Because the metabolic products of these reactions serve as substrates for later conversion steps, the distribution of reaction flux among parallel pathways influences the overall efficiency of methane production [8].

When these reaction pathways occur within granular biomass, their behavior becomes coupled to the spatial substrate distribution within the microbial aggregate. Diffusion limitations within the granule modify the substrate concentrations experienced by different microbial populations, which in turn affects the relative rates of competing metabolic reactions [6,20]. Microorganisms located near the granule surface may experience higher concentrations of the primary substrate, while those located deeper within the aggregate operate under more substrate-limited conditions. These spatial variations can alter the balance between sequential and parallel reaction pathways within the microbial network.

The mathematical representation of sequential and parallel reactions within the reaction network follows directly from the stoichiometric framework introduced previously. Each metabolic pathway is represented by a rate expression associated with a particular microbial population, while the stoichiometric matrix defines the coupling between substrate consumption and product formation. The complete formulation of this reaction network is presented in Appendix A (Eqs. A.14–A.19), where the volume-averaged reaction rates are defined through spatial integration of the local reaction terms within the granule.

Because these reactions share common intermediates, the rates of individual pathways become interdependent through the spatial distribution of chemical species within the aggregate. Transport limitations can therefore modify the apparent reaction rates by altering the local concentrations of intermediate compounds that regulate microbial activity. In particular, hydrogen plays a central role in regulating syntrophic interactions in anaerobic digestion systems. Variations in hydrogen concentration within the granule can influence the thermodynamic feasibility and kinetic rate of volatile fatty acid oxidation reactions, thereby modifying the distribution of reaction flux within the microbial network [31].

The coupling between reaction network structure and transport processes introduces an additional level of complexity beyond the single-substrate kinetic behavior discussed previously.

Even when intrinsic kinetic parameters remain unchanged, diffusion limitations within the aggregate can alter the relative activity of competing metabolic pathways [32]. As a result, the effective substrate conversion behavior observed at the reactor scale reflects not only intrinsic microbial kinetics but also the interaction between reaction network topology and transport processes within the granular biomass.

The following section examines this interaction in greater detail by evaluating how transport limitations influence the apparent selectivity between competing reactions within the microbial network. By analyzing the relative activity of these reactions across a range of transport conditions, the model provides insight into how diffusion gradients within granular biomass influence the distribution of metabolic activity within anaerobic microbial communities.

3.3 Influence of Reaction Network on Observed Rates

The reaction network formulation developed in the preceding sections establishes that microbial reactions within anaerobic digestion systems occur through a set of metabolically coupled pathways. When this network structure is embedded within granular biomass, the behavior of each reaction pathway becomes influenced by the spatial distribution of intermediate species within the aggregate. Consequently, the apparent rates observed at the reactor scale reflect not only intrinsic microbial kinetics but also the interaction between reaction network topology and transport processes within the granule.

To investigate this interaction, the reaction–diffusion framework developed previously was extended to include a reduced two-species representation of the microbial network. In this formulation, volatile fatty acid oxidation produces hydrogen as an intermediate species, while hydrogenotrophic methanogenesis consumes hydrogen to form methane. The rates of these reactions depend on the local concentrations of the participating species and therefore become coupled through the spatial hydrogen concentration field within the granule. The mathematical formulation describing this reduced reaction network is derived in Appendix A (Eqs. A.14–A.19).

Because both reactions occur throughout the aggregate volume, the effective contribution of each pathway must be evaluated using the volume-averaged reaction rate definition derived previously. For each reaction j , the volume-averaged rate is obtained by integrating the local reaction rate over the granule volume as demonstrated in equation 33,

$$\bar{r}_j = \frac{1}{V} \int_0^R r_j(r) 4\pi r^2 dr \quad [\text{eqn. 33}]$$

which corresponds to the definition provided in Appendix A. This formulation preserves the spatial transport structure of the system while allowing the aggregate-scale behavior of each reaction pathway to be quantified.

To evaluate the influence of transport limitations on reaction network behavior, the model was solved numerically across a range of transport and kinetic conditions using the numerical methods described in Appendix B. The resulting simulations allow the relative contribution of the competing metabolic pathways to be quantified through a selectivity metric comparing the apparent and intrinsic reaction rates.

The intrinsic selectivity between two competing reactions can be defined using the local reaction rates evaluated at the granule surface as shown in equation 34, which corresponds to the intrinsic selectivity definition given in Appendix A.

$$\Sigma_{int} = \frac{r_1(S_{H_2}(R))}{r_3(S_{H_2}(R))} \quad [\text{eqn. 34}]$$

In contrast, the apparent selectivity observed at the aggregate scale is determined from the volume-averaged reaction rates shown in equation 35, as defined in Appendix A.

$$\Sigma_{app} = \frac{\bar{r}_1}{\bar{r}_3} \quad [\text{eqn. 35}]$$

The ratio between these two quantities provides a measure of the degree to which transport processes alter the relative activity of competing microbial pathways.

Figure 3-1 Selectivity regime: $\Sigma_{app}/\Sigma_{int}^{surf}$ versus hydrogen transport–reaction modulus $\phi_{H_2}^2$ (two-dimensional sweep).

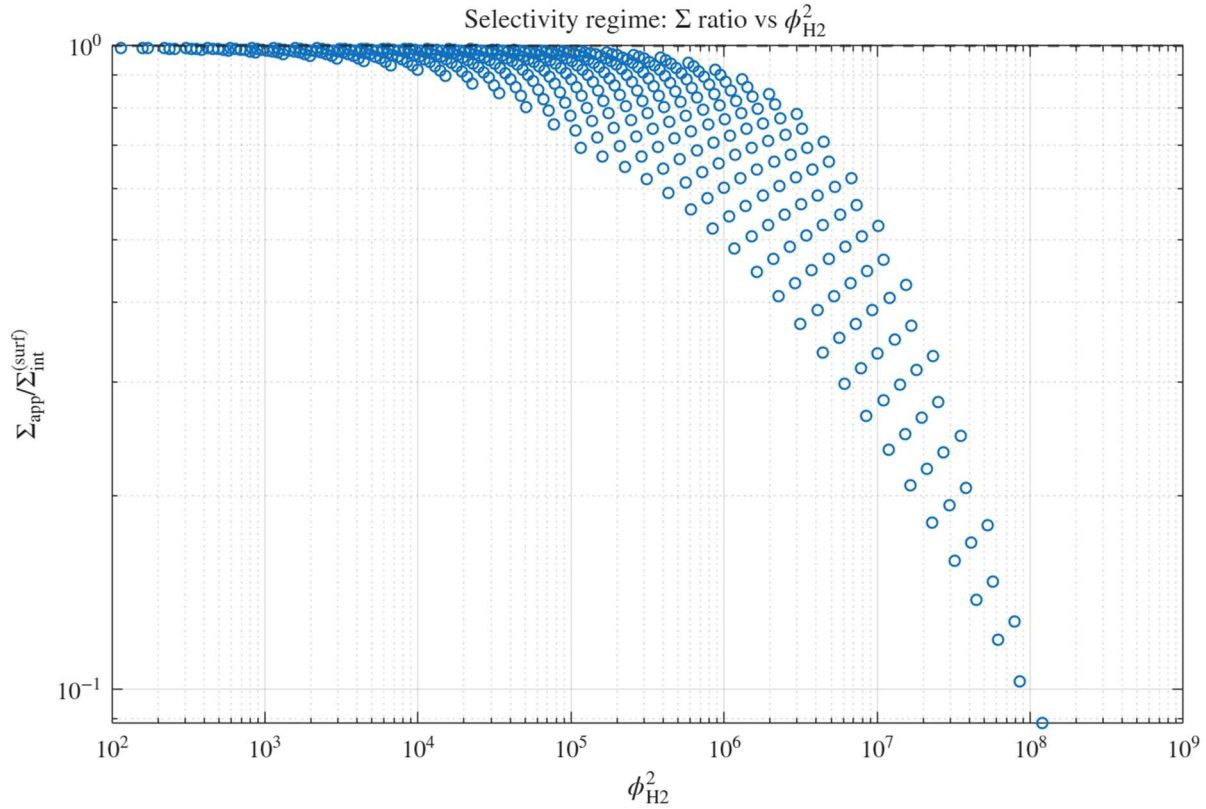
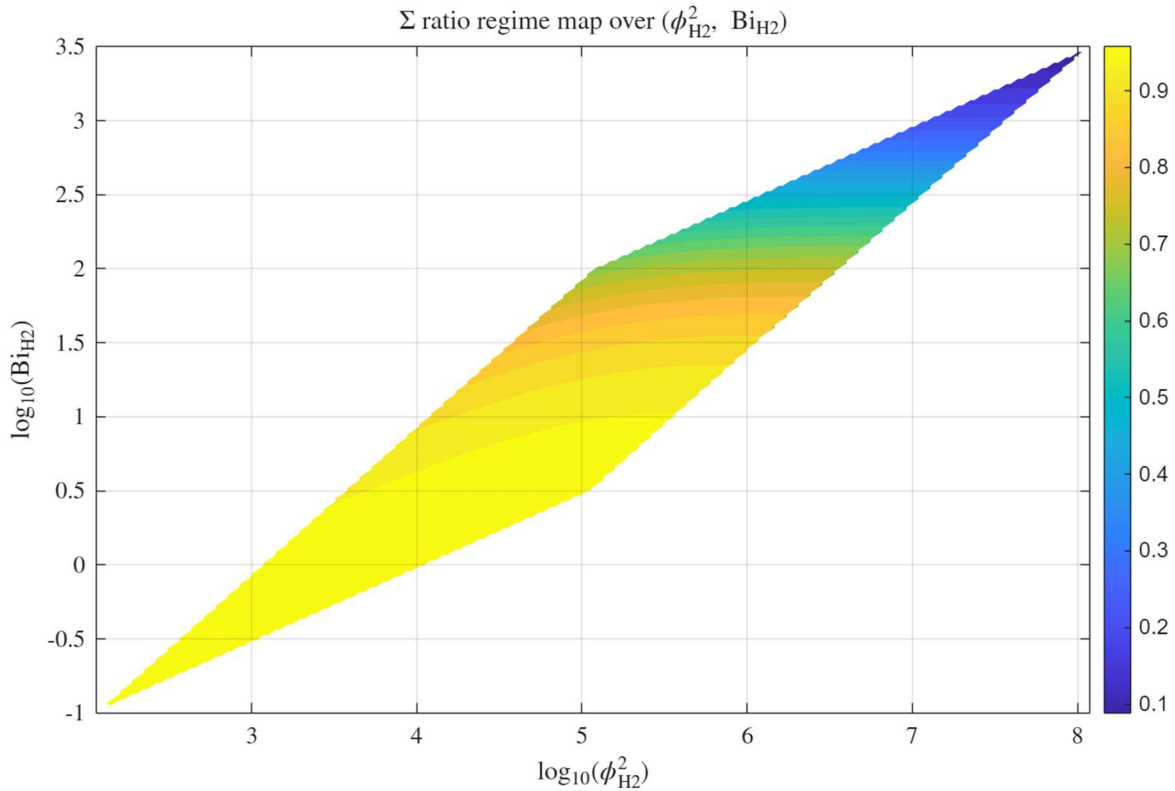


Figure 3-1 shows the variation of the selectivity ratio $\Sigma_{app}/\Sigma_{int}$ as a function of the squared hydrogen transport–reaction modulus $\phi_{H_2}^2$. At low values of this transport parameter, diffusion limitations are weak and hydrogen concentrations remain nearly uniform throughout the aggregate. Under these conditions, the apparent selectivity remains close to the intrinsic value predicted from the reaction kinetics. As the transport parameter increases, however, diffusion limitations lead to the accumulation of hydrogen within the granule interior. Because the competing reactions respond differently to hydrogen concentration, this accumulation modifies the relative activity of the pathways and produces a shift in the apparent selectivity. Transport limitations therefore influence not only the magnitude of reaction rates but also the distribution of metabolic flux within the microbial reaction network.

The combined influence of internal diffusion and external mass transfer is illustrated more clearly in the regime map shown in Figure 3-2, which presents the selectivity ratio across the parameter space defined by the hydrogen transport modulus and the hydrogen mass-transfer Biot

number. The regime map shown in Figure 3-2 is constructed from interpolation of discrete simulation results obtained from the parameter sweep described in Appendix B. The contours therefore represent a visualization of transport-conditioned selectivity trends rather than an exact analytical boundary between regimes.

Figure 3-2 Selectivity regime map in $(\phi_{H_2}^2, Bi_{H_2})$ space.



The regime map reveals distinct regions in which the reaction network behaves differently depending on the balance between reaction kinetics and transport processes. In the region corresponding to low transport resistance, both reactions operate close to their intrinsic kinetic behavior and the selectivity ratio remains near unity. As diffusion limitations increase, spatial gradients in hydrogen concentration alter the relative rates of the competing reactions, leading to a progressive deviation of the apparent selectivity from the intrinsic value.

The numerical stability of the computational framework used to generate these results was evaluated across the parameter ranges explored in the transport analysis. The Newton solver used to compute the coupled reaction–diffusion system converged robustly for all parameter combinations considered in the regime sweep. The corresponding convergence diagnostics are

provided in Appendix C (Figure C.1), which illustrates solver convergence across the (D_h , R) parameter domain examined in the selectivity analysis.

Together, the results presented in this section demonstrate that the structure of the microbial reaction network can strongly influence the effective substrate conversion behavior observed in granular anaerobic systems. Even when intrinsic kinetic parameters remain unchanged, diffusion limitations and external mass transfer resistance can alter the spatial distribution of intermediate species within the aggregate. These transport-induced gradients modify the relative activity of competing metabolic pathways and therefore influence the apparent reaction rates observed at the reactor scale.

The analysis developed here establishes a mechanistic connection between microbial interaction networks and transport phenomena within granular biomass. The next section extends this framework by examining how these transport processes influence the broader regime behavior of the system and by identifying the dimensionless parameters that determine whether granular biomass operates under kinetic control, internal diffusion limitation, or external mass transfer limitation.

4 Coupling of Transport Phenomena and Reaction Rates in Anaerobic Granules

4.1 External Mass Transfer and Hydrodynamic Boundary Condition

Substrate transport from the bulk liquid to the surface of anaerobic granules is controlled initially by external mass transfer through the hydrodynamic boundary layer surrounding the biomass particle. Before substrate can diffuse into the interior of the granule and participate in microbial metabolism, it must first cross this external liquid film. The resistance associated with this step depends on the local hydrodynamic environment and can influence the substrate concentration available at the granule surface.

In high-rate anaerobic reactors, external transport is governed by the interaction between bulk liquid motion, mixing conditions, and the stagnant or partially stagnant liquid layer adjacent to the granule surface. Although the thickness of this boundary layer is typically small relative to the granule radius, its influence becomes important when microbial reaction rates are high or when mixing conditions are insufficient to maintain rapid substrate renewal at the particle surface [22,24,25]. Under such conditions, the substrate concentration at the granule surface can deviate significantly from the bulk liquid concentration [22,34].

The transport process at the granule surface is described by the external mass transfer boundary condition derived in Appendix A. At the granule surface $r = R$, continuity of flux between the liquid phase and the granule interior requires that the diffusive flux inside the granule equal the flux through the external liquid film. This condition is expressed in equation 36 which corresponds to the boundary condition presented in Appendix A.

$$-D_e \frac{dS}{dr} \Big|_{r=R} = k_L(S_b - S_s) \quad [\text{eqn. 36}]$$

In this expression, k_L represents the liquid-film mass transfer coefficient, S_b represents the bulk liquid substrate concentration, and $S_s = S(R)$ represents the substrate concentration at the granule surface. This relation links the external transport environment of the reactor to the internal diffusion processes occurring within the biomass.

The external mass transfer coefficient depends on the hydrodynamic conditions surrounding the granule and is commonly related to dimensionless transport correlations involving the Sherwood number. The Sherwood number is defined in equation 37 and corresponds

$$Sh = \frac{k_L d_p}{D_b} \quad [\text{eqn. 37}]$$

where $d_p = 2R$ represents the particle diameter and D_b represents the molecular diffusivity of the substrate in the bulk liquid. Correlations of the Sherwood number with Reynolds and Schmidt numbers provide a means of relating hydrodynamic flow conditions to the magnitude of the external mass transfer coefficient [22].

Hydrodynamic conditions in anaerobic reactors are influenced by factors such as reactor geometry, mixing intensity, and superficial liquid velocity. Tracer-based hydrodynamic studies and residence time distribution analyses have shown that the flow environment experienced by granular biomass can deviate substantially from ideal mixing behavior, producing spatial variations in shear stress and mass transfer conditions within the reactor [24,26]. Computational fluid dynamics simulations of granular sludge reactors further demonstrate that local mixing patterns and velocity distributions can influence the transport environment surrounding microbial aggregates [25].

Because the external mass transfer coefficient depends on the reactor hydrodynamics, it represents a coupling between the macroscopic reactor environment and the microscopic transport processes occurring within individual granules. The surface substrate concentration S_s determined by the boundary condition above therefore becomes the interfacial condition that governs diffusion into the granule interior. When external transport is rapid, the surface concentration approaches the bulk concentration and the effect of the hydrodynamic film becomes negligible [21,22]. When external transport is limited, however, the surface concentration decreases relative to the bulk concentration, reducing the driving force for diffusion into the biomass.

The external transport formulation introduced in this section therefore provides the first component of the complete granule transport model. By explicitly representing the coupling between hydrodynamic transport and intragranular diffusion, the boundary condition establishes how reactor-scale flow conditions influence the local substrate environment experienced by microbial aggregates. The following section couples this external boundary condition with the

internal reaction–diffusion formulation to describe substrate transport and microbial consumption throughout the granule volume.

4.2 Internal Diffusion and Reaction Diffusion Formulation

Once substrate reaches the surface of the microbial granule, it must diffuse through the porous biomass matrix before it can be consumed by the microorganisms embedded within the aggregate. The transport of substrate within the granule therefore occurs simultaneously with microbial metabolism, producing a coupled reaction–diffusion system that governs the spatial distribution of substrate concentration inside the biomass.

For a spherical aggregate with effective intragranular diffusivity D_e and Monod reaction kinetics, the steady-state transport–reaction balance is written out in equation 38 as derived in Appendix A.

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 D_e \frac{dS}{dr} \right) - \frac{\mu_{\max} X_0}{Y} \frac{S}{K_s + S} = 0 \quad [\text{eqn. 38}]$$

where the first term represents radial diffusion of substrate within the granule and the second term represents microbial consumption of substrate through growth-associated metabolism. The derivation of this equation follows directly from conservation of mass applied to a differential spherical control volume and is presented in Appendix A.

Together with the boundary conditions defined in Appendix A (Eqs. A.20–A.21), this relation forms a nonlinear boundary-value problem describing the substrate concentration field within the microbial aggregate. The resulting spatial distribution of substrate determines the metabolic activity of the biomass because the local microbial growth rate depends on the local substrate concentration through the intrinsic Monod kinetic relation.

A convenient measure of the influence of diffusion limitations on microbial activity is the effectiveness factor. The effectiveness factor represents the ratio between the actual reaction rate occurring within the granule and the reaction rate that would occur if the entire biomass were exposed to the substrate concentration present at the granule surface. Using the definitions introduced in Appendix A, the effectiveness factor is written out in equation 39.

$$\eta = \frac{R_{obs}}{R_{intrinsic}} \quad [\text{eqn. 39}]$$

which corresponds to the effectiveness definition given in Appendix. Values of the effectiveness factor close to unity indicate that diffusion limitations are weak and the entire granule participates in substrate conversion. As diffusion resistance becomes more significant, substrate penetration into the granule interior becomes restricted and the effectiveness factor decreases because a smaller fraction of the biomass remains metabolically active [19,20,28].

The effectiveness behavior of the granular reaction–diffusion system was evaluated numerically using the computational method described in Appendix B. The nonlinear boundary-value problem was discretized in the radial coordinate using finite differences and solved iteratively using a Newton method until the residual of the governing equations satisfied the convergence tolerance. The resulting substrate concentration profile was then used to compute the observed reaction rate R_{obs} and the corresponding effectiveness factor.

Figure 4-1 Numerical effectiveness factor η_{num} versus Thiele modulus Φ (Monod kinetics, film boundary condition) with k_L overlays.

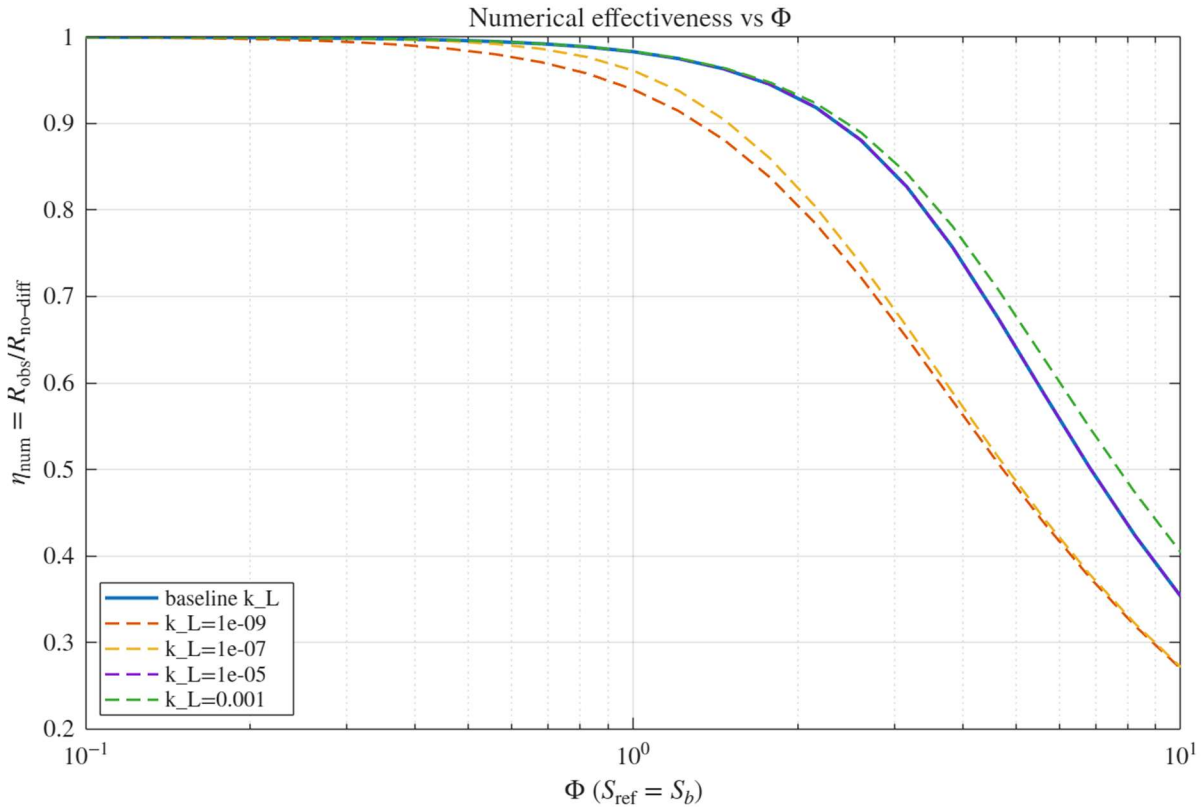


Figure 4-1 shows the variation of the numerical effectiveness factor η_{num} as a function of the dimensionless reaction–diffusion parameter Φ . At small values of this parameter, diffusion is

sufficiently rapid that substrate concentrations remain nearly uniform throughout the granule. Under these conditions the effectiveness factor remains close to unity, indicating that the entire microbial aggregate participates in substrate conversion. As the reaction–diffusion parameter increases, substrate consumption near the granule surface becomes sufficiently rapid that diffusion cannot replenish substrate throughout the interior of the aggregate. The resulting concentration gradients restrict microbial activity to the outer regions of the granule, causing the effectiveness factor to decrease.

The influence of the external mass transfer coefficient on the internal diffusion behavior is also illustrated in Figure 4-1. For small values of k_L , external transport resistance lowers the substrate concentration at the granule surface, reducing the driving force for diffusion into the aggregate interior. As the external mass transfer coefficient increases, the surface concentration approaches the bulk liquid concentration and the internal diffusion behavior approaches the limit determined solely by the intragranular transport process. The relationship between the surface substrate concentration and the reaction–diffusion parameter is shown in Figure 4-2.

Figure 4-2 Surface substrate concentration $S_s = S(R)$ versus Thiele modulus Φ under film boundary condition.

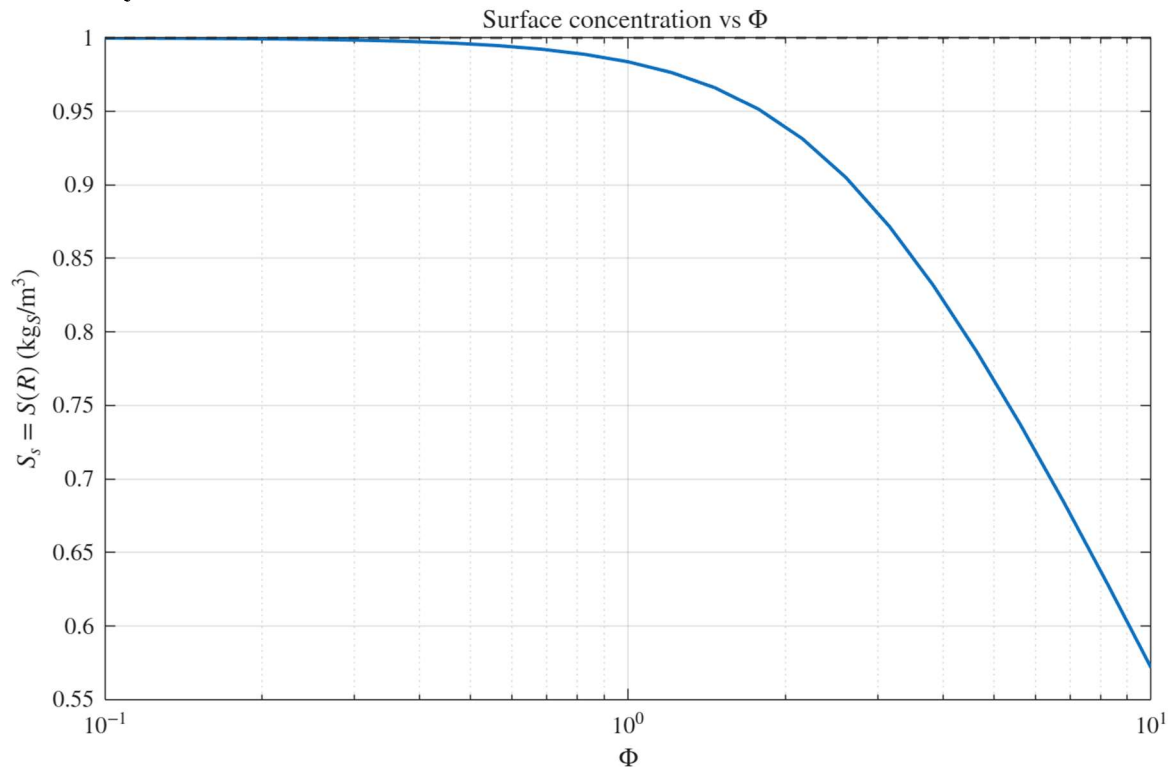


Figure 4-2 shows that the substrate concentration at the granule surface decreases gradually as the reaction–diffusion parameter increases. At low values of Φ , both internal diffusion resistance and external mass transfer resistance are small, and the surface concentration remains nearly equal to the bulk substrate concentration. As reaction rates increase relative to diffusion, substrate consumption within the granule begins to influence the interfacial transport balance, causing the surface concentration to decrease. This behavior reflects the coupling between the internal reaction–diffusion process and the external mass transfer boundary condition.

The results presented in this section demonstrate how internal diffusion and external mass transfer interact to determine the substrate concentration field within granular biomass. The reaction–diffusion formulation therefore provides the mechanistic link between intrinsic microbial kinetics and the effective reaction behavior of the microbial aggregate. In the following section, this formulation is expressed in dimensionless form to identify the governing parameters that determine the transport regime of the system and to construct regime maps that classify the conditions under which microbial activity is controlled by kinetics, internal diffusion, or external mass transfer resistance.

4.3 Dimensionless Analysis and Governing Regime Identification

The reaction–diffusion formulation presented in the previous section can be expressed in dimensionless form to identify the governing transport parameters that determine the behavior of granular anaerobic systems. Non-dimensionalization provides a compact representation of the coupled reaction–diffusion problem and reveals the key parameters controlling the relative influence of microbial kinetics, internal diffusion, and external mass transfer.

Following the derivation presented in Appendix A, the radial coordinate and substrate concentration are expressed in dimensionless form as shown in equation 40.

$$\rho = \frac{r}{R}, s(\rho) = \frac{S}{S_{ref}} \quad [\text{eqn. 40}]$$

Where R is the granule radius and S_{ref} is a reference substrate concentration. Substituting these variables into the reaction–diffusion equation yields the dimensionless transport–reaction

formulation as shown in equation 41,

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{ds}{d\rho} \right) - \Phi^2 \frac{s}{\kappa + s} = 0 \quad [\text{eqn. 41}]$$

which corresponds to the dimensionless governing equation presented in Appendix A. In this expression, the dimensionless group represents the reaction diffusion parameter, oftentimes referred to as the Monod-based Thiel modulus as defined in equation 42, which corresponds to the definition provided in Appendix A.

$$\Phi^2 = \frac{R^2}{D_e} \left(\frac{\mu_{\max} X_0}{Y S_{ref}} \right) \quad [\text{eqn. 42}]$$

This parameter characterizes the relative strength of microbial reaction rates compared with diffusive transport within the granule.

The influence of external transport resistance is captured through the mass-transfer Biot number defined in equation 43 which corresponds to the transport parameter defined in Appendix A.

$$Bi_m = \frac{k_L R}{D_e} \quad [\text{eqn. 43}]$$

The Biot number represents the ratio of external mass transfer resistance to internal diffusion resistance and therefore determines the extent to which the external hydrodynamic boundary condition influences the substrate concentration field within the aggregate.

Together, the parameters Φ and Bi_m define the transport regime of the granular system. The reaction–diffusion parameter determines the magnitude of internal concentration gradients produced by microbial metabolism, while the Biot number determines whether the external hydrodynamic boundary layer imposes an additional transport limitation at the granule surface.

To evaluate the behavior of the system across this parameter space, the reaction–diffusion model described in Appendix B was solved numerically over a wide range of values of Φ and Bi_m . The resulting effectiveness factors were then used to construct regime maps describing the influence of transport limitations on microbial activity within granular biomass.

Figure 4-3 Effectiveness regime map η_{num} in (Φ, Bi_m) space.

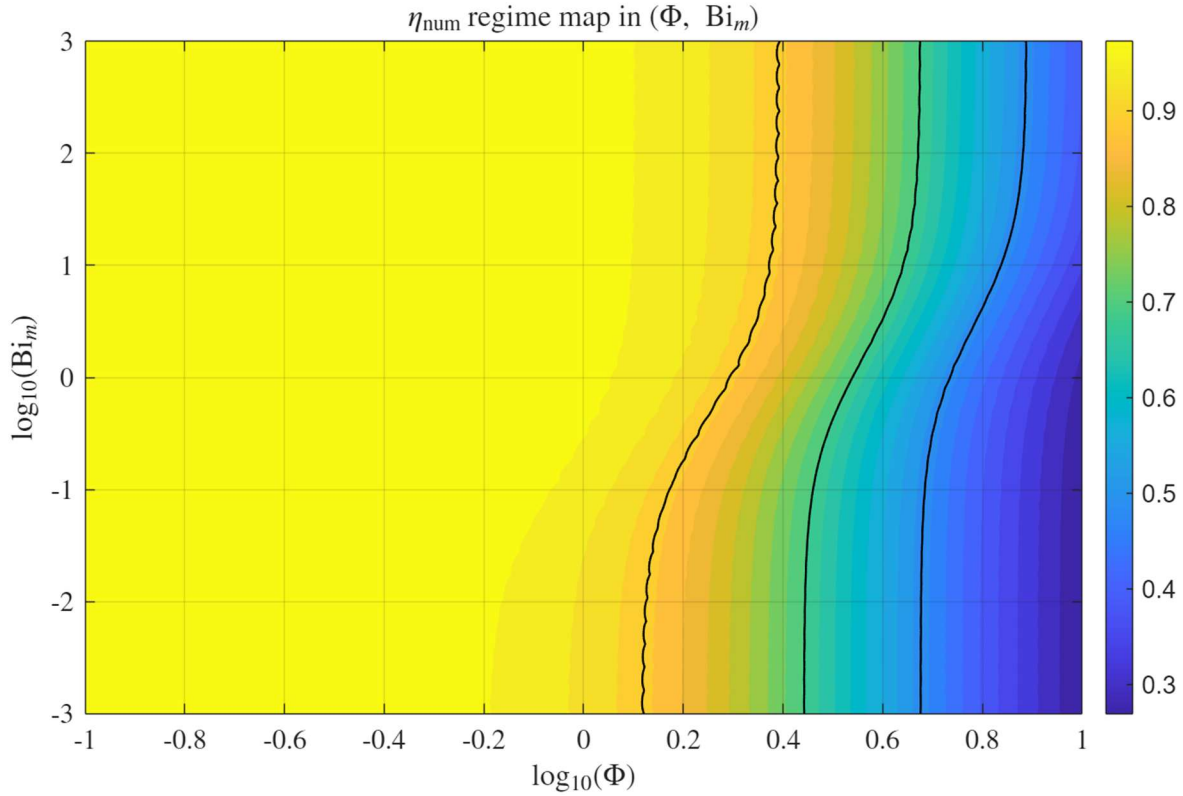


Figure 4-3 presents the effectiveness factor η_{num} across the dimensionless parameter space defined by the reaction–diffusion parameter and the mass-transfer Biot number. Regions of high effectiveness correspond to kinetically controlled conditions in which diffusion limitations are weak and most of the biomass participates in substrate conversion. As the reaction–diffusion parameter increases, internal diffusion resistance becomes more significant, producing a gradual transition toward diffusion-limited behavior in which microbial activity becomes confined to the outer regions of the aggregate. The regime map therefore provides a practical diagnostic tool for determining whether a granular reactor operates under kinetic control, internal diffusion limitation, or external mass-transfer limitation.

An additional question arises when interpreting this regime map: under what conditions can the influence of the external mass transfer boundary condition be neglected? If external transport resistance becomes sufficiently small, the reaction–diffusion system should collapse to a behavior determined solely by internal diffusion and reaction kinetics. This collapse condition can be evaluated by examining the variation of the effectiveness factor across different values of

the Biot number. The results of this collapse analysis are shown in Figure 4-4 and 4-5.

Figure 4-4 Collapse diagnostic: variation in $\Delta\eta_{\max}$ across Bi_m bins for $\text{Bi}_m \geq 1$.

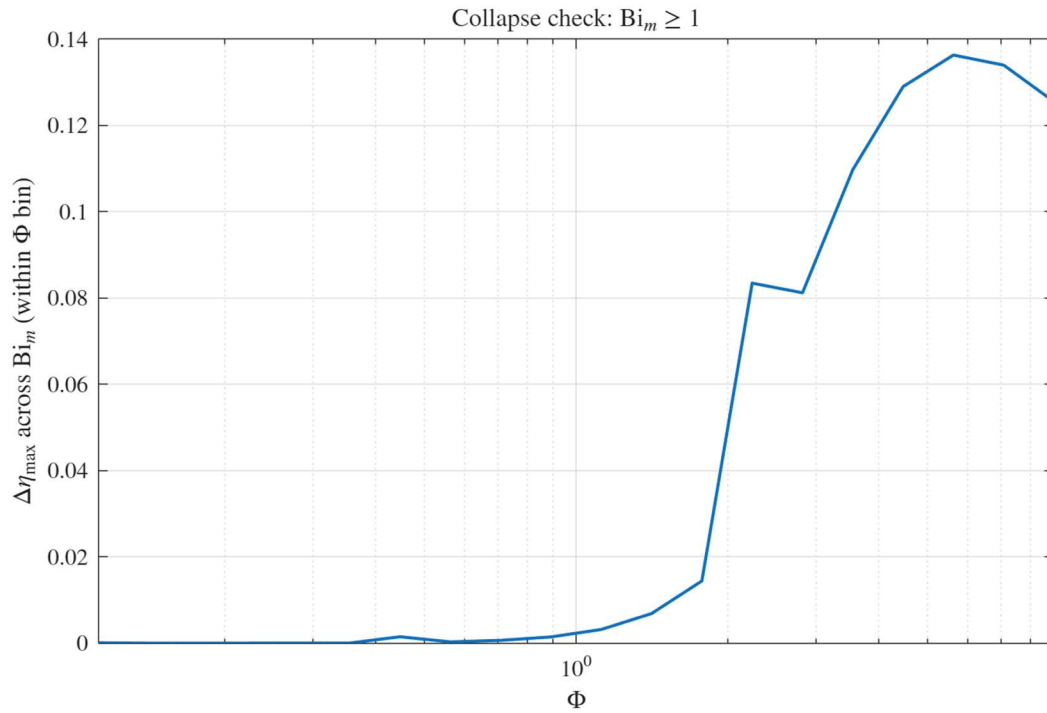
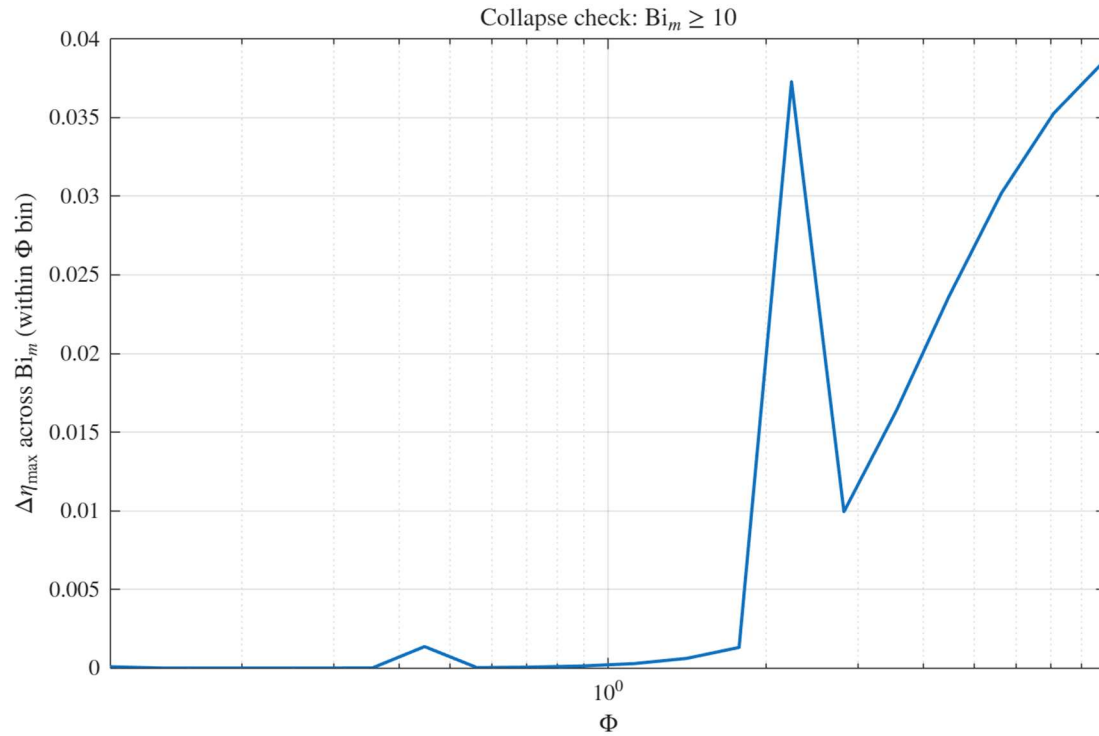


Figure 4-5 Collapse diagnostic: variation in $\Delta\eta_{\max}$ across Bi_m bins for $\text{Bi}_m \geq 10$.



These figures show the variation in effectiveness factor across bins of the reaction–diffusion parameter when the Biot number exceeds specified threshold values. When the Biot number is sufficiently large, the variation in effectiveness behavior across different external transport conditions becomes small [22]. Under these conditions, the system behaves as if the surface substrate concentration were equal to the bulk concentration, and the reaction–diffusion system effectively collapses to the internal diffusion limit.

Using this observation, a series of numerical experiments were performed to determine the minimum Biot number required for regime collapse under specified accuracy tolerances. The resulting design rules are presented in Figures 4-6 and 4-7.

Figure 4-6 Design rule: minimum Bi_m required for regime collapse within tolerance $\Delta\eta \leq 0.02$

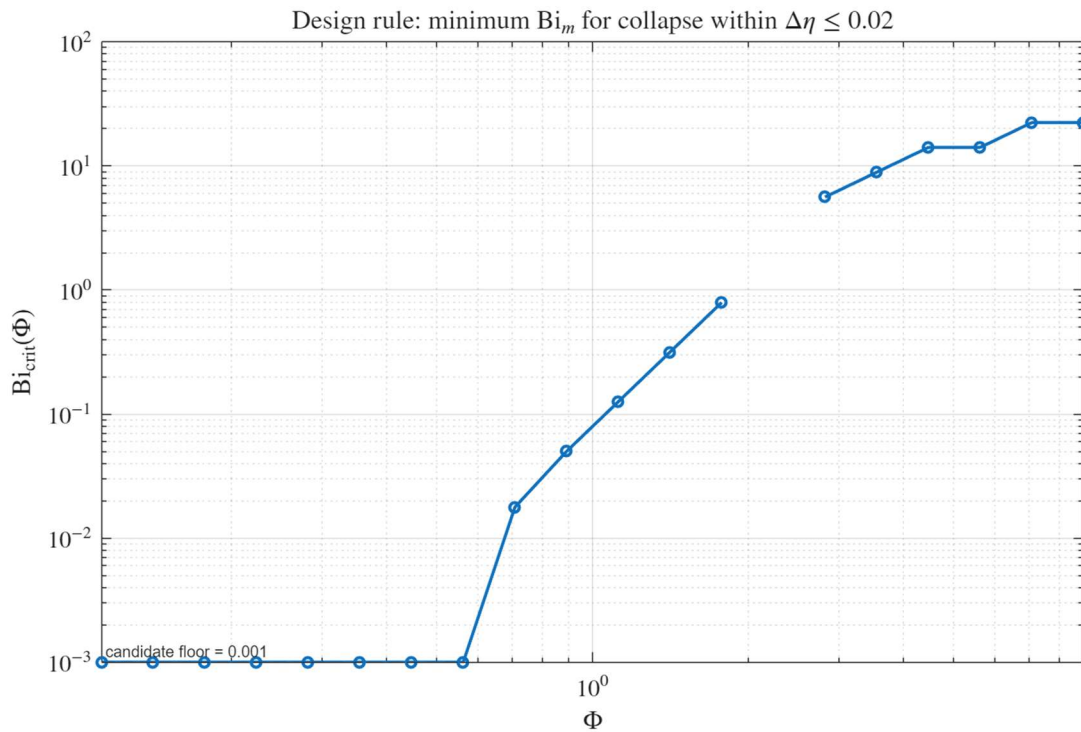


Figure 4-7 Design rule: minimum Bi_m required for regime collapse within tolerance $\Delta\eta \leq 0.05$.

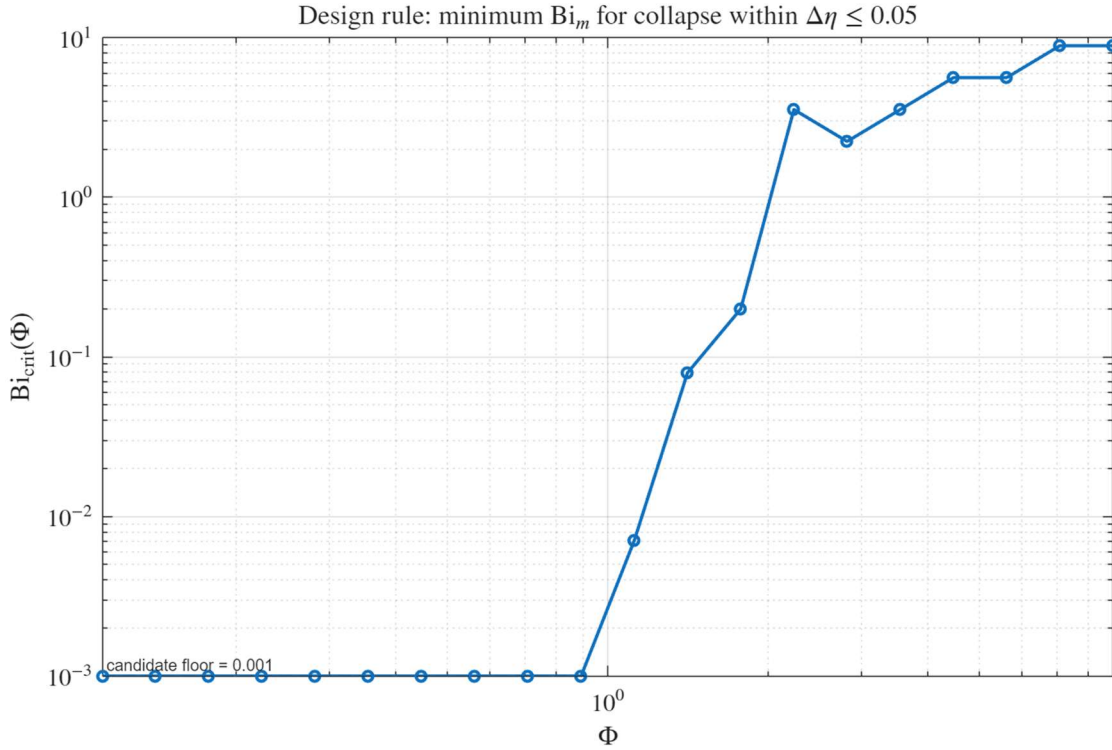


Figure 4-6 shows the minimum Biot number required to ensure that the deviation in effectiveness remains below a tolerance of $\Delta\eta \leq 0.02$, while Figure 4-7 presents the corresponding result for a tolerance of $\Delta\eta \leq 0.05$. These figures demonstrate that the required external mass transfer strength increases as the reaction–diffusion parameter becomes larger. When reaction rates are high relative to diffusion, maintaining sufficiently strong external transport becomes necessary to prevent additional transport limitations at the granule surface.

The numerical robustness of the solution procedure used to generate these regime maps was evaluated across the parameter ranges considered in the transport analysis. The Newton solver used to compute the nonlinear reaction–diffusion system converged consistently for the combinations of reaction and mass-transfer parameters examined in this study. The corresponding convergence diagnostics are provided in Appendix C (Figure C.2), which illustrates solver convergence across the (μ_{max}, k_L) parameter domain used in the regime analysis.

To develop a compact analytical representation of the regime boundary identified in this analysis, the critical Biot numbers obtained from the collapse calculations were fitted using a

power-law relationship with respect to the reaction–diffusion parameter. The resulting regression relationship is shown in Figure 4-8.

Figure 4-8 Multi-tolerance overlay of Bi_{crit} versus Φ with fitted scaling curves.

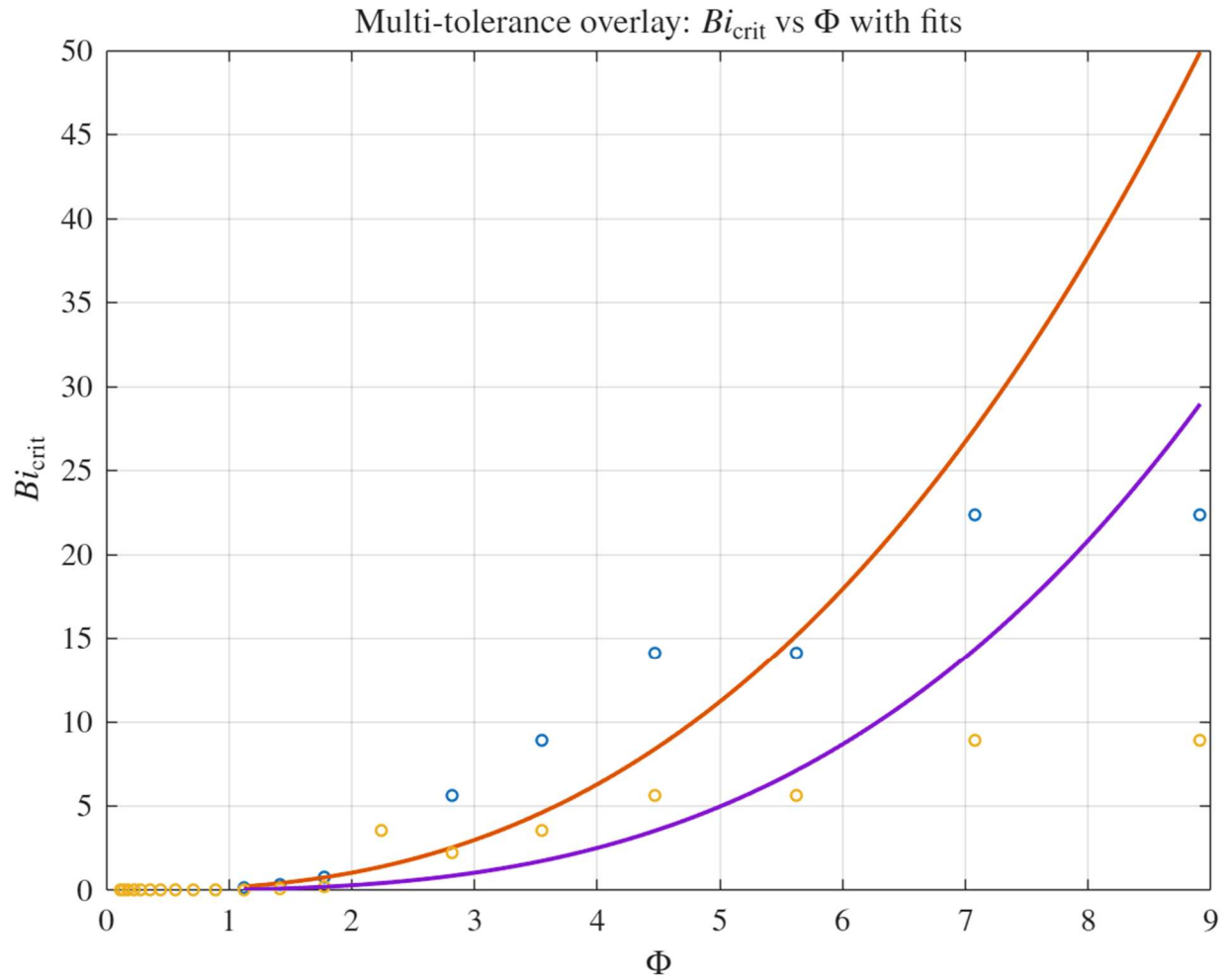
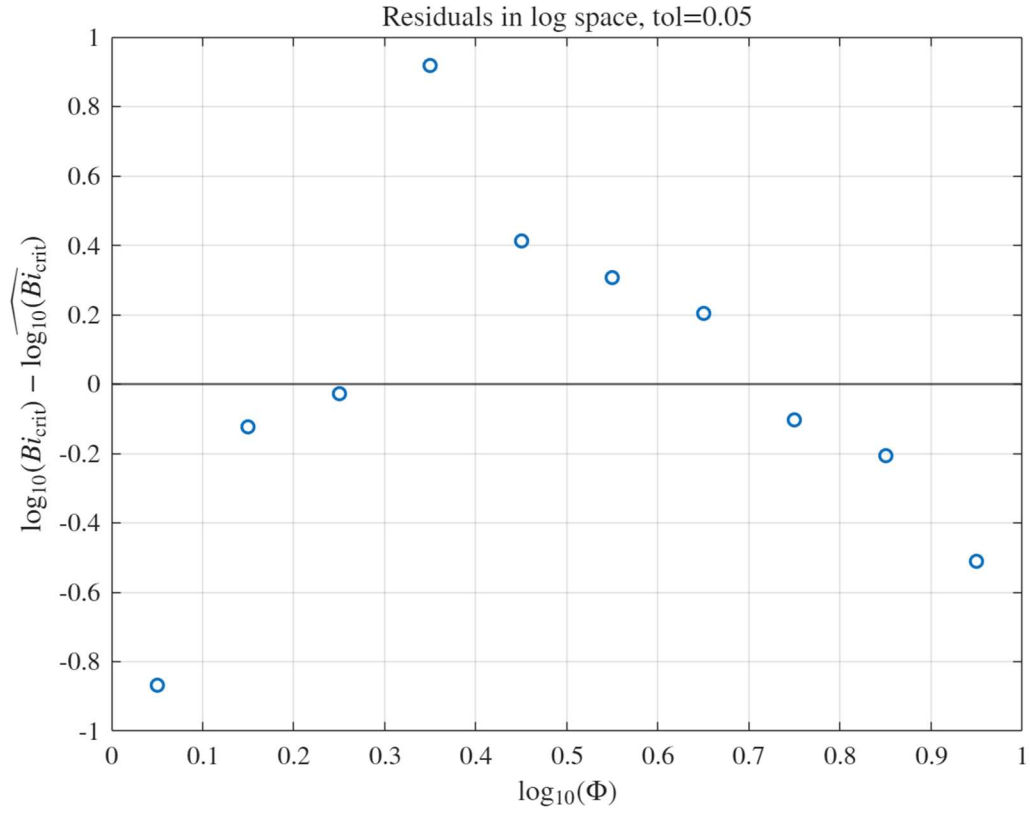
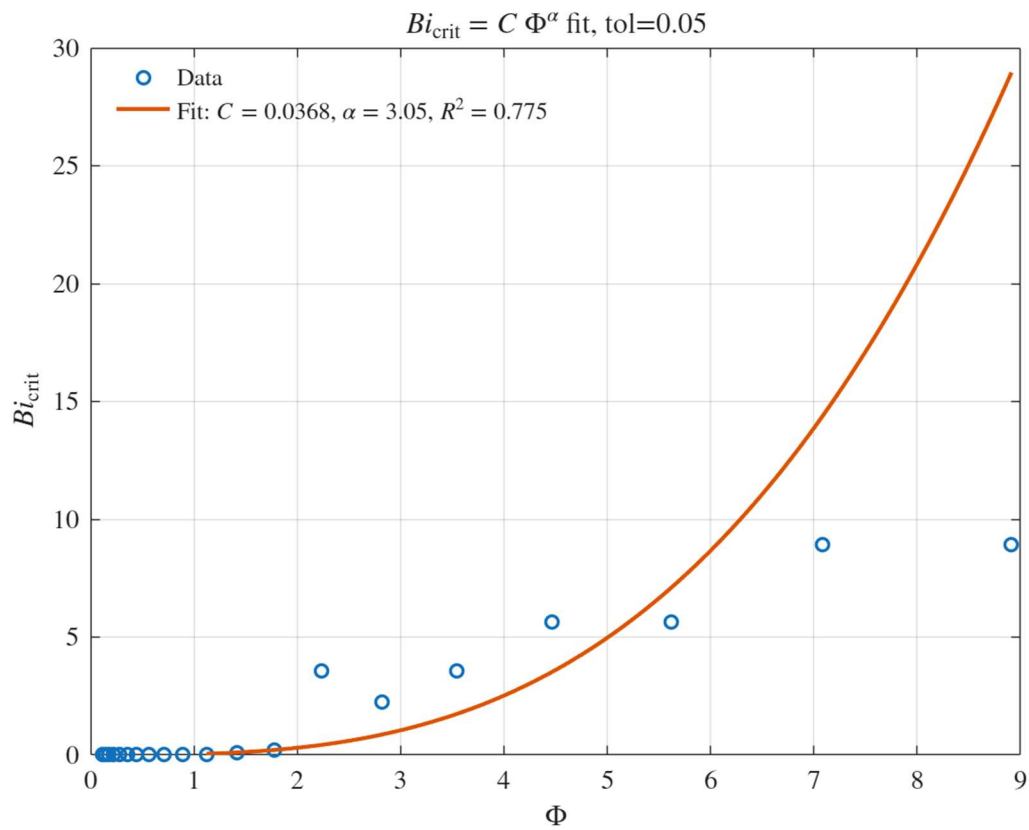


Figure 4-9 Residuals in logarithmic space for Bi_{crit} scaling fit with tolerance $\Delta\eta \leq 0.05$.



The quality of the regression fit is evaluated in Figures 4-9 and 4-10 for the tolerance criterion $\Delta\eta \leq 0.05$. These regression relationships are intended to provide approximate engineering guidance for estimating regime boundaries rather than universal scaling laws derived directly from first-principles asymptotic analysis.

Figure 4-10 Power-law fit $Bi_{crit} = C\Phi^\alpha$ for tolerance $\Delta\eta \leq 0.05$.



A similar analysis was performed for the more restrictive tolerance criterion $\Delta\eta \leq 0.02$, with the corresponding residuals and fitted power-law relationship shown in Figures 4-11 and 4-12

Figure 4-11 Residuals in logarithmic space for Bi_{crit} scaling fit with tolerance $\Delta\eta \leq 0.02$.

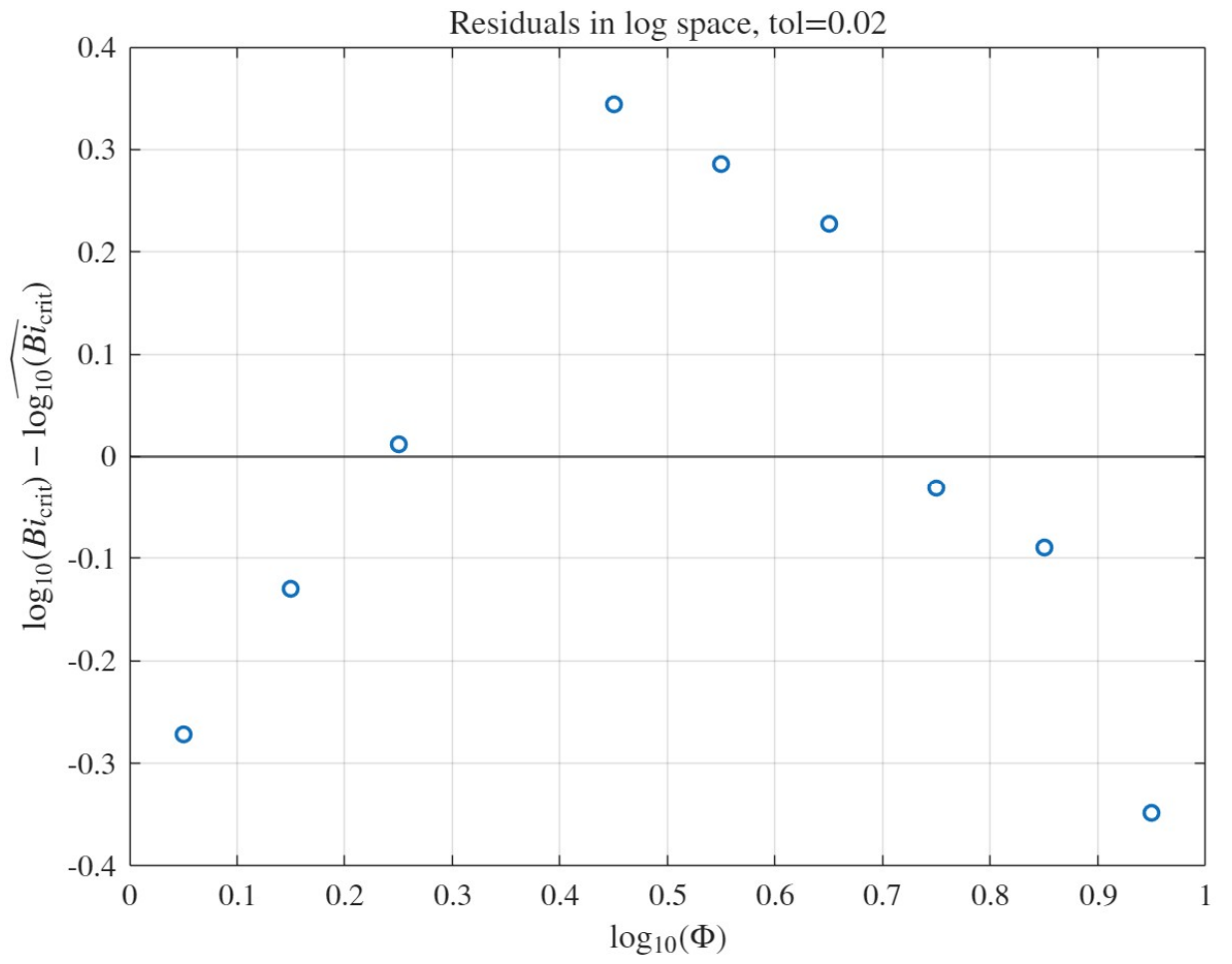
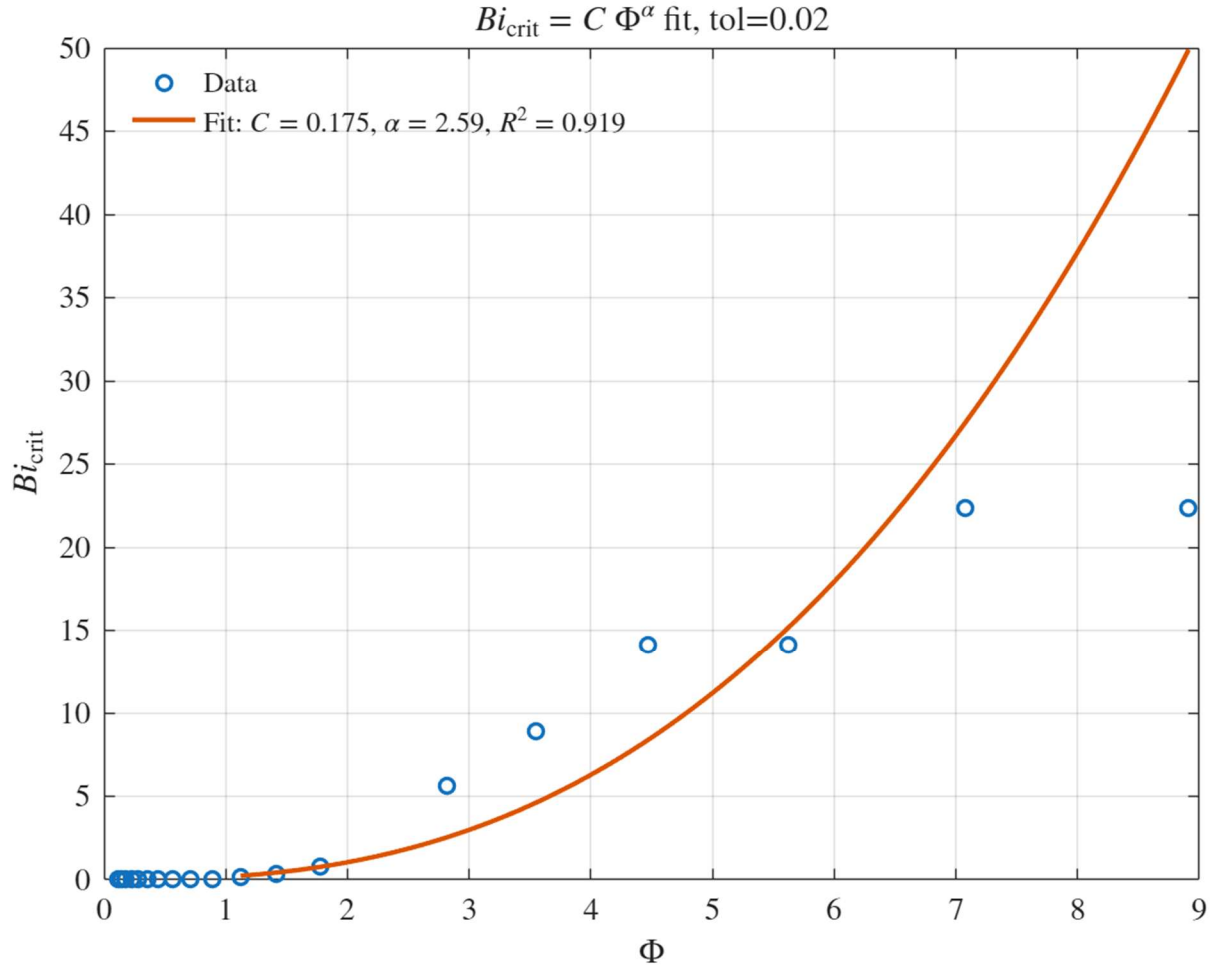


Figure 4-12 Power-law fit $Bi_{crit} = C\Phi^\alpha$ for tolerance $\Delta\eta \leq 0.02$.



These results show that the regime boundary separating internal diffusion control from combined internal and external transport limitation can be represented using the approximate scaling relationship described in equation 44 which corresponds to the regime boundary scaling relationship described in Appendix A.

$$Bi_{m,crit}(\Phi) \approx C\Phi^\alpha \quad [\text{eqn. 44}]$$

This relationship provides a compact engineering criterion for estimating the external mass-transfer strength required to prevent additional transport limitations at the granule surface. The expression therefore offers a practical design guideline for evaluating whether external mass transfer resistance can be neglected for a given granular system. The critical Biot number

relationship presented here is derived from numerical collapse analysis of the simulation results rather than from an analytical asymptotic derivation of the governing equations. The resulting power-law representation should therefore be interpreted as an empirical engineering correlation describing the numerical regime boundary within the parameter ranges investigated in this work.

The dimensionless framework developed in this section therefore provides a systematic method for identifying the governing transport regime in granular anaerobic systems. By evaluating the relative magnitudes of the reaction–diffusion parameter and the mass-transfer Biot number, it becomes possible to determine whether microbial activity within granular biomass is controlled primarily by intrinsic kinetics, internal diffusion limitations, or external mass transfer resistance. This regime identification framework forms the basis for the stability analysis developed in the following section.

5 Reaction Effectiveness & Stability Implications in Granular Biomass

5.1 Effectiveness Factors for Granular Anaerobic Systems

The transport analysis developed previously demonstrated that microbial activity within granular biomass depends strongly on the interaction between intrinsic microbial kinetics, internal diffusion, and external mass transfer. When transport limitations are present, the substrate concentration experienced by microorganisms within the aggregate differs from the bulk liquid concentration surrounding the granule. As a result, the effective reaction rate of the microbial community deviates from the intrinsic kinetic rate predicted from bulk concentration measurements.

A convenient metric for quantifying the influence of transport limitations on microbial activity is the effectiveness factor. The effectiveness factor represents the ratio between the actual reaction rate occurring within the granule and the reaction rate that would occur if the entire biomass were exposed to the substrate concentration present at the granule surface. This concept arises naturally from the reaction–diffusion formulation presented earlier and provides a compact measure of the extent to which diffusion limitations reduce the metabolic activity of the microbial aggregate.

Using the definitions introduced in Appendix A, the observed substrate utilization rate of a granule is obtained by integrating the local reaction rate throughout the aggregate volume as shown in equation 45.

$$R_{obs} = \int_0^R r_S(S(r)) 4\pi r^2 dr \quad [\text{eqn. 45}]$$

The intrinsic reference rate is defined as the rate that would occur if the entire granule were exposed to the substrate concentration at the surface, which is defined in equation 46.

$$R_{intrinsic} = r_S(S_s, X_{avg}) \frac{4}{3} \pi R^3 \quad [\text{eqn. 46}]$$

The effectiveness factor is then written as shown in equation 47 which corresponds to the effectiveness factor definition presented in Appendix A.

$$\eta = \frac{R_{obs}}{R_{intrinsic}} \quad [\text{eqn. 46}]$$

Values of the effectiveness factor close to unity indicate that diffusion limitations are weak and that the majority of the biomass within the granule participates in substrate conversion. As diffusion resistance becomes more significant, substrate penetration into the interior of the aggregate becomes restricted. Under these conditions, only a fraction of the microbial population remains metabolically active, causing the effectiveness factor to decrease.

The effectiveness factor therefore provides a quantitative link between intrinsic microbial kinetics and the effective reaction behavior observed at the granule scale. Because the effectiveness factor depends on the spatial substrate concentration field within the aggregate, it reflects the combined influence of the transport parameters identified in the regime analysis of the previous section.

The effectiveness behavior of granular anaerobic systems is particularly important because it determines the fraction of biomass that actively contributes to substrate conversion. As the reaction–diffusion parameter increases, substrate gradients within the granule become more pronounced, and the active microbial region becomes confined to the outer layers of the aggregate. Microorganisms located deeper within the granule experience lower substrate concentrations and may contribute little to the overall reaction rate [19,28].

This concept provides a direct connection between the reaction–diffusion analysis developed earlier and the broader question of granule stability. Because microbial growth depends on the local reaction rate within the biomass, diffusion limitations that reduce the effective reaction rate can also influence the long-term persistence of granular aggregates. When substrate transport becomes insufficient to sustain metabolic activity throughout the granule, the net biomass growth rate may decrease, potentially affecting the stability of the aggregate within the reactor.

The effectiveness framework developed in this section therefore provides the foundation for analyzing the relationship between microbial growth and biomass stability in granular anaerobic systems. By quantifying the fraction of biomass that remains metabolically active under different transport conditions, the effectiveness factor provides a mechanistic link between the reaction–diffusion transport behavior of the granule and the growth dynamics of the microbial community. The following section builds on this framework by examining how the interaction

between microbial growth and biomass detachment determines whether a granule experiences net growth, neutral stability, or shrinkage under a given set of operating conditions.

5.2 Transport Limitations & Apparent Granule Stability

The effectiveness framework introduced in the previous section provides a quantitative measure of how transport limitations influence the metabolic activity of granular biomass. While the effectiveness factor describes how diffusion and external mass transfer affect substrate utilization rates, the long-term persistence of granular aggregates depends on whether the resulting microbial growth is sufficient to offset biomass loss from the granule surface. The stability of granular biomass therefore emerges from the balance between internal microbial growth and surface detachment processes.

The growth–detachment balance governing granule stability is derived in Appendix A. The total biomass within a spherical granule is defined in equation 47.

$$M_X = \int_0^R X(r) 4\pi r^2 dr \quad [\text{eqn. 47}]$$

time rate of change of the total biomass within the granule is then written in equation 48.

$$\frac{dM_X}{dt} = \int_0^R [\mu(S(r)) - b] X(r) 4\pi r^2 dr - J_{det} 4\pi R^2 \quad [\text{eqn. 48}]$$

which corresponds to the biomass balance derived in Appendix A (Eq. A.47). The first term represents the volumetric biomass production resulting from microbial growth minus endogenous decay, while the second term represents biomass loss from the granule surface due to detachment or erosion.

The surface detachment flux is modeled as a hydrodynamically driven process proportional to the local shear stress, the constitutive closure corresponds to the detachment model presented in Appendix A using equation 49.

$$J_{det} = k_d \tau \quad [\text{eqn. 49}]$$

where k_d is a detachment proportionality constant and τ represents the hydrodynamic shear stress acting on the granule surface. Equation 50 corresponds to the hydrodynamic scaling relation derived in Appendix A. The shear stress is related to the fluid velocity surrounding the granule

through

$$\tau = \frac{1}{2}\rho U^2 f \quad [\text{eqn. 50}]$$

In this expression, U represents a characteristic fluid velocity, f represents a friction factor associated with the flow regime, and ρ represents the fluid density.

The competition between biomass growth and detachment defines the stability condition for the granular aggregate. A convenient measure of this balance is the stability ratio shown in equation 51.

$$\Lambda(R, U) = \frac{\int_0^R [\mu(S(r)) - b] X(r) 4\pi r^2 dr}{k_d \tau 4\pi R^2} \quad [\text{eqn. 51}]$$

which corresponds to the stability diagnostic defined in Appendix A. This ratio provides a direct measure of the balance between biomass production and hydrodynamic erosion within the granular aggregate. Values of this parameter greater than unity indicate that biomass production exceeds surface loss and the granule experiences net growth. When the stability ratio is less than unity, biomass loss dominates and the granule is predicted to shrink.

To evaluate the stability behavior of granular biomass, the reaction–diffusion model described previously was coupled with the growth–detachment formulation described above. The resulting model was evaluated across a range of granule radii and hydrodynamic velocities using the numerical procedure described in Appendix B.

Figure 5-1 Granule stability map (1 = growth, 0 = neutral, -1 = shrink) in (U, R) space.

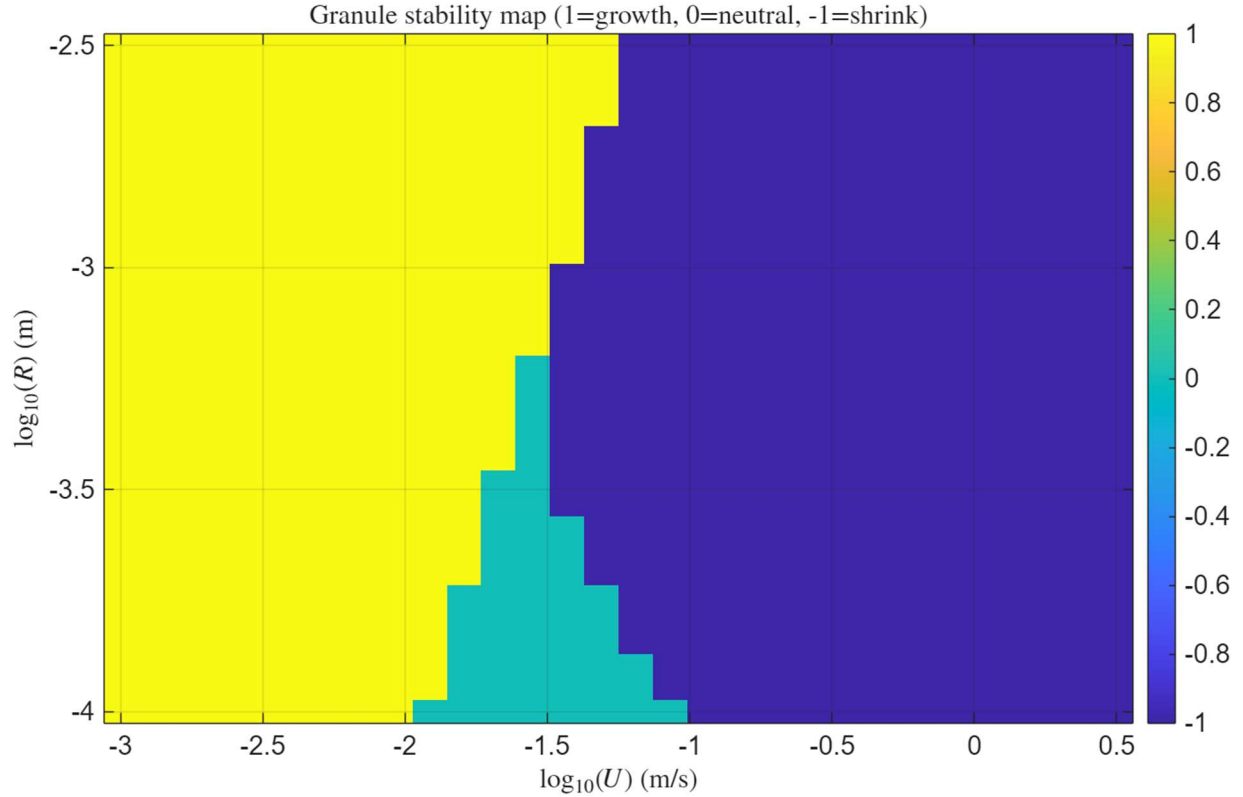


Figure 5-1 presents the resulting stability map in the parameter space defined by the superficial fluid velocity U and the granule radius R . The color scale indicates whether the predicted biomass balance corresponds to net growth, neutral stability, or shrinkage. Regions of positive stability correspond to conditions under which microbial activity within the granule produces sufficient biomass to offset detachment losses at the granule surface.

The stability map reveals a clear relationship between granule size and the hydrodynamic conditions required to maintain stable biomass. For small granules, internal diffusion limitations are weak, and substrate penetrates throughout most of the aggregate volume. Under these conditions, microbial activity remains close to intrinsic kinetic behavior and the granule can sustain growth over a wide range of hydrodynamic environments. In the present analysis the external mass-transfer coefficient was held constant while hydrodynamic velocity was varied to represent detachment effects. In practical reactor systems these quantities may be coupled through hydrodynamic correlations, and therefore the stability boundary should be interpreted as illustrating the balance between growth and detachment under the assumed transport conditions.

As the granule radius increases, internal diffusion resistance becomes more significant. Substrate penetration into the interior of the aggregate becomes restricted, causing the metabolically active region of the biomass to become confined to the outer layers of the granule. Because microbial growth occurs primarily within this diffusion-penetrated shell, the effective biomass production rate decreases relative to the total granule volume. As granules increase in size, diffusion limitations restrict substrate penetration into the aggregate interior, reducing the fraction of metabolically active biomass while hydrodynamic detachment losses continue to scale with the granule surface area.

Under these conditions, stronger external hydrodynamic transport is required to maintain sufficient substrate supply to the active biomass region. Higher fluid velocities increase the external mass transfer coefficient and reduce the thickness of the hydrodynamic boundary layer surrounding the granule. This increases the substrate concentration at the granule surface and partially compensates for the internal diffusion limitations within the biomass.

The curved stability boundary observed in Figure 5-1 therefore reflects the combined influence of internal diffusion and external transport resistance on microbial growth within the aggregate. Larger granules require stronger hydrodynamic transport conditions to remain stable because the effective growth region becomes increasingly confined to the outer portion of the biomass.

This result provides a mechanistic explanation for the granule size distributions commonly observed in high-rate anaerobic reactors. Granules that grow beyond the transport-limited stability boundary will experience reduced metabolic activity relative to surface detachment, causing them to shrink until they return to the stable operating region. Conversely, granules operating within the growth region can continue to develop until internal diffusion limitations become sufficiently strong to reduce the effective growth rate.

The stability behavior observed in this analysis therefore emerges directly from the interaction between microbial kinetics, transport limitations, and hydrodynamic forcing. The next section integrates these effects to provide a unified interpretation of how kinetic, transport, and structural factors together govern the behavior of granular biomass in anaerobic reactor systems.

5.3 Integrated Interpretation of Kinetic, Transport, & Structural Effects

The preceding sections developed a framework for analyzing microbial reaction behavior in granular anaerobic systems by progressively incorporating intrinsic microbial kinetics, reaction network structure, and transport limitations. The stability analysis presented in the previous section demonstrated that the persistence of granular biomass depends on the balance between microbial growth occurring within the aggregate and hydrodynamically driven biomass loss at the granule surface. This section integrates these components to provide a unified interpretation of the processes governing granule behavior in high-rate anaerobic reactors.

The stability condition derived in Appendix A defines the boundary between granule growth and shrinkage as the condition for which the net biomass accumulation rate is zero as shown in equation 52,

$$\frac{dM_X}{dt} = 0 \quad [\text{eqn. 52}]$$

which corresponds to the neutral stability condition implied by the biomass balance equation presented in Appendix A. Under this condition, microbial growth integrated over the active region of the granule exactly balances biomass loss through detachment at the granule surface. The resulting stability boundary therefore represents the combinations of granule size and hydrodynamic transport conditions for which the aggregate can persist without net growth or decay.

The critical hydrodynamic velocity required to maintain this balance can be obtained by solving the growth-detachment equation for the velocity that satisfies the stability condition. This calculation was performed numerically using the reaction–diffusion solution described previously, combined with the growth integral defined in Appendix A (Eq. A.47). The resulting relationship between the critical superficial velocity and the granule radius is shown in Figure 5-2.

Figure 5-2 Stability boundary $U_{\text{crit}}(R)$ determined from $dM/dt = 0$ using bisection.

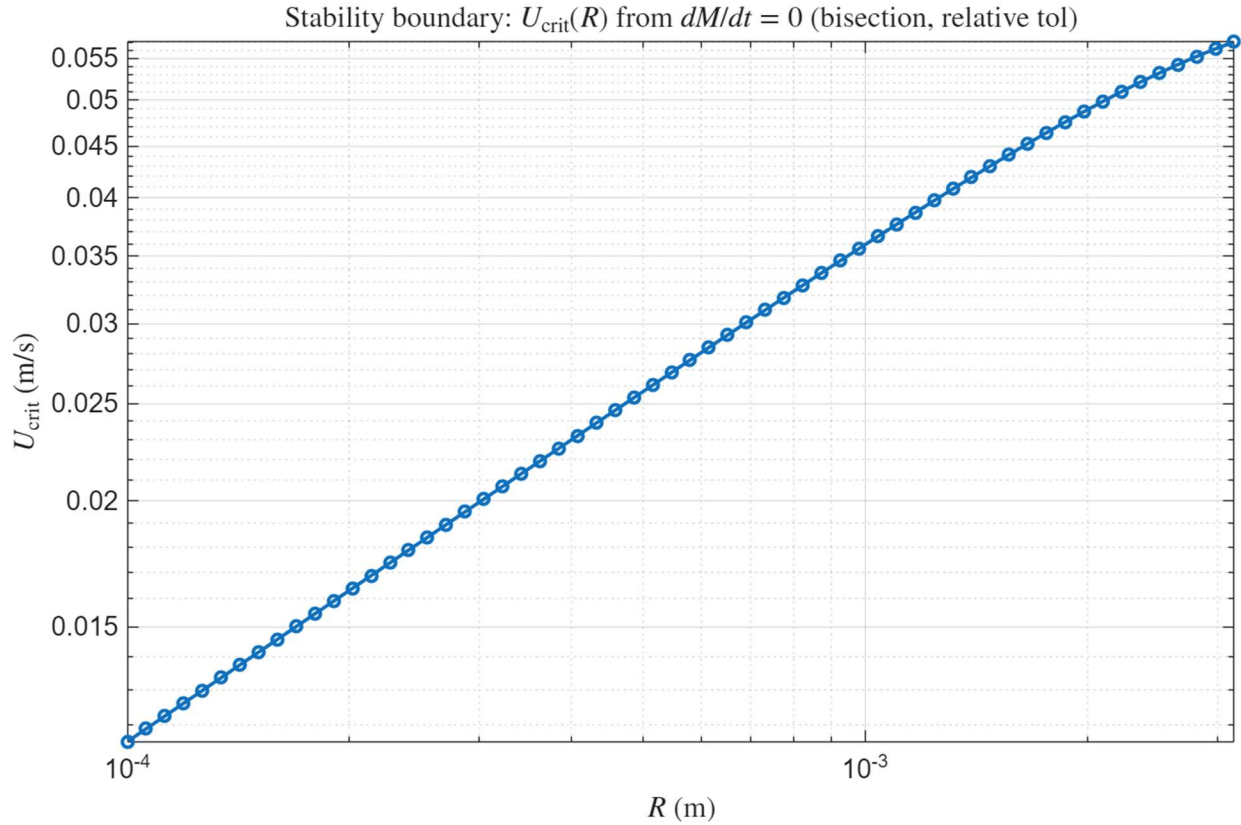


Figure 5-2 shows the combinations of granule radius and superficial velocity for which the net biomass accumulation rate is zero. The curve separates the parameter space into regions corresponding to net biomass growth and net biomass loss. The monotonic increase in the critical velocity with increasing granule radius reflects the increasing importance of internal diffusion limitations as granules become larger. When the radius of the aggregate increases, substrate must diffuse over longer distances to reach microorganisms located in the interior of the granule. This reduces the fraction of biomass that remains metabolically active and therefore decreases the effective growth rate of the aggregate.

To maintain stability under these conditions, the external hydrodynamic environment must provide sufficient mass transfer to sustain substrate supply to the active region of the granule. Increasing the external fluid velocity enhances substrate transport across the hydrodynamic boundary layer surrounding the granule, increasing the substrate concentration at the surface and partially offsetting the internal diffusion limitations within the biomass. The stability boundary

therefore represents the hydrodynamic conditions required to maintain a balance between microbial growth and surface detachment.

The numerical accuracy of the stability boundary was verified by evaluating the stability ratio along the computed curve. The resulting values are shown in Figure 5-3.

Figure 5-3 Stability diagnostic ratio $\Lambda(R, U_{\text{crit}})$ evaluated along the stability boundary (target $\Lambda \approx 1$).

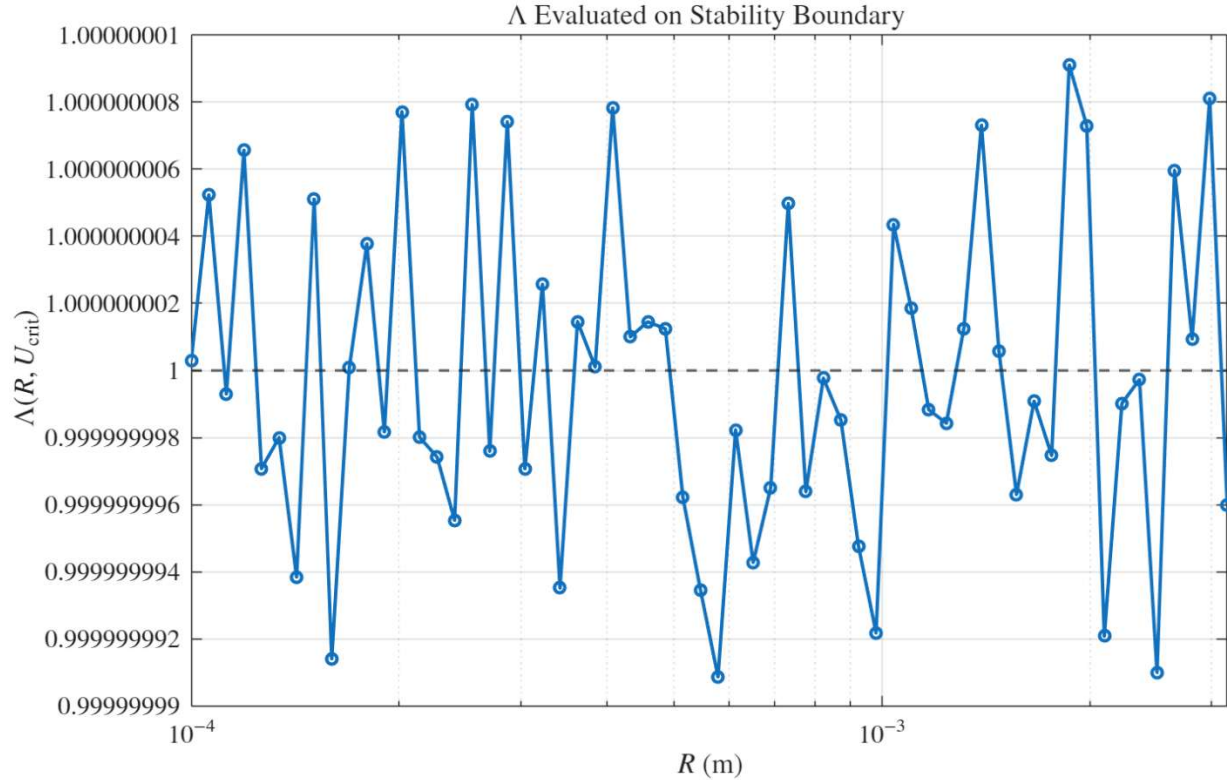


Figure 5-3 presents the stability ratio Λ evaluated along the predicted neutral stability boundary. Because the stability boundary corresponds to the condition $dM_X/dt = 0$, the stability ratio should remain approximately equal to unity along the curve. The values shown in the figure remain close to this expected value, confirming that the numerical solution procedure correctly identifies the stability condition defined by the biomass balance equation.

A broader view of the stability behavior can be obtained by evaluating the stability ratio across the full velocity–radius parameter space. The resulting stability field is shown in Figure 5-4.

Figure 5-4 Contour map of $\log_{10}(\Lambda)$ with $\Lambda = 1$ stability boundary superimposed.

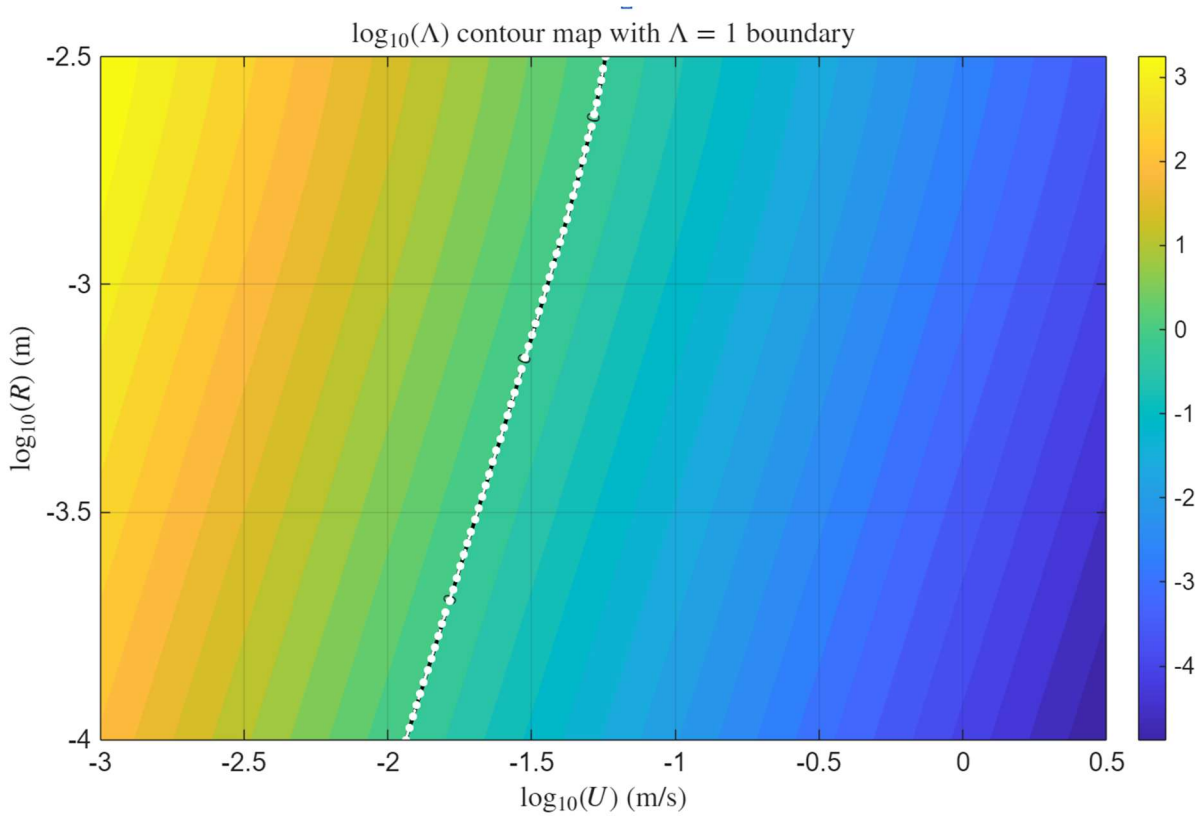


Figure 5-4 presents contours of $\log_{10}(\Lambda)$ across the parameter space defined by fluid velocity and granule radius. The contour corresponding to $\Lambda = 1$ represents the neutral stability boundary separating the growth and shrinkage regimes. Regions where $\Lambda > 1$ correspond to conditions under which microbial growth exceeds detachment losses, allowing the granule to increase in size. Conversely, regions where $\Lambda < 1$ correspond to conditions under which detachment dominates, leading to a gradual reduction in granule size.

The stability structure revealed by these results highlights the coupled influence of microbial kinetics, transport processes, and hydrodynamic conditions on the behavior of granular biomass. Intrinsic microbial kinetics determine the potential growth rate of the biomass, while diffusion limitations restrict the fraction of biomass that remains metabolically active within the granule. External hydrodynamic conditions then determine the magnitude of biomass detachment through shear-driven erosion at the granule surface.

Together, these factors determine whether a given granular aggregate can persist under a specific set of reactor operating conditions. The framework developed here therefore provides a

mechanistic interpretation of granule stability in terms of transport-limited microbial growth and hydrodynamically controlled biomass detachment. This integrated perspective provides a foundation for understanding the behavior of granular sludge systems and for interpreting the variability in granule size distributions observed in high-rate anaerobic reactors.

The synthesis presented in this section establishes the connection between microscale transport phenomena and the macroscopic behavior of granular anaerobic systems. The final section summarizes the key findings of this work and discusses their implications for reactor operation, design, and future research directions.

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6 Conclusions and Future Outlook

6.1 Summary of Key Findings

This work developed a transport-based framework for interpreting microbial reaction behavior in granular anaerobic systems. The analysis began by examining the relationship between intrinsic microbial kinetics and the apparent reaction rates observed at the reactor scale. Although microbial growth is commonly described using Monod-type kinetic expressions, the results presented in this study demonstrate that granular biomass operates within a transport-limited environment in which the substrate concentration experienced by microorganisms varies spatially within the aggregate. Consequently, the reaction rates measured at the reactor scale represent spatially averaged quantities determined by the coupled effects of microbial metabolism and substrate transport.

The reaction–diffusion formulation derived in Appendix A provided the foundation for analyzing these transport effects. By solving the nonlinear reaction–diffusion boundary-value problem governing substrate transport and microbial consumption within a spherical granule, the spatial substrate distribution within the biomass was obtained. Integration of the local reaction rate across the aggregate volume yielded the effective substrate conversion rate of the granule, providing a direct connection between intrinsic microbial kinetics and apparent reaction behavior.

The results showed that transport limitations can significantly influence the kinetic parameters inferred from reactor-scale measurements. When diffusion limitations are present, the substrate concentration within the granule interior becomes lower than the bulk liquid concentration. Regression of Monod-type models using bulk concentrations therefore produces apparent kinetic parameters that differ from the intrinsic microbial constants. In particular, the apparent half-saturation constant was shown to increase as external mass-transfer resistance becomes stronger, demonstrating that transport limitations can bias the interpretation of microbial kinetic measurements [12].

The analysis was then extended to consider the influence of reaction network structure within granular biomass. Anaerobic digestion proceeds through a series of metabolically coupled reactions involving multiple microbial populations. By representing these reactions as a reduced

network embedded within the granular transport framework, the model demonstrated how diffusion limitations can alter the spatial distribution of intermediate species and thereby modify the relative activity of competing metabolic pathways. The resulting transport-conditioned selectivity provides a mechanistic explanation for variations in apparent pathway activity observed in anaerobic microbial communities [8], [31].

A dimensionless analysis of the reaction–diffusion system revealed that the behavior of granular biomass is governed primarily by two transport parameters: the reaction–diffusion parameter Φ and the mass-transfer Biot number Bi_m . These parameters characterize the relative importance of internal diffusion resistance and external hydrodynamic transport. Numerical simulations across this parameter space were used to construct regime maps that classify the conditions under which microbial activity is controlled by intrinsic kinetics, internal diffusion limitations, or external mass transfer resistance. The boundary separating these regimes was shown to follow an approximate power-law scaling relationship between the reaction–diffusion parameter and the critical Biot number.

Finally, the reaction–diffusion framework was coupled with a biomass growth–detachment balance to examine the stability of granular aggregates. The resulting model showed that granule persistence is determined by the balance between volumetric microbial growth within the aggregate and shear-driven biomass loss at the granule surface. Larger granules experience stronger internal diffusion limitations, which reduce the fraction of metabolically active biomass. As a result, stronger hydrodynamic transport conditions are required to sustain growth as granule size increases. The stability maps generated in this work illustrate how the combined effects of microbial kinetics, transport limitations, and hydrodynamic forcing determine the conditions under which granular biomass can persist in high-rate anaerobic reactors.

Together, these results demonstrate that granular anaerobic systems must be interpreted as transport-limited reacting particles rather than as well-mixed microbial suspensions. The apparent kinetics, pathway selectivity, and structural stability of granular biomass all emerge from the interaction between microbial metabolism and transport processes within the aggregate. Understanding this coupling provides a mechanistic basis for interpreting reactor-scale observations and for predicting the behavior of granular sludge systems under different operating conditions.

6.2 Implications for Reactor Operation and Design

The transport-based framework developed in this work provides several insights relevant to the operation and design of high-rate anaerobic reactors. Because granular biomass behaves as a transport-limited reacting particle, reactor performance depends strongly on maintaining conditions that allow substrate to penetrate the metabolically active region of the granule. Reactor hydrodynamics therefore play a critical role in determining the effectiveness of substrate transport to and within the biomass.

External hydrodynamic conditions influence the mass-transfer coefficient governing substrate transport across the liquid film surrounding the granule. Increased mixing intensity or higher superficial velocities reduce the thickness of the hydrodynamic boundary layer and increase the external mass-transfer coefficient. Under these conditions, the substrate concentration at the granule surface approaches the bulk concentration, minimizing external transport resistance and allowing the internal diffusion process to dominate substrate delivery to the biomass.

The regime analysis presented in this study provides a systematic method for evaluating whether external mass transfer limitations are likely to influence reactor performance. By estimating the reaction–diffusion parameter and the mass-transfer Biot number for a given reactor system, it is possible to determine whether microbial activity is primarily limited by intrinsic kinetics, internal diffusion resistance, or external hydrodynamic transport. This type of analysis can help guide reactor design decisions related to mixing intensity, hydraulic loading, and granule size management.

The stability analysis presented in Chapter 5 also highlights the importance of hydrodynamic conditions in maintaining stable granular biomass populations. Granules that grow beyond the transport-limited stability boundary may experience reduced metabolic activity relative to surface detachment, leading to gradual shrinkage or structural instability. Conversely, granules operating within the stable region of the parameter space can maintain sustained microbial growth while resisting hydrodynamic erosion.

These results suggest that reactor operation strategies should consider both microbial kinetics and transport processes when evaluating system performance. Monitoring granule size distributions, mixing intensity, and hydraulic loading conditions may provide useful indicators of

whether granular biomass is operating within a favorable transport regime. Incorporating transport-based criteria into reactor design and operation could therefore improve the predictability and stability of high-rate anaerobic treatment systems. The dimensionless framework developed in this work provides a systematic method for evaluating the transport environment experienced by granular biomass. By estimating the reaction-diffusion parameter and the mass-transfer Biot number for a given reactor configuration, it becomes possible to assess whether microbial activity is likely to be controlled primarily by intrinsic kinetics, internal diffusion, or external mass transfer. This perspective provides a mechanistic basis for interpreting variations in reactor performance across different hydrodynamic conditions.

6.3 Opportunities for Future Research

While the reaction-diffusion framework developed in this work captures the fundamental transport processes governing microbial activity within granular biomass, several opportunities remain for extending and refining the model. The present analysis considered a simplified spherical granule geometry with uniform biomass distribution. In practice, microbial aggregates often exhibit complex internal structures, including layered microbial populations, spatial variations in biomass density, and heterogeneous pore structures. Incorporating these structural features into transport models could improve the accuracy of predictions for real granular systems.

The modeling framework developed in this work represents a simplified description of granular biomass behavior intended to isolate the fundamental coupling between microbial kinetics and transport processes. The reaction network representation is reduced relative to the full metabolic complexity of anaerobic digestion, and the regime boundaries identified in the transport analysis are based on numerical parameter sweeps rather than analytical asymptotic solutions. Future work could extend the present framework by incorporating additional microbial populations, experimentally constrained transport coefficients, and hydrodynamic models that explicitly couple shear stress and external mass transfer.

The reaction network representation used in this study was intentionally simplified to illustrate how transport processes influence metabolic pathway interactions. More detailed models incorporating additional intermediate species and microbial populations could provide deeper insight into the dynamics of anaerobic digestion systems. Integration of such models with

established anaerobic digestion frameworks, such as the Anaerobic Digestion Model No. 1 (ADM1), may provide a pathway toward more comprehensive descriptions of microbial community behavior in granular reactors [8].

Another important direction for future work involves coupling the reaction–diffusion framework with hydrodynamic models describing the flow environment within anaerobic reactors. Computational fluid dynamics simulations and tracer studies have shown that flow patterns within granular sludge reactors can influence mass transfer conditions and granule motion within the reactor volume [24], [25]. Integrating these hydrodynamic effects with the transport model developed here could provide a more complete representation of the interaction between reactor-scale flow behavior and microscale microbial activity.

Experimental validation of the transport-based predictions developed in this work also represents an important area for future research. Measurements of substrate concentration profiles, metabolic activity distributions, and granule stability under controlled hydrodynamic conditions could provide valuable data for testing the reaction–diffusion framework. Such experiments could help clarify the relationship between microbial kinetics, transport limitations, and structural stability in granular anaerobic systems.

This work reframes granular anaerobic biomass as a transport-limited reacting particle system and demonstrates how diffusion and hydrodynamic transport modify apparent kinetics, pathway selectivity, and structural stability. The dimensionless regime framework and stability criteria developed here provide a physically interpretable basis for evaluating transport constraints in high-rate anaerobic reactors. The transport-based perspective presented in this work highlights the importance of considering spatial transport processes when interpreting the behavior of microbial aggregates. The transport-based framework developed in this study provides a mechanistic foundation for interpreting granular anaerobic systems and highlights the importance of integrating microbial kinetics, transport phenomena, and reactor engineering principles when analyzing and designing high-rate biological treatment processes.

References

- [1] L.W. Hulshoff Pol,, S.I. De Castro Lopes,, G. Lettinga,, P.N.L. Lens, *Water Res.* 38(6) (2004) 1376–89. 10.1016/j.watres.2003.12.002.
- [2] Y. Liu,, J.-H. Tay, *Biotechnol. Adv.* 22 (2004) 533–653. 10.1016/j.biotechadv.2004.05.001.
- [3] R. Mulder, *Biological wastewater treatment for industrial effluents: technology and operation*, P. Thomas, Paques B.V., Balk, The Netherlands, 2003.
- [4] S. Mills,, A.C. Trego,, M. Prevedello,, J. De Vrieze,, V. O’Flaherty,, P.N.L. Lens,, G. Collins, *Environmental Science and Ecotechnology* (2024). 10.1016/j.esse.2023.100310.
- [5] J. Van Lier,, J. Sanz Martin,, G. Lettinga, *Water Res.* 30(1) (1996) 199–207. 10.1016/0043-1354(95)00107-V.
- [6] B. Wilen,, D. Gapes,, J. Keller, *Biotechnol. Bioeng.* 86(4) (2004) 445–57. 10.1002/bit.20058.
- [7] J. Palasti,, R. Affes,, B. Fernandez,, M. Pereira,, M. Alves,, X. Flotats, *Water Res.* 46 (2012) 5268–78. 10.1016/h.watres.2012.07.008.
- [8] R. Mo,, W. Guo,, D. Batstone,, J. Makinia,, Y. Li, *Water Res.* (2023). 10.1016/j.watres.2023.120504.
- [9] L. Hinken,, M. Huber,, D. Weichgrebe,, K.H. Rosenwinkel, *Water Res.* 64 (2014) 82–93. 10.1016/j.watres.2014.06.044.
- [10] Y. Huang,, Y. Ma,, J. Wan,, Y. Wang, *Front. Microbiol.* 12 (2021). 10.3389/fmicb.2021.755398.
- [11] A. Doloman,, H. Varghese,, C. Miller,, N. Flann, *BMC Syst. Biol.* 11(69) (2017). 10.1186/s12918-017-0443-z.
- [12] E. Giraldo-Gomez,, S. Goodwin,, M. Switzenbaum, *Biotechnol. Bioeng.* 40(7) (1992) 768–76. 10.1002/bit.260400704.
- [13] A. Alphenaar, *ANAEROBIC GRANULAR SLUDGE: CHARACTERIZATION, AND FACTORS AFFECTING ITS FUNCTIONING*. Ph.D. Thesis, Wageningen Agricultural University, 1994.
- [14] A. Vlyssides,, E.M. Barampouti,, S. Mai, *J. Environ. Manage.* 86(4) (2008) 660–4. 10.1016/j.jenvman.2006.12.018.
- [15] X. Liu,, D. Pan,, Q. Yuan,, X. Feng,, M. Li,, X. Song,, M. Li,, Y. Ge,, Y. Xing,, Y. Yu,, Z. Jin, *Science of the Total Environment* 912 (2024). 10.1016/j.scitotenv.2023.169064.

- [16] Z. Wang,, K. Jiang,, Y. Zhu,, L. Liu,, X. Zou,, X. Yang,, Y. Xu,, J. Zhang,, Y. Chen,, W. Gao,, S. Wang, *Journal of Water Process Engineering* (2023).
10.1016/j.jwpe.2023.103695.
- [17] J. Tay,, Q. Liu,, Y. Liu, *Appl. Microbiol. Biotechnol.* 57 (2001) 227–33.
10.1007/s002530100766.
- [18] Y. Liu,, J.-H. Tay, *Water Res.* 36(7) (2002) 1653–65. 10.1016/S0043-1354(01)00379-7.
- [19] P.N.L. Lens,, R. Gastesi,, F. Vergeldt,, A. Van Aelst,, A. Pisabarro,, H. Van As, *Appl. Environ. Microbiol.* 69(11) (2003) 6644–9. 10.1128/AEM.69.11.6644-6649.2003.
- [20] G. Gonzalez,, L. Seghezze,, G. Lettinga,, R. Kleerebezem, *Biotechnol. Bioeng.* 73(2) (2000) 125–34. 10.1002/bit.1044.
- [21] H.S. Fogler, *Elements of Chemical Reaction Engineering Fifth Edition*, 5th ed., Prentice Hall / Pearson Education, Philadelphia, PA, USA, 2016.
- [22] L.A. Glasgow, *Transport Phenomena: An introduction to Advanced Topics*, 1st ed., John Wiley & Sons, Inc., Hoboken, NJ, USA, 2010.
- [23] A. Tenore,, F. Russo,, M.R. Mattei,, B. D’Acunto,, G. Collins,, L. Frunzo, *Bull. Math. Biol.* 83(12) (2021). 10.1007/s11538-021-00951-y.
- [24] B. Patel,, P. Gundaliya,, U. Patel,, U. Khare, *Environmental Challenges* 5 (2021).
10.1016/j.envc.2021.100358.
- [25] C. Bastiani,, D. Kennedy,, A. Reynolds, *Water Res.* 242 (2023).
10.1016/j.watres.2023.120220.
- [26] A. Rodrigues, *Chem. Eng. Sci.* 230 (2021). 10.1015/j.ces.2020.116188.
- [27] B. Xing,, X. Tang,, L. Lu,, Y. Fu,, J. Liu,, Y. Wang,, X. Sun,, Y. Li,, R. Chen,, R. Jin, *Bioresour. Technol.* 400 (2024). 10.1016/j.biortech.2024.130700.
- [28] P.N.L. Lens,, D. De Beer,, C. Cronenberg,, F. Houwen,, S. Ottengraf,, W. Verstraete, *Appl. Environ. Microbiol.* 59(11) (1993) 3803–15. <https://doi.org/10.1128/aem.59.11.3803-3815.1993>.
- [29] D. De Beer,, J. Huisman,, J. Van Den Heuvel,, S. Ottengraf, *Water Res.* 26(10) (1992) 1329–36. 10.1016/0043-1354(92)90127-P.
- [30] M. Wu,, C. Criddle,, R. Hickey, *Biotechnol. Bioeng.* 46(5) (1995) 465–75.
10.1002/bit.260460511.
- [31] Y. Liu,, H.-L. Xu,, S.-F. Yang,, J.-H. Tay, *Mechanisms and models for anaerobic granulation in upflow anaerobic sludge blanket reactor*, Vol. 37, 2003.

- [32] R. Voolapalli,, D. Stuckey, *Appl. Environ. Microbiol.* 65(11) (1999) 5009–16. 10.1128/aem.65.11.5009-5016.1999.
- [33] M.A. Pereira,, O.C. Pires,, M. Mota,, M.M. Alves, *Biotechnol. Bioeng.* 92(1) (2005) 15–23. 10.1002/bit.20548.
- [34] M. Wu,, R. Hickey, *Journal of Environmental Engineering* 123(3) (1997) 244–52. 10.1061/(ASCE)0733-9372(1997)123:3(244).
- [35] R. Turton,, J. Shaeiwitz,, D. Bhattacharyya, *Analysis, Synthesis, and Design of Chemical Processes*, 5th ed., Prentice Hall / Pearson Education Inc., Boston, MA, USA, 2018.
- [36] M. Hajaya,, R. Alkaraki,, N. Kurnikova,, S. Bordel,, R. Munoz, *Journal of Water Process Engineering* 71 (2025). 10.1016/j.jwpe.2025.107230.
- [37] D. Poggio,, M. Walker,, W. Nimmo,, L. Ma,, M. Pourkashanian, *Waste Management* 53 (2016) 40–54. 10.1016/j.wasman.2016.04.024.
- [38] M.R. Mattei,, B. D’Acunto,, G. Esposito,, L. Frunzo,, F. Pirozzi, *Desalination Water Treat.* 55(3) (2015) 740–8. 10.1080/19443994.2014.937764.
- [39] S. Astals,, M. Esteban-Gutiérrez,, T. Fernández-Arévalo,, E. Aymerich,, J.L. García-Heras,, J. Mata-Alvarez, *Water Res.* 47(16) (2013) 6033–43. 10.1016/j.watres.2013.07.019.
- [40] A. Ding,, M. Hounslow,, C. Biggs, *Chem. Eng. Sci.* 61 (2006) 63–74. 10.1016/j.ces.2005.02.074.
- [41] G. Gonzalez,, P.N.L. Lens,, A. Van Aelst,, H. Van As,, A.I. Versprille,, G. Lettinga, *Applied and Environmental Biology* 67(8) (2001) 3683–962. 10.1128/AEM.67.8.3683-3692.2001.

Appendix A - Governing Equations

The notation used in this appendix follows the definitions provided in the Nomenclature section of the report. Only variables introduced specifically for intermediate derivations are defined locally where they appear.

A.1 System Geometry and Model Variables

The granule is modeled as a sphere of radius R with radial coordinate r , where

$$0 \leq r \leq R$$

Substrate transport is assumed to occur only in the radial direction, consistent with a spherically symmetric granule. The local limiting-substrate concentration is denoted $S(r)$, the bulk liquid concentration is S_b , and the granule surface concentration is

$$S_s = S(R)$$

For the substrate transport calculations used in the numerical model, the biomass concentration is prescribed as spatially uniform and constant within the granule,

$$X(r) = X_0$$

This permits the substrate field to be solved from a steady diffusion–reaction balance while retaining intrinsic Monod kinetics in the local reaction term.

The external liquid phase is represented through a film model with liquid-side mass-transfer coefficient k_L . Internal transport resistance is captured through an effective diffusivity D_e , which lumps the effects of porosity, tortuosity, and constriction.

The framework developed in this appendix is subsequently extended to effectiveness calculations, reduced network selectivity diagnostics, and a granule stability criterion based on the competition between biomass growth and shear-driven detachment.

A.2 Governing Transport–Reaction Equations

For a spherical granule with steady radial diffusion and local substrate consumption, the substrate balance is

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 D_e \frac{dS}{dr} \right) - r_S(S) = 0 \quad [\text{A.1}]$$

For the present model, D_e is taken as constant, so Eq. (A.1) reduces to

$$D_e \left(\frac{d^2 S}{dr^2} + \frac{2}{r} \frac{dS}{dr} \right) - r_S(S) = 0 \quad [\text{A.2}]$$

The reaction term is coupled to intrinsic microbial kinetics through a growth-associated consumption law. With biomass fixed at X_0 in the transport calculation, the local substrate sink becomes

$$r_S(S) = \frac{\mu(S)X_0}{Y} \quad [\text{A.3}]$$

Substituting the Monod expression from Section A.3 gives

$$r_S(S) = \frac{\mu_{\max} X_0}{Y} \frac{S}{K_S + S} \quad [\text{A.4}]$$

Hence the steady spherical reaction–diffusion equation solved in the model is

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 D_e \frac{dS}{dr} \right) - \frac{\mu_{\max} X_0}{Y} \frac{S}{K_S + S} = 0 \quad [\text{A.5}]$$

The observed total substrate uptake rate is obtained by integrating the local consumption over the full granule volume,

$$R_{\text{obs}} = \int_0^R r_S(r) 4\pi r^2 dr \quad [\text{A.6}]$$

Using Eq. (A.4), this may also be written as

$$R_{\text{obs}} = \int_0^R \frac{\mu_{\max} X_0}{Y} \frac{S(r)}{K_S + S(r)} 4\pi r^2 dr \quad [\text{A.7}]$$

Flux continuity at the granule surface gives an equivalent expression

$$R_{\text{obs}} = -4\pi R^2 J_{\text{out}}(R) \quad [\text{A.8}]$$

where the outward diffusive flux is

$$J_{\text{out}}(R) = -D_e \frac{dS}{dr} \big|_{r=R} \quad [\text{A.9}]$$

An apparent specific growth rate can then be defined by normalizing the observed uptake rate to the total biomass:

$$R_{\text{obs}} = \frac{1}{Y} \mu_{\text{app}} M_X \quad [\text{A.10}]$$

with

$$\mu_{\text{app}} = \frac{\int_0^R \mu(S(r)) X(r) 4\pi r^2 dr}{\int_0^R X(r) 4\pi r^2 dr} \quad [\text{A.11}]$$

For the numerical implementation in this report, $X(r) = X_0$, so Eq. (A.11) reduces to a volume-weighted average of $\mu(S)$.

A.3 Reaction Kinetics

The intrinsic microbial growth law is written in Monod form:

$$\mu(S) = \mu_{\text{max}} \frac{S}{K_S + S} \quad [\text{A.12}]$$

where μ_{max} is the maximum specific growth rate and K_S is the half-saturation constant.

The corresponding biomass balance including endogenous decay is

$$\frac{dX}{dt} = \mu(S)X - bX \quad [\text{A.13}]$$

Equation (A.13) provides the intrinsic kinetic statement used to distinguish synthesis from decay. In the transport calculations of this report, biomass is prescribed and Eq. (A.13) is not solved directly. Instead, its kinetic structure informs the local reaction term and the later stability analysis.

For the reduced reaction-network interpretation, the bulk species balances are written compactly as

$$\frac{dS_b}{dt} = N\bar{r} \quad [\text{A.14}]$$

The state vector for the reduced subsystem is

$$S_b = \begin{bmatrix} S_{\text{Pr},b} \\ S_{\text{Bu},b} \\ S_{\text{Ac},b} \\ S_{\text{H}_2,b} \\ S_{\text{CO}_2,b} \\ S_{\text{CH}_4,b} \end{bmatrix} \quad [\text{A.15}]$$

with stoichiometric matrix

$$N = \begin{bmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 2 & 0 & -1 \\ 3 & 2 & -4 & 0 \\ 1 & 0 & -1 & 1 \\ 0 & 0 & 1 & 1 \end{bmatrix} \quad [\text{A.16}]$$

The volume-averaged rate of reaction j is defined as

$$\bar{r}_j = \frac{1}{V} \int_0^R r_j(r) 4\pi r^2 dr \quad [\text{A.17}]$$

Intrinsic and apparent selectivity ratios are then

$$\Sigma_{\text{int}} = \frac{r_1(S_{\text{H}_2}(R))}{r_3(S_{\text{H}_2}(R))} \quad [\text{A.18}]$$

$$\Sigma_{\text{app}} = \frac{\bar{r}_1}{\bar{r}_3} \quad [\text{A.19}]$$

A.4 Boundary Conditions

At the granule center, spherical symmetry requires

$$\frac{dS}{dr} \big|_{r=0} = 0 \quad [\text{A.20}]$$

At the granule surface, continuity of flux between the granule and liquid film gives

$$-D_e \frac{dS}{dr} \big|_{r=R} = k_L (S_b - S_s) \quad [\text{A.21}]$$

For analytical reference, a Dirichlet condition may also be imposed

$$S(R) = S_s \quad [\text{A.22}]$$

The total biomass in a granule is

$$M_X(t) = \int_0^R X(r, t) 4\pi r^2 dr \quad [\text{A.23}]$$

The biomass balance becomes

$$\frac{dM_X}{dt} = \int_0^R [\mu(S(r, t)) - b] X(r, t) 4\pi r^2 dr - J_{\text{det}} 4\pi R^2 \quad [\text{A.24}]$$

The detachment flux is modeled as

$$J_{\text{det}} = k_d \tau \quad [\text{A.25}]$$

with hydrodynamic shear stress approximated as

$$\tau = \frac{1}{2} \rho U^2 f \quad [\text{A.26}]$$

A.5 Dimensionless Formulation

Define the dimensionless variables

$$\rho = \frac{r}{R}, s(\rho) = \frac{S}{S_{\text{ref}}} \quad [\text{A.27}]$$

and

$$\kappa = \frac{K_s}{S_{\text{ref}}} \quad [\text{A.28}]$$

Substitution into Eq. (A.5) yields

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{ds}{d\rho} \right) - \Phi^2 \frac{s}{\kappa + s} = 0 \quad [\text{A.29}]$$

where

$$\Phi^2 = \frac{R^2}{D_e} \left(\frac{\mu_{\text{max}} X_0}{Y S_{\text{ref}}} \right) \quad [\text{A.30}]$$

Boundary conditions become

$$\frac{ds}{d\rho} \big|_{\rho=0} = 0 \quad [\text{A.31}]$$

$$s(1) = \frac{S_s}{S_{\text{ref}}} \quad [\text{A.32}]$$

For finite film resistance

$$-\frac{ds}{d\rho} \big|_{\rho=1} = \text{Bi}_m (1 - s(1)) \quad [\text{A.33}]$$

with

$$\text{Bi}_m = \frac{k_L R}{D_e} \quad [\text{A.34}]$$

Using the Sherwood definition

$$\text{Sh} = \frac{k_L d_p}{D_b}, d_p = 2R \quad [\text{A.35}]$$

$$k_L = \frac{\text{Sh} D_b}{d_p} \quad [\text{A.36}]$$

$$\text{Bi}_m = \frac{D_b}{2D_e} \text{Sh} \quad [\text{A.37}]$$

and

$$\text{Sh} = 2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3} \quad [\text{A.38}]$$

Analytical Reference Relations

Classical first-order spherical effectiveness factor

$$\eta = \frac{3}{\phi_1^2} (\phi_1 \coth \phi_1 - 1) \quad [\text{A.39}]$$

First-order Thiele modulus

$$\phi_1^2 = \frac{k_1 R^2}{D_e} \quad [\text{A.40}]$$

Bulk-based effectiveness definition

$$\Omega = \frac{R_{\text{obs}}}{R_{\text{bulk}}} \quad [\text{A.41}]$$

A.6 Final Model Equations

The boundary-value problem solved numerically is

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{ds}{d\rho} \right) - \Phi^2 \frac{s}{\kappa+s} = 0 \quad [\text{A.42}]$$

subject to

$$\frac{ds}{d\rho} \big|_{\rho=0} = 0 \quad [\text{A.43}]$$

$$-\frac{ds}{d\rho} \big|_{\rho=1} = \text{Bi}_m (1 - s(1)) \quad [\text{A.44}]$$

The dimensional uptake rate is

$$R_{\text{obs}} = \int_0^R \frac{\mu_{\text{max}} X_0}{Y} \frac{S(r)}{K_s + S(r)} 4\pi r^2 dr \quad [\text{A.45}]$$

The numerical effectiveness factor is

$$\eta_{\text{num}} = \frac{R_{\text{obs}}}{R_{\text{no-diff}}} \quad [\text{A.46}]$$

The stability model is

$$\frac{dM_X}{dt} = \int_0^R [\mu(S) - b] X 4\pi r^2 dr - k_d \tau 4\pi R^2 \quad [\text{A.47}]$$

Define the stability ratio

$$\Lambda(R, U) = \frac{\int_0^R [\mu(S) - b] X 4\pi r^2 dr}{k_d \tau 4\pi R^2} \quad [\text{A.48}]$$

with interpretation

$$\Lambda > 1 \Rightarrow \frac{dM_X}{dt} > 0$$

$$\Lambda = 1 \Rightarrow \frac{dM_X}{dt} = 0$$

$$\Lambda < 1 \Rightarrow \frac{dM_x}{dt} < 0$$

Finally, the regime-boundary scaling is represented as

$$\text{Bi}_{m,\text{crit}}(\Phi) \approx C \Phi^\alpha \quad [\text{A.50}]$$

This expression provides a compact analytical representation of the numerically identified transition between transport regimes.

Appendix B — MATLAB Code

The MATLAB scripts in this appendix implement the numerical models developed in Appendix A (Governing Equations). These scripts compute the steady spherical reaction–diffusion solution, evaluate effectiveness factors, analyze transport regimes, and determine granule stability boundaries.

B.1 Numerical Solution of the Monod Reaction–Diffusion Boundary Value

Problem

This script implements the Newton iteration solution of the nonlinear spherical reaction–diffusion equation defined in Equations (A.42–A.44). The solver computes the steady substrate concentration profile within a granule subject to Monod kinetics and an external film mass transfer boundary condition.

MATLAB Code

```
function out = solve_RD_sphere_monod_newton(p)

R      = p.R;
N      = p.N;
De     = p.De;
mu_max = p.mu_max;
X0     = p.X0;
Y      = p.Y;
Ks     = p.Ks;
kL     = p.kL;
Sb     = p.Sb;

alpha = mu_max * X0 / Y;

r = linspace(0, R, N).';
dr = r(2) - r(1);

maxit   = p.newton.maxit;
tolF    = p.newton.tolF;
tolS    = p.newton.tolS;
lambda0 = p.newton.lambda0;

S = Sb * (0.95 + 0.05*(r/R));

for k = 1:maxit

    [F,J] = build_residual_and_jacobian(r, dr, De, alpha, Ks, kL, Sb, S);

    if norm(F,inf) < tolF
```

```

        break
    end

    dS = -J \ F;

    if norm(dS,inf) < tolS
        S = S + dS;
        break
    end

    lambda = lambda0;

    S_trial = S + lambda*dS;
    [F_trial,~] = build_residual_and_jacobian(r, dr, De, alpha, Ks, kL, Sb,
    S_trial);

    while norm(F_trial,inf) > norm(F,inf) && lambda > 1e-6
        lambda = 0.5*lambda;
        S_trial = S + lambda*dS;
        [F_trial,~] = build_residual_and_jacobian(r, dr, De, alpha, Ks, kL,
    Sb, S_trial);
    end

    S = S_trial;

end

dSdr_R = (3*S(end) - 4*S(end-1) + S(end-2))/(2*dr);

Jout = -De*dSdr_R;

Robs = -Jout*(4*pi*R^2);

out.r = r;
out.S = S;
out.Jout = Jout;
out.Robs = Robs;

```

B.2 Residual and Jacobian Assembly for the Newton Solver

This script constructs the residual vector and Jacobian matrix corresponding to the discretized spherical reaction–diffusion equation described by Equation (A.42) with the boundary conditions in Equations (A.43–A.44).

MATLAB Code

```

function [F,J] = build_residual_and_jacobian(r, dr, De, alpha, Ks, kL, Sb, S)

N = numel(S);

```

```

F = zeros(N,1);
J = zeros(N,N);

F(1) = -3*S(1) + 4*S(2) - S(3);
J(1,1) = -3;
J(1,2) = 4;
J(1,3) = -1;

for i = 2:(N-1)

    ri = r(i);

    rph = ri + 0.5*dr;
    rmh = ri - 0.5*dr;

    aip = (rph^2 * De) / (dr^2);
    aim = (rmh^2 * De) / (dr^2);

    diff_i = (1/(ri^2))*(aip*(S(i+1)-S(i)) - aim*(S(i)-S(i-1)));

    reac_i = alpha*(S(i)/(Ks+S(i)));

    F(i) = diff_i - reac_i;

    dF_dSim1 = (1/(ri^2))*aim;
    dF_dSi    = (1/(ri^2))*(-aip - aim);
    dF_dSip1 = (1/(ri^2))*aip;

    dReac_dSi = alpha*(Ks/(Ks+S(i))^2);

    J(i,i-1) = dF_dSim1;
    J(i,i)    = dF_dSi - dReac_dSi;
    J(i,i+1) = dF_dSip1;

end

dSdr_R = (3*S(N) - 4*S(N-1) + S(N-2))/(2*dr);

```

```
F(N) = (-De*dSdr_R) - kL*(S(N) - Sb);
```

```
J(N,N) = -De*(3/(2*dr)) - kL;
```

```
J(N,N-1) = -De*(-4/(2*dr));
```

```
J(N,N-2) = -De*(1/(2*dr));
```

B.3 Monod Kinetic Function

This function evaluates the Monod growth law used in Equation (A.12).

MATLAB Code

```
function mu = monod_mu(mu_max, Ks, S)
```

```
mu = mu_max .* (S ./ (Ks + S));
```

B.4 Nonlinear Regression for Apparent Monod Parameters

This script performs nonlinear regression to estimate apparent kinetic parameters by fitting simulated uptake rates to the Monod form.

MATLAB Code

```
function fit = fit_monod_nls(Sb, mu_app)
```

```
Sb = Sb(:);
```

```
mu_app = mu_app(:);
```

```
mask = isfinite(Sb) & isfinite(mu_app) & (Sb > 0) & (mu_app >= 0);
```

```
Sb = Sb(mask);
```

```
mu_app = mu_app(mask);
```

```
mu_max0 = max(mu_app);
```

```
target = 0.5 * mu_max0;
```

```
[~, idx] = min(abs(mu_app - target));
```

```
Ks0 = Sb(idx);
```

```

x0 = [log(mu_max0); log(Ks0)];

obj = @(x) sse_logparams(x, Sb, mu_app);

opts = optimset('Display','off','MaxIter',2000);

[xopt,fval] = fminsearch(obj,x0,opts);

mu_max_fit = exp(xopt(1));
Ks_fit = exp(xopt(2));

fit.mu_max = mu_max_fit;
fit.Ks = Ks_fit;
fit.SSE = fval;
fit.mu_fit = monod_mu(mu_max_fit, Ks_fit, Sb);

end

```

B.5 Post-Processing of Uptake Rate, Surface Concentration, and Effectiveness Factor

This script post-processes the numerical solution of the Monod reaction–diffusion boundary value problem. It computes the surface concentration, observed uptake rate, hypothetical no-diffusion uptake rate, numerical effectiveness factor, and the dimensionless groups appearing in Equations (A.41), (A.46), and (A.34).

MATLAB Code

```

function pp = postprocess_effectiveness_monod(p,out)
    R      = p.R;
    De     = p.De;
    mu_max = p.mu_max;
    X0     = p.X0;
    Y      = p.Y;
    Ks     = p.Ks;
    kL     = p.kL;
    Sb     = p.Sb;

```

```

Ss = out.S(end);

mu_s = mu_max * (Ss/(Ks + Ss));
mu_b = mu_max * (Sb/(Ks + Sb));

V = (4/3)*pi*R^3;
A = 4*pi*R^2;

rS_nodiff = (1/Y) * mu_s * X0;
R_nodiff = rS_nodiff * V;

eta_num = out.Robs / R_nodiff;

Sref = Sb;
Phi2 = (R^2/De) * (mu_max*X0/(Y*Sref));
Bi_m = (kL*R)/De;

pp.Ss = Ss;
pp.mu_s = mu_s;
pp.mu_b = mu_b;
pp.gamma = mu_s / mu_b;

pp.V = V;
pp.A = A;

pp.Robs = out.Robs;
pp.R_nodiff = R_nodiff;
pp.eta_num = eta_num;

pp.Phi2 = Phi2;
pp.Phi = sqrt(Phi2);
pp.Bi_m = Bi_m;

pp.flags.S_order_ok = (out.S(1) <= out.S(end)) && (out.S(end) <= Sb);
pp.flags.eta_ok = (eta_num >= 0) && (eta_num <= 1.5);
end

```

B.6 Evaluation of the Biomass Growth Integral for Stability Analysis

This script evaluates the net biomass growth integral used in the stability formulation. It implements the volumetric growth term appearing in Equations (A.47–A.48).

MATLAB Code

```
function G = compute_growth_integral(p,out)
    r = out.r;
    S = out.S;

    mu = p.mu_max .* (S ./ (p.Ks + S));
    net = (mu - p.b) .* p.X0;

    integrand = net .* (4*pi*r.^2);
    G = trapz(r,integrand);
end
```

B.7 Chapter 2 Single-Case Solution and Newton Convergence Demonstration

This script solves the steady spherical Monod reaction–diffusion model for a representative parameter set. It generates the substrate profile and Newton convergence behavior corresponding to Figures 2-1 and 2-2 and directly implements the numerical problem defined by Equations (A.42–A.45).

MATLAB Code

```
clear; clc; close all;

p.R      = 1.0e-3;
p.N      = 201;
p.De     = 1.0e-9;
p.mu_max = 1.0e-5;
p.X0     = 10.0;
p.Y      = 0.1;
p.Ks     = 1.0;
p.kL     = 1.0e-5;
p.Sb     = 1.0;
```

```

p.newton.maxit = 60;
p.newton.tolF = 1e-12;
p.newton.tolS = 1e-14;
p.newton.lambda0 = 1.0;

out = solve_RD_sphere_monod_newton(p);

fprintf('Converged: %d, iters: %d\n', out.info.converged, out.info.iters);
fprintf('S(0)=%.6f, S(R)=%.6f, Sb=%.6f\n', out.S(1), out.S(end), p.Sb);
fprintf('BC check dS/dr|0 = %.3e\n', out.info.check.dSdr0);
fprintf('BC check film residual = %.3e\n', out.info.check.film_res);
fprintf('dS/dr|R = %.3e\n', out.info.check.dSdrR);
fprintf('Jout = %.3e (kgS/m^2/s)\n', out.Jout);
fprintf('Robs = %.6e (kgS/s)\n', out.Robs);

figure;
plot(out.r,out.S,'LineWidth',2); hold on;
yline(p.Sb,'--','$S_b$', 'LineWidth',1.5,'Interpreter','latex');
xlabel('$r$ (m)', 'Interpreter','latex');
ylabel('$S(r)$ (kg$_S$/m$^3$)', 'Interpreter','latex');
title('Granule Substrate Profile, Steady Spherical Monod RD (Film BC)', 'Interpreter','latex');
grid on;

figure;
semilogy(1:numel(out.info.Finf),out.info.Finf,'LineWidth',2);
xlabel('Newton iteration','Interpreter','latex');
ylabel('$\\|F|_{\\infty}$', 'Interpreter','latex');
title('Newton Convergence', 'Interpreter','latex');
grid on;

```

B.8 Chapter 2 Grid Refinement Check

This script evaluates numerical grid convergence of the reaction–diffusion solution by tracking the observed uptake rate and surface concentration as the number of grid points increases. It supports verification of the numerical implementation used for the Chapter 2 and 4 results.

MATLAB Code

```

clear; clc; close all;

p.R      = 1.0e-3;
p.De     = 1.0e-9;
p.mu_max = 1.0e-5;
p.X0     = 10.0;
p.Y      = 0.1;
p.Ks     = 1.0;
p.kL     = 1.0e-5;
p.Sb     = 1.0;

p.newton.maxit = 80;
p.newton.tolF = 1e-12;
p.newton.tolS = 1e-14;
p.newton.lambda0 = 1.0;

N_list = [51, 101, 201, 401];
Robs_list = zeros(size(N_list));
Ss_list = zeros(size(N_list));

for k = 1:numel(N_list)
    p.N = N_list(k);
    out = solve_RD_sphere_monod_newton(p);

    if ~out.info.converged
        error('Newton failed at N=%d',p.N);
    end

    pp = postprocess_effectiveness_monod(p,out);
    Robs_list(k) = pp.Robs;
    Ss_list(k) = pp.Ss;
end

figure;
plot(N_list,Robs_list,'-o','LineWidth',2);
xlabel('N grid points');
ylabel('R_{obs} (kg_S/s)');
title('Grid refinement: R_{obs} vs N');

```

```

grid on;

figure;
plot(N_list, Ss_list, '-o', 'LineWidth', 2); hold on;
yline(p.Sb, '--', 'S_b', 'LineWidth', 1.5);
xlabel('N grid points');
ylabel('S_s (kg_S/m^3)');
title('Grid refinement: surface concentration vs N');
grid on;

```

B.9 Chapter 2 Apparent Kinetic Bias Validation by Monod Regression

This script generates the Chapter 2 apparent-kinetics analysis by sweeping bulk concentration and external mass-transfer coefficient, fitting apparent Monod parameters, and comparing the fitted half-saturation constant to the analytical bias prediction. It supports Figures 2-3 through 2-6 and connects directly to the apparent-rate framework in Equations (A.10–A.12) and the film-transfer formulation in Equations (A.21), (A.34).

MATLAB Code

```

clear; clc; close all;

p.R      = 1.0e-3;
p.N      = 201;
p.De     = 1.0e-9;
p.mu_max = 1.0e-5;
p.X0     = 10.0;
p.Y      = 0.1;
p.Ks     = 1.0;
p.Sb     = 1.0;
p.kL     = 1.0e-5;

p.newton.maxit = 80;
p.newton.tolF = 1e-12;
p.newton.tolS = 1e-14;
p.newton.lambda0 = 1.0;

Sb_list = logspace(-2, 1.3, 30);

```

```

kL_list = logspace(-7,-3,9);

Ks_fit_list      = zeros(size(kL_list));
mu_fit_list      = zeros(size(kL_list));
Ks_theory_list   = zeros(size(kL_list));
SSE_list         = zeros(size(kL_list));

V = (4/3)*pi*p.R^3;

for j = 1:numel(kL_list)
    p.kL = kL_list(j);
    mu_app_data = zeros(size(Sb_list));

    for i = 1:numel(Sb_list)
        p.Sb = Sb_list(i);
        out = solve_RD_sphere_monod_newton(p);

        if ~out.info.converged
            error('Newton failed at kL=%g, Sb=%g',p.kL,p.Sb);
        end

        mu_app_data(i) = p.Y * out.Robs / (p.X0 * V);

        if mu_app_data(i) < 0
            mu_app_data(i) = 0;
        end
    end
end

fit = fit_monod_nls(Sb_list,mu_app_data);

mu_fit_list(j) = fit.mu_max;
Ks_fit_list(j) = fit.Ks;
SSE_list(j)     = fit.SSE;

Ks_theory_list(j) = p.Ks + (p.mu_max * p.X0 * p.R) / (6 * p.Y * p.kL);

fprintf('kL=%.3e: Ks_fit=%.4g, Ks_theory=%.4g, mu_max_fit=%.4g,
SSE=%.3e\n', ...

```

```

    p.kL,Ks_fit_list(j),Ks_theory_list(j),mu_fit_list(j),SSE_list(j));

    if j == ceil(numel(kL_list)/2)
        figure;
        loglog(Sb_list,mu_app_data,'o','LineWidth',1.5); hold on;
        mu_curve = monod_mu(fit.mu_max,fit.Ks,Sb_list);
        loglog(Sb_list,mu_curve,'-','LineWidth',2);
        xlabel('$S_b$ (kg$_S$/m$^3$)','Interpreter','latex');
        ylabel('$\mu_{\mathrm{app}}$ (s$^{-1}$)','Interpreter','latex');
        title(sprintf('Monod fit to $\mu_{\mathrm{app}}(S_b)$ at
$K_L=0.2e$',p.kL), ...
            'Interpreter','latex');
        legend('$\mu_{\mathrm{app}}$ simulated','Monod regression fit', ...
            'Location','best','Interpreter','latex');
        grid on;
    end
end

figure;
loglog(kL_list,Ks_fit_list,'o-','LineWidth',2); hold on;
loglog(kL_list,Ks_theory_list,'s--','LineWidth',2);
xlabel('$K_L$ (m/s)','Interpreter','latex');
ylabel('$K_{s,\mathrm{app}}$ (kg$_S$/m$^3$)','Interpreter','latex');
title('Apparent $K_s$ from regression vs analytical bias
prediction','Interpreter','latex');
legend('$K_{s,\mathrm{fit}}$ (NLS
regression)', '$K_{s,\mathrm{theory}}$', 'Location','best','Interpreter','latex
');
grid on;

figure;
semilogx(kL_list,Ks_fit_list ./ Ks_theory_list,'o-','LineWidth',2);
yline(1,'--','LineWidth',1.5);
xlabel('$K_L$ (m/s)','Interpreter','latex');
ylabel('$K_{s,\mathrm{fit}}/K_{s,\mathrm{theory}}$', 'Interpreter','latex');
title('Bias validation ratio','Interpreter','latex');
grid on;

```

```

figure;
loglog(kL_list,mu_fit_list,'o-','LineWidth',2); hold on;
yline(p.mu_max,'--
','\mu_{\max,\mathrm{intrinsic}}$', 'LineWidth',1.5,'Interpreter','latex');
xlabel('$k_L$ (m/s)', 'Interpreter','latex');
ylabel('$\mu_{\max,\mathrm{fit}}$ (s$^{-1}$)', 'Interpreter','latex');
title('$\mu_{\max}$ regression drift vs $k_L$', 'Interpreter','latex');
grid on;

```

B.10 Two-Species Reaction–Diffusion Newton Solver for VFA-Hydrogen

Coupling

This script solves the coupled two-species spherical reaction–diffusion problem for the Chapter 3 selectivity analysis. It extends the single-species formulation of Equation (A.42) to a reduced reaction network in which substrate conversion and hydrogen dynamics are solved simultaneously, consistent with the Chapter 3 balances summarized in Equations (A.14–A.19).

MATLAB Code

```

function out = solve_RD_sphere_2species_newton(p,y_init)
    if nargin < 2
        y_init = [];
    end

    R = p.R;
    N = p.N;
    r = linspace(0,R,N).';
    dr = r(2)-r(1);

    if isfield(p,'nuH1_eff')
        nuH1 = p.nuH1_eff;
    else
        nuH1 = p.nuH1;
    end

    maxit = p.newton.maxit;
    tolF = p.newton.tolF;

```

```

tolS      = p.newton.tolS;
lambda0 = p.newton.lambda0;

y_floor = 1e-20;

if isempty(y_init)
    P0 = p.Pb * (0.98 + 0.02*(r/R));
    if p.Hb == 0
        H0 = 1e-10 * ones(size(r));
    else
        H0 = max(p.Hb,y_floor) * ones(size(r));
    end
    y = [P0;H0];
else
    y = max(y_init,y_floor);
end

Fhist = zeros(maxit,1);
dhist = zeros(maxit,1);
lhist = zeros(maxit,1);

converged = false;
k = 0;

for k = 1:maxit
    [F,J] = build_residual_and_jacobian_2species(r,dr,p,nuH1,y);
    Fn = norm(F,inf);
    Fhist(k) = Fn;

    if Fn < tolF
        converged = true;
        break
    end

    dy = -J \ F;
    dn = norm(dy,inf);
    dhist(k) = dn;

```

```

if dn < tolS
    y = y + dy;
    y = max(y,y_floor);
    converged = true;
    break
end

lam = lambda0;

while lam > 1e-12
    y_try = y + lam*dy;
    if all(y_try > y_floor)
        break
    end
    lam = 0.5*lam;
end

if lam <= 1e-12
    break
end

y_try = y + lam*dy;
[F_try,~] = build_residual_and_jacobian_2species(r,dr,p,nuH1,y_try);

while norm(F_try,inf) > Fn && lam > 1e-12
    lam = 0.5*lam;
    y_try = y + lam*dy;
    if any(y_try <= y_floor)
        continue
    end
    [F_try,~] =
build_residual_and_jacobian_2species(r,dr,p,nuH1,y_try);
end

lhist(k) = lam;

if lam <= 1e-12
    break

```

```

        end

        y = max(y_try, y_floor);
    end

    P = y(1:N);
    H = y(N+1:end);

    dPdr0 = (-3*P(1) + 4*P(2) - P(3))/(2*dr);
    dHdr0 = (-3*H(1) + 4*H(2) - H(3))/(2*dr);
    dPdrR = (3*P(end) - 4*P(end-1) + P(end-2))/(2*dr);
    dHdrR = (3*H(end) - 4*H(end-1) + H(end-2))/(2*dr);

    filmP_res = (-p.Dp*dPdrR) - p.kLP*(P(end) - p.Pb);
    filmH_res = (-p.Dh*dHdrR) - p.kLH*(H(end) - p.Hb);

    out.r = r;
    out.P = P;
    out.H = H;

    out.info.converged = converged;
    out.info.iters = k;
    out.info.Finf = Fhist(1:k);
    out.info.dinf = dhist(1:k);
    out.info.lambda = lhist(1:k);

    out.info.check.dPdr0 = dPdr0;
    out.info.check.dHdr0 = dHdr0;
    out.info.check.filmP_res = filmP_res;
    out.info.check.filmH_res = filmH_res;
    out.info.check.minP = min(P);
    out.info.check.minH = min(H);
end

```

B.11 Residual and Jacobian Assembly for the Two-Species Reaction–Diffusion

Solver

This script constructs the residual vector and Jacobian matrix for the coupled VFA–hydrogen reaction–diffusion model used in Chapter 3. It supplies the Newton system for the two-species solver and supports the selectivity quantities defined in Equations (A.17–A.19).

MATLAB Code

```
function [F,J] = build_residual_and_jacobian_2species(r,dr,p,nuH1,y)
    N = numel(r);
    P = y(1:N);
    H = y(N+1:end);

    F = zeros(2*N,1);
    J = zeros(2*N,2*N);

    F(1) = -3*P(1) + 4*P(2) - P(3);
    J(1,1) = -3;
    J(1,2) = 4;
    J(1,3) = -1;

    F(N+1) = -3*H(1) + 4*H(2) - H(3);
    J(N+1,N+1) = -3;
    J(N+1,N+2) = 4;
    J(N+1,N+3) = -1;

    for i = 2:(N-1)
        ri = r(i);
        rph = ri + 0.5*dr;
        rmh = ri - 0.5*dr;

        aipP = (rph^2 * p.Dp) / (dr^2);
        aimP = (rmh^2 * p.Dp) / (dr^2);
        aipH = (rph^2 * p.Dh) / (dr^2);
        aimH = (rmh^2 * p.Dh) / (dr^2);
```

```

diffP = (1/(ri^2))*(aipP*(P(i+1)-P(i)) - aimP*(P(i)-P(i-1)));
diffH = (1/(ri^2))*(aipH*(H(i+1)-H(i)) - aimH*(H(i)-H(i-1)));

P_i = P(i);
H_i = H(i);

denomP = p.Kp + P_i;
denomHinh = 1 + H_i/p.KI;
denomH = p.Kh + H_i;

r1 = p.k1 * (P_i/denomP) * (1/denomHinh);
r3 = p.k3 * (H_i/denomH);

ip = i;
ih = N + i;

F(ip) = diffP - r1;
F(ih) = diffH - (nuH1*r1 - p.nuH3*r3);

dFp_dPim1 = (1/(ri^2))*aimP;
dFp_dPi = (1/(ri^2))*(-aipP - aimP);
dFp_dPip1 = (1/(ri^2))*aipP;

dr1_dP = p.k1 * (p.Kp/(denomP^2)) * (1/denomHinh);
dr1_dH = p.k1 * (P_i/denomP) * (-1/p.KI) / (denomHinh^2);

J(ip,i-1) = dFp_dPim1;
J(ip,i) = dFp_dPi - dr1_dP;
J(ip,i+1) = dFp_dPip1;
J(ip,N+i) = -dr1_dH;

dFh_dHim1 = (1/(ri^2))*aimH;
dFh_dHi = (1/(ri^2))*(-aipH - aimH);
dFh_dHip1 = (1/(ri^2))*aipH;

dr3_dH = p.k3 * (p.Kh / (denomH^2));

J(ih,N+i-1) = dFh_dHim1;

```

```

J(ih,N+i) = dFh_dHi + (-nuH1*dr1_dH + p.nuH3*dr3_dH);
J(ih,N+i+1) = dFh_dHip1;
J(ih,i) = -nuH1 * dr1_dP;
end

dPdrR = (3*P(end) - 4*P(end-1) + P(end-2))/(2*dr);
dHdrR = (3*H(end) - 4*H(end-1) + H(end-2))/(2*dr);

F(N) = (-p.Dp*dPdrR) - p.kLP*(P(end) - p.Pb);
J(N,N) = -p.Dp*(3/(2*dr)) - p.kLP;
J(N,N-1) = -p.Dp*(-4/(2*dr));
J(N,N-2) = -p.Dp*(1/(2*dr));

F(2*N) = (-p.Dh*dHdrR) - p.kLH*(H(end) - p.Hb);
J(2*N,2*N) = -p.Dh*(3/(2*dr)) - p.kLH;
J(2*N,2*N-1) = -p.Dh*(-4/(2*dr));
J(2*N,2*N-2) = -p.Dh*(1/(2*dr));
end

```

B.12 Chapter 3 Demonstration of Coupled Selectivity in a Representative

Granule

This script evaluates a representative two-species case for the Chapter 3 selectivity analysis. It computes the radial VFA and hydrogen profiles and evaluates the intrinsic and apparent selectivity metrics corresponding to Equations (A.18–A.19).

MATLAB Code

```

clear; clc; close all;

p.N = 201;
p.Dp = 1.0e-9;
p.Dh = 3.0e-9;
p.kLP = 1.0e-5;
p.kLH = 1.0e-5;
p.Pb = 1.0;
p.Hb = 0.0;
p.k1 = 2.0e-4;

```

```

p.Kp = 1.0;
p.KI = 1.0e-2;
p.k3 = 3.0e-3;
p.Kh = 1.0e-4;
p.nuH1 = 3.0;
p.nuH3 = 4.0;

p.newton.maxit = 200;
p.newton.tolF = 1e-11;
p.newton.tolS = 1e-13;
p.newton.lambda0 = 1.0;

gamma_list = [0.02,0.05,0.1,0.2,0.4,0.7,1.0];

r1_fun = @(P,H,pp) pp.k1 .* (P./(pp.Kp + P)) .* (1./(1 + H/pp.KI));
r3_fun = @(H,pp) pp.k3 .* (H./(pp.Kh + H));

p.R = 1.0e-3;

[out_base,y_init,ok] = solve_ch3_at_R_with_Pbaseline(p,gamma_list);

if ~ok
    error('Failed at baseline R=1e-3 even with P-only baseline.');
```

end

```

figure;
plot(out_base.r,out_base.P,'LineWidth',2); hold on;
yline(p.Pb,'--','P_b','LineWidth',1.5);
xlabel('r (m)');
ylabel('P(r) (kg/m^3)');
title('VFA (P) Profile in Granule (Film BC)');
grid on;

figure;
plot(out_base.r,out_base.H,'LineWidth',2); hold on;
yline(p.Hb,'--','H_b','LineWidth',1.5);
xlabel('r (m)');
ylabel('H(r) (kg/m^3)');
```

```

title('Hydrogen Profile in Granule (Film BC, H_b=0)');
grid on;

fprintf('\nBaseline checks at R=%g:\n',p.R);
fprintf('Min(P)=%.3e, Min(H)=%.3e\n',min(out_base.P),min(out_base.H));
fprintf('BC residuals: filmP=%.3e,
filmH=%.3e\n',out_base.info.check.filmP_res,out_base.info.check.filmH_res);

R_list = logspace(-4,-2.5,30);
Sigma_ratio = NaN(size(R_list));
H_center = NaN(size(R_list));

y_warm = [];

for i = 1:numel(R_list)
    p.R = R_list(i);
    [out_i,y_warm,ok_i] = solve_ch3_at_R_with_Pbaseline(p,gamma_list,y_warm);

    if ~ok_i
        warning('Skip R=%g (failed).',p.R);
        continue
    end

    r = out_i.r;
    P = out_i.P;
    H = out_i.H;

    r1 = r1_fun(P,H,p);
    r3 = r3_fun(H,p);

    V = (4/3)*pi*p.R^3;
    r1_bar = trapz(r,r1 .* 4*pi.*r.^2) / V;
    r3_bar = trapz(r,r3 .* 4*pi.*r.^2) / V;

    Sigma_app = r1_bar / max(r3_bar,realmin);

    Href = 1e-8;
    Sigma_int = r1_fun(p.Pb,Href,p) / max(r3_fun(Href,p),realmin);

```

```

        Sigma_ratio(i) = Sigma_app / Sigma_int;
        H_center(i) = H(1);
end

figure;
semilogx(R_list,Sigma_ratio,'o-','LineWidth',2);
yline(1,'--','LineWidth',1.5);
xlabel('R (m)');
ylabel('\Sigma_{app}/\Sigma_{int}');
title('Transport selectivity shift: \Sigma_{app}/\Sigma_{int} vs R');
grid on;

figure;
semilogx(R_list,H_center,'o-','LineWidth',2);
xlabel('R (m)');
ylabel('H(0) (kg/m^3)');
title('Hydrogen accumulation metric: H center vs R');
grid on;

fprintf('\nDone.\n');

function [out_last,y_out,ok] =
solve_ch3_at_R_with_Pbaseline(p,gamma_list,y_in)
    if nargin < 3
        y_in = [];
    end

    ok = false;
    y_out = y_in;
    out_last = [];

    p1.R = p.R;
    p1.N = p.N;
    p1.De = p.Dp;
    p1.kL = p.kLP;
    p1.Sb = p.Pb;
    p1.mu_max = p.k1;

```

```

p1.X0 = 1.0;
p1.Y = 1.0;
p1.Ks = p.Kp;
p1.newton = p.newton;

outP = solve_RD_sphere_monod_newton(p1);

if ~outP.info.converged
    fprintf(' FAIL P-only baseline at R=%g\n',p.R);
    ok = false;
    return
end

Pseed = outP.S;
Hseed = 1e-10 * ones(size(Pseed));

if ~isempty(y_out)
    N = numel(Pseed);
    Pseed = y_out(1:N);
    Hseed = y_out(N+1:end);
end

y_out = [Pseed;Hseed];

for g = gamma_list
    p.nuH1_eff = g * p.nuH1;
    out_try = solve_RD_sphere_2species_newton(p,y_out);

    if ~out_try.info.converged
        fprintf(' FAIL at R=%g, gamma=%g,
iters=%d\n',p.R,g,out_try.info.iters);
        ok = false;
        return
    end

    y_out = [out_try.P;out_try.H];
    out_last = out_try;
end

```

```
    ok = true;
end
```

B.13 Chapter 3 Segregated Coupling Demonstration for the Reduced Reaction Network

This script demonstrates a segregated outer-iteration solution strategy for the reduced Chapter 3 reaction network. It alternates between hydrogen and VFA updates to illustrate the coupling between transport and selectivity behavior in the reduced network.

MATLAB Code

```
clear; clc; close all;

N = 201;
R = 1.0e-3;
Dp = 1.0e-9;
Dh = 3.0e-9;
kLP = 1.0e-5;
kLH = 1.0e-5;
Pb = 1.0;
Hb = 0.0;
k1 = 2.0e-4;
Kp = 1.0;
KI = 1.0e-2;
k3 = 3.0e-3;
Kh = 1.0e-4;
nuH1 = 3.0;
nuH3 = 4.0;

max_outer = 60;
tol_outer = 1e-8;

newton.maxit = 80;
newton.tolF = 1e-12;
newton.tolS = 1e-14;
newton.lambda0 = 1.0;
```

```

r = linspace(0,R,N)';

r1_fun = @(P,H) k1 .* (P./(Kp + P)) .* (1./(1 + H/KI));
r3_fun = @(H) k3 .* (H./(Kh + H));

P = Pb * (0.98 + 0.02*(r/R));
H = 1e-10 * ones(size(r));

fprintf('\n--- Segregated solve: P <-> H coupling ---\n');

for it = 1:max_outer
    P_old = P;
    H_old = H;

    dr = r(2)-r(1);
    A = sparse(N,N);
    bvec = zeros(N,1);

    A(1,1) = -3;
    A(1,2) = 4;
    A(1,3) = -1;
    bvec(1) = 0;

    for iN = 2:N-1
        ri = r(iN);
        rph = ri + 0.5*dr;
        rmh = ri - 0.5*dr;

        aip = (rph^2 * Dh) / (dr^2);
        aim = (rmh^2 * Dh) / (dr^2);

        c_im1 = (1/(ri^2))*aim;
        c_i    = (1/(ri^2))*(-aip - aim);
        c_ip1 = (1/(ri^2))*aip;

        sink_coeff = nuH3 * k3 / (Kh + max(H_old(iN),1e-20));

```

```

    A(iN,iN-1) = c_im1;
    A(iN,iN)    = c_i - sink_coeff;
    A(iN,iN+1) = c_ip1;

    bvec(iN) = -nuH1 * r1_fun(P(iN),H_old(iN));
end

A(N,N)    = -Dh*(3/(2*dr)) - kLH;
A(N,N-1) = -Dh*(-4/(2*dr));
A(N,N-2) = -Dh*(1/(2*dr));
bvec(N)   = -kLH*(-Hb);

H = A \ bvec;
H = max(H,1e-20);

mu_eff = k1 * mean(1./(1 + H/KI));

p1.R = R;
p1.N = N;
p1.De = Dp;
p1.kL = kLP;
p1.Sb = Pb;
p1.mu_max = mu_eff;
p1.X0 = 1.0;
p1.Y  = 1.0;
p1.Ks = Kp;
p1.newton = newton;

outP = solve_RD_sphere_monod_newton(p1);

if ~outP.info.converged
    error('P-solve failed in outer iteration %d',it);
end

P = outP.S;

relP = norm(P-P_old,inf)/max(norm(P_old,inf),1e-20);
relH = norm(H-H_old,inf)/max(norm(H_old,inf),1e-20);

```

```

fprintf('outer %02d: relP=%.3e, relH=%.3e\n',it,relP,relH);

if max(relP,relH) < tol_outer
    fprintf('Converged in %d outer iterations.\n',it);
    break
end

if it == max_outer
    warning('Reached max outer iterations without full convergence.');
```

end

end

```

figure;
plot(r,P,'LineWidth',2); hold on;
yline(Pb,'--','P_b','LineWidth',1.5);
xlabel('r (m)');
ylabel('P(r) (kg/m^3)');
title('Chapter 3 demo: P profile (segregated coupling)');
grid on;

figure;
plot(r,H,'LineWidth',2); hold on;
yline(Hb,'--','H_b','LineWidth',1.5);
xlabel('r (m)');
ylabel('H(r) (kg/m^3)');
title('Chapter 3 demo: H profile (segregated coupling)');
grid on;

r1_local = r1_fun(P,H);
r3_local = r3_fun(H);

V = (4/3)*pi*R^3;
r1_bar = trapz(r,r1_local .* 4*pi.*r.^2) / V;
r3_bar = trapz(r,r3_local .* 4*pi.*r.^2) / V;
Sigma_app = r1_bar / max(r3_bar,realmin);

Href = 1e-8;
```

```

Sigma_int = r1_fun(Pb,Href) / max(r3_fun(Href),realmin);

fprintf('\n--- Selectivity metrics at R=%.3e ---\n',R);
fprintf('r1_bar=%.3e, r3_bar=%.3e\n',r1_bar,r3_bar);
fprintf('Sigma_app=%.3e, Sigma_int=%.3e, Sigma_app/Sigma_int=%.3e\n', ...
        Sigma_app,Sigma_int,Sigma_app/Sigma_int);

```

B.14 Chapter 3 Selectivity Regime Sweep over Radius and Hydrogen

Diffusivity

This script performs the full Chapter 3 parameter sweep used to generate the selectivity collapse and regime-map results. It supports Figures 3-1 through 3-3 and maps the apparent-to-intrinsic selectivity ratio over the hydrogen transport–reaction modulus and the hydrogen mass-transfer Biot number.

MATLAB Code

```

clear; clc; close all;

N = 201;
R_list = logspace(-4,-2.5,22);
Dp = 1.0e-9;
Dh_list = logspace(-11,-8,18);
kLP = 1.0e-5;
kLH = 1.0e-5;
Pb = 1.0;
Hb = 0.0;

k1 = 2.0e-4;
Kp = 1.0;
KI = 1.0e-2;
k3 = 3.0e-3;
Kh = 1.0e-4;

nuH1 = 3.0;
nuH3 = 4.0;

```

```

max_outer = 80;
tol_outer = 1e-8;
H_floor = 1e-20;

r1_fun = @(P,H) k1 .* (P./(Kp + P)) .* (1./(1 + H/KI));
r3_fun = @(H) k3 .* (H./(Kh + H));

Sigma_ratio_map = NaN(numel(R_list),numel(Dh_list));
phiH2_sq_map = NaN(numel(R_list),numel(Dh_list));
BiH2_map = NaN(numel(R_list),numel(Dh_list));
conv_map = false(numel(R_list),numel(Dh_list));

fprintf('\n--- Chapter 3: 2D regime sweep over (R, Dh) ---\n');
fprintf('R: %d points, Dh: %d points\n',numel(R_list),numel(Dh_list));

for iR = 1:numel(R_list)
    R = R_list(iR);
    r = linspace(0,R,N)';
    dr = r(2)-r(1);

    w = 4*pi.*r.^2;
    wsum = trapz(r,w);

    for jD = 1:numel(Dh_list)
        Dh = Dh_list(jD);

        P = Pb * (0.98 + 0.02*(r/R));
        H = 1e-10 * ones(size(r));

        converged = false;

        for it = 1:max_outer
            P_old = P;
            H_old = H;

            A = sparse(N,N);
            bvec = zeros(N,1);

```

```

A(1,1) = -3;
A(1,2) = 4;
A(1,3) = -1;
bvec(1) = 0;

for iN = 2:N-1
    ri = r(iN);
    rph = ri + 0.5*dr;
    rmh = ri - 0.5*dr;

    aip = (rph^2 * Dh) / (dr^2);
    aim = (rmh^2 * Dh) / (dr^2);

    c_im1 = (1/(ri^2))*aim;
    c_i    = (1/(ri^2))*(-aip - aim);
    c_ip1 = (1/(ri^2))*aip;

    sink_coeff = nuH3 * k3 / (Kh + max(H_old(iN),H_floor));

    A(iN,iN-1) = c_im1;
    A(iN,iN)    = c_i - sink_coeff;
    A(iN,iN+1) = c_ip1;

    bvec(iN) = -nuH1 * r1_fun(P(iN),H_old(iN));
end

A(N,N)    = -Dh*(3/(2*dr)) - kLH;
A(N,N-1) = -Dh*(-4/(2*dr));
A(N,N-2) = -Dh*(1/(2*dr));
bvec(N)   = -kLH*(-Hb);

H = A \ bvec;
H = max(H,H_floor);

inhib_field = 1./(1 + H/KI);
inhib_vw = trapz(r,inhib_field .* w) / wsum;
mu_eff = k1 * inhib_vw;

```

```

p1.R = R;
p1.N = N;
p1.De = Dp;
p1.kL = kLP;
p1.Sb = Pb;
p1.mu_max = mu_eff;
p1.X0 = 1.0;
p1.Y = 1.0;
p1.Ks = Kp;
p1.newton.maxit = 80;
p1.newton.tolF = 1e-12;
p1.newton.tolS = 1e-14;
p1.newton.lambda0 = 1.0;

outP = solve_RD_sphere_monod_newton(p1);

if ~outP.info.converged
    break
end

P = outP.S;

relP = norm(P-P_old,inf)/max(norm(P_old,inf),H_floor);
relH = norm(H-H_old,inf)/max(norm(H_old,inf),H_floor);

if max(relP,relH) < tol_outer
    converged = true;
    break
end
end

if ~converged
    continue
end

conv_map(iR,jD) = true;

r1_local = r1_fun(P,H);

```

```

r3_local = r3_fun(H);

V = (4/3)*pi*R^3;
r1_bar = trapz(r,r1_local .* 4*pi.*r.^2) / V;
r3_bar = trapz(r,r3_local .* 4*pi.*r.^2) / V;

Sigma_app = r1_bar / max(r3_bar,realmin);

Hs = H(end);
Sigma_int_surf = r1_fun(Pb,Hs) / max(r3_fun(Hs),realmin);

Sigma_ratio_map(iR,jD) = Sigma_app / Sigma_int_surf;
BiH2_map(iR,jD) = (kLH*R)/Dh;

Href = max(Hs,H_floor);
Pref = Pb;

termP = (Pref/(Kp + Pref));
dr1dH = k1 * termP * (-(1/KI) / (1 + Href/KI)^2);
dr3dH = k3 * (Kh / (Kh + Href)^2);

dRH2dH_ref = (-nuH1)*dr1dH + (nuH3)*dr3dH;
kH2_ref = abs(dRH2dH_ref);

phiH2_sq_map(iR,jD) = (R^2/Dh) * kH2_ref;
end
end

ok = conv_map & isfinite(Sigma_ratio_map) & isfinite(phiH2_sq_map) &
(phiH2_sq_map > 0);

figure;
loglog(phiH2_sq_map(ok),Sigma_ratio_map(ok),'o','LineWidth',1.2);
yline(1,'--','LineWidth',1.5);
xlabel('$\phi_{\mathrm{H2}}^2$','Interpreter','latex');
ylabel('$\Sigma_{\mathrm{app}}/\Sigma_{\mathrm{int}}^{\mathrm{surf}}$','Interpreter','latex');
title('Selectivity regime: $\Sigma$ ratio vs $\phi_{\mathrm{H2}}^2$ (2D

```

```

sweep) ', 'Interpreter', 'latex');
grid on;

X = log10(phiH2_sq_map(ok));
Y = log10(BiH2_map(ok));
Z = Sigma_ratio_map(ok);

xg = linspace(min(X),max(X),250);
yg = linspace(min(Y),max(Y),250);
[XG,YG] = meshgrid(xg,yg);

F = scatteredInterpolant(X,Y,Z,'natural','none');
ZG = F(XG,YG);

figure;
contourf(XG,YG,ZG,25,'LineStyle','none');
colorbar;
grid on;
xlabel('$\log_{10}(\phi_{\mathrm{H2}}^2)$','Interpreter','latex');
ylabel('$\log_{10}(\mathrm{Bi}_{\mathrm{H2}})$','Interpreter','latex');
title('$\Sigma$ ratio regime map over $\phi_{\mathrm{H2}}^2$, $\mathrm{Bi}_{\mathrm{H2}}$','Interpreter','latex');

figure;
imagesc(log10(Dh_list),log10(R_list),conv_map);
set(gca,'YDir','normal');
colorbar;
xlabel('$\log_{10}(D_h)$ (m$^2$/s)','Interpreter','latex');
ylabel('$\log_{10}(R)$ (m)','Interpreter','latex');
title('Convergence map (1=converged, 0=failed)','Interpreter','latex');
grid on;

```

B.15 Chapter 4 Numerical Effectiveness Sweep over the Monod Thiele

Modulus

This script evaluates the numerical effectiveness factor as a function of the Monod-based Thiele modulus Φ for the single-species reaction–diffusion model. It supports Figures 4-1 and 4-2 and

connects directly to the dimensionless formulation in Equations (A.29–A.38) and the numerical effectiveness definition in Equation (A.46).

MATLAB Code

```
clear; clc; close all;

p.R      = 1.0e-3;
p.N      = 201;
p.De     = 1.0e-9;
p.mu_max = 1.0e-5;
p.X0     = 10.0;
p.Y      = 0.1;
p.Ks     = 1.0;
p.kL     = 1.0e-5;
p.Sb     = 1.0;

p.newton.maxit = 80;
p.newton.tolF  = 1e-12;
p.newton.tolS  = 1e-14;
p.newton.lambda0 = 1.0;

mu_list = logspace(-7,-3,25);

Phi_list = zeros(size(mu_list));
eta_list = zeros(size(mu_list));
Ss_list  = zeros(size(mu_list));
Robs_list = zeros(size(mu_list));

for k = 1:numel(mu_list)
    p.mu_max = mu_list(k);

    out = solve_RD_sphere_monod_newton(p);
    if ~out.info.converged
        error('Newton failed at k=%d (mu=%g).',k,p.mu_max);
    end

    pp = postprocess_effectiveness_monod(p,out);
```

```

    Phi_list(k) = pp.Phi;
    eta_list(k) = pp.eta_num;
    Ss_list(k) = pp.Ss;
    Robs_list(k) = pp.Robs;
end

figure;
semilogx(Phi_list,eta_list,'LineWidth',2); hold on;
xlabel('$\Phi$ (Monod Thiele-like,
$S_{\mathrm{ref}}=S_b$)','Interpreter','latex');
ylabel('$\eta_{\mathrm{num}}=R_{\mathrm{obs}}/R_{\mathrm{no}\!-\!
\!diff}$','Interpreter','latex');
title('Numerical effectiveness vs $\Phi$ (Monod, film
BC)','Interpreter','latex');
grid on;

do_overlay_Bi = true;
if do_overlay_Bi
    kL_overlay = [1e-9, 1e-7, 1e-5, 1e-3];
    for q = 1:numel(kL_overlay)
        p.kL = kL_overlay(q);

        eta_q = zeros(size(mu_list));
        Phi_q = zeros(size(mu_list));

        for k = 1:numel(mu_list)
            p.mu_max = mu_list(k);

            out = solve_RD_sphere_monod_newton(p);
            if ~out.info.converged
                eta_q(k) = NaN;
                Phi_q(k) = NaN;
                continue
            end

            pp = postprocess_effectiveness_monod(p,out);
            Phi_q(k) = pp.Phi;

```

```

        eta_q(k) = pp.eta_num;
    end

    semilogx(Phi_q,eta_q,'--','LineWidth',1.4);
end

    legend_entries = [{'baseline k_L'}, arrayfun(@(v)
sprintf('k_L=%g',v),kL_overlay,'UniformOutput',false)];
    legend(legend_entries{:},'Location','southwest');
end
hold off;

figure;
semilogx(Phi_list,Ss_list,'LineWidth',2); hold on;
yline(p.Sb,'--','$S_b$', 'LineWidth',1.5,'Interpreter','latex');
xlabel('$\Phi$', 'Interpreter','latex');
ylabel('$S_s=S(R)$ (kg$_{S}$/m$^3$)', 'Interpreter','latex');
title('Surface concentration vs $\Phi$ (film BC)', 'Interpreter','latex');
grid on;

```

B.16 Chapter 4 Regime Map over (Φ , Bi_m) and Collapse Boundary Extraction

This script generates the Chapter 4 transport regime maps by sweeping the intrinsic rate and the external mass-transfer coefficient. It computes the effectiveness field, exports collapse-boundary data, evaluates regime collapse, and produces the design-rule quantities used in Figures 4-3 through 4-8. It connects directly to Equations (A.29–A.38) and the boundary-scaling framework summarized in Equation (A.50).

MATLAB Code

```

clear; clc; close all;

p.R      = 1.0e-3;
p.N      = 201;
p.De     = 1.0e-9;
p.mu_max = 1.0e-5;
p.X0     = 10.0;
p.Y      = 0.1;

```

```

p.Ks      = 1.0;
p.kL      = 1.0e-5;
p.Sb      = 1.0;

p.newton.maxit    = 80;
p.newton.tolF     = 1e-12;
p.newton.tolS     = 1e-14;
p.newton.lambda0  = 1.0;

mu_list = logspace(-7,-3,24);
kL_list = logspace(-9,-3,30);

Phi_map = zeros(numel(mu_list),numel(kL_list));
Bi_map  = zeros(numel(mu_list),numel(kL_list));
eta_map = zeros(numel(mu_list),numel(kL_list));
Ss_map  = zeros(numel(mu_list),numel(kL_list));
conv_map = false(numel(mu_list),numel(kL_list));

for i = 1:numel(mu_list)
    for j = 1:numel(kL_list)
        p.mu_max = mu_list(i);
        p.kL     = kL_list(j);

        out = solve_RD_sphere_monod_newton(p);
        conv_map(i,j) = out.info.converged;

        if ~out.info.converged
            Phi_map(i,j) = NaN;
            Bi_map(i,j)  = NaN;
            eta_map(i,j) = NaN;
            Ss_map(i,j)  = NaN;
            continue
        end

        pp = postprocess_effectiveness_monod(p,out);
        Phi_map(i,j) = pp.Phi;
        Bi_map(i,j)  = pp.Bi_m;
        eta_map(i,j) = pp.eta_num;
    end
end

```

```

        Ss_map(i,j) = pp.Ss;
    end
end

outdir = 'CH4_boundary_exports';
if ~exist(outdir,'dir'); mkdir(outdir); end

X = log10(Phi_map(:));
Y = log10(Bi_map(:));
Z = eta_map(:);

mask = isfinite(X) & isfinite(Y) & isfinite(Z) & conv_map(:) & (Phi_map(:) >
0) & (Bi_map(:) > 0);

X = X(mask);
Y = Y(mask);
Z = Z(mask);

xg = linspace(min(X),max(X),300);
yg = linspace(min(Y),max(Y),300);
[XG,YG] = meshgrid(xg,yg);

F = scatteredInterpolant(X,Y,Z,'natural','none');
ZG = F(XG,YG);

figure;
contourf(XG,YG,ZG,26,'LineStyle','none');
colorbar; grid on;
xlabel('$\log_{10}(\Phi)$','Interpreter','latex');
ylabel('$\log_{10}(\mathrm{Bi}_m)$','Interpreter','latex');
title('$\eta_{\mathrm{num}}$ regime map in $(\Phi,\mathrm{Bi}_m)$','Interpreter','latex');

levels = [0.90 0.70 0.50];
boundaries = struct([]);
fit_rows = [];

for ii = 1:numel(levels)

```

```

eta0 = levels(ii);
C = contourc(xg,yg,ZG,[eta0 eta0]);

k = 1;
curves_log = {};
while k < size(C,2)
    npts = C(2,k);
    pts = C(:,k+1:k+npts);
    k = k + npts + 1;
    curves_log{end+1} = pts;
end

curve_out = {};
for c = 1:numel(curves_log)
    x = curves_log{c}(1,:);
    y = curves_log{c}(2,:);

    Phi = 10.^x;
    Bi = 10.^y;

    M = [Phi(:),Bi(:)];
    curve_out{c} = M;

    fname =
sprintf('%s/boundary_eta_%0.2f_curve_%02d.csv',outdir,eta0,c);
    writematrix(M,fname);

    lx = log10(M(:,1));
    ly = log10(M(:,2));
    ok2 = isfinite(lx) & isfinite(ly);

    if nnz(ok2) >= 10
        Pfit = polyfit(lx(ok2),ly(ok2),1);
        b = Pfit(1);
        a = Pfit(2);

        ly_hat = polyval(Pfit,lx(ok2));
        SSres = sum((ly(ok2) - ly_hat).^2);
    end
end

```

```

        SStot = sum((ly(ok2) - mean(ly(ok2))).^2);
        r2 = 1 - SSres/max(SStot,eps);

        fit_rows = [fit_rows; eta0, c, a, b, nnz(ok2), r2];
    else
        fit_rows = [fit_rows; eta0, c, NaN, NaN, nnz(ok2), NaN];
    end
end

boundaries(ii).eta = eta0;
boundaries(ii).curves = curve_out;
end

save(sprintf('%s/regime_boundaries_eta.mat',outdir),'boundaries');

fit_file = sprintf('%s/boundary_fits.csv',outdir);
fid = fopen(fit_file,'w');
fprintf(fid,'eta_level,curve_id,a_intercept,b_slope,npts,R2\n');
fclose(fid);
dlmwrite(fit_file,fit_rows,'-append');

hold on;
for ii = 1:numel(boundaries)
    for c = 1:numel(boundaries(ii).curves)
        M = boundaries(ii).curves{c};
        plot(log10(M(:,1)),log10(M(:,2)),'k-','LineWidth',1.2);
    end
end
hold off;

Phi_all = Phi_map(:);
Bi_all = Bi_map(:);
eta_all = eta_map(:);
ok = isfinite(Phi_all) & isfinite(Bi_all) & isfinite(eta_all) & conv_map(:) &
(Phi_all > 0) & (Bi_all > 0);

Phi_all = Phi_all(ok);
Bi_all = Bi_all(ok);

```

```

eta_all = eta_all(ok);

logPhi = log10(Phi_all);
Bi_thresh_list = [1,10,100];

nbins = 20;
edges = linspace(min(logPhi),max(logPhi),nbins+1);
centers = 0.5*(edges(1:end-1)+edges(2:end));

collapse_report = [];

for t = 1:numel(Bi_thresh_list)
    Bi_thresh = Bi_thresh_list(t);

    use = (Bi_all >= Bi_thresh);
    dmax = NaN(nbins,1);
    drms = NaN(nbins,1);

    for b = 1:nbins
        inbin = (logPhi >= edges(b)) & (logPhi < edges(b+1)) & use;
        n = nnz(inbin);

        if n >= 8
            e = eta_all(inbin);
            dmax(b) = max(e) - min(e);
            drms(b) = sqrt(mean((e - mean(e)).^2));
        end
    end

    has = isfinite(dmax);
    if any(has)
        max_spread = max(dmax(has));
        rms_spread = mean(drms(has),'omitnan');
        Phi_lo = 10^(min(centers(has)));
        Phi_hi = 10^(max(centers(has)));
        nb_used = nnz(has);
    else
        max_spread = NaN;
    end
end

```

```

        rms_spread = NaN;
        Phi_lo = NaN;
        Phi_hi = NaN;
        nb_used = 0;
    end

    collapse_report = [collapse_report; Bi_thresh, Phi_lo, Phi_hi,
max_spread, rms_spread, nb_used];

    figure;
    plot(10.^centers,dmax,'LineWidth',2); grid on;
    set(gca,'XScale','log');
    xlabel('$\Phi$', 'Interpreter','latex');
    ylabel('$\Delta\eta_{\{\max\}}$ across $\mathrm{Bi}_m$ (within
$\Phi$ bin)', 'Interpreter','latex');
    title(sprintf('Collapse check: $\mathrm{Bi}_m$
\\ge %g$',Bi_thresh), 'Interpreter','latex');
end

collapse_file = sprintf('%s/collapse_report.csv',outdir);
fid = fopen(collapse_file,'w');
fprintf(fid,'Bi_threshold,Phi_low,Phi_high,delta_eta_max_over_bins,delta_eta_
rms_mean_over_bins,nbins_used\n');
fclose(fid);
dlmwrite(collapse_file,collapse_report,'-append');

tols = [0.02,0.05];
Bi_candidates = logspace(-3,3,121);
Bi_floor = min(Bi_candidates);

for tt = 1:numel(tols)
    tol = tols(tt);
    Bi_crit = NaN(nbins,1);
    Phi_bin_center = 10.^centers(:);

    for b = 1:nbins
        inPhi = (logPhi >= edges(b)) & (logPhi < edges(b+1));
        if nnz(inPhi) < 10

```

```

        continue
    end

    found = false;
    for bc = 1:numel(Bi_candidates)
        Bth = Bi_candidates(bc);
        sel = inPhi & (Bi_all >= Bth);

        if nnz(sel) < 8
            continue
        end

        e = eta_all(sel);
        spread = max(e) - min(e);

        if spread <= tol
            Bi_crit(b) = Bth;
            found = true;
            break
        end
    end

    if ~found
        Bi_crit(b) = NaN;
    end
end

figure;
loglog(Phi_bin_center,Bi_crit,'o-','LineWidth',2); grid on;
xlabel('$\Phi$', 'Interpreter', 'latex');
ylabel('$\mathrm{Bi}_{\mathrm{crit}}(\Phi)$', 'Interpreter', 'latex');
title(sprintf('Design rule: minimum $\mathrm{Bi}_m$ for collapse within
$\Delta \eta \leq %.2f$',tol), ...
    'Interpreter', 'latex');
hold on;
yline(Bi_floor,'--',sprintf('candidate floor = %g',Bi_floor), ...
    'LabelHorizontalAlignment','left','Interpreter','none');
hold off;

```

```

Mout = [Phi_bin_center,Bi_crit];
fname = sprintf('%s/Bi_crit_vs_Phi_tol_%0.2f.csv',outdir,tol);
writematrix(Mout,fname);
end

figure;
imagesc(log10(kL_list),log10(mu_list),conv_map);
set(gca,'YDir','normal');
colorbar;
xlabel('$\log_{10}(k_L)$ (m/s)', 'Interpreter','latex');
ylabel('$\log_{10}(\mu_{\max})$ (s$^{-1}$)', 'Interpreter','latex');
title('Newton convergence map (1=converged,
0=failed)', 'Interpreter','latex');
grid on;

```

B.17 Chapter 4 Power-Law Fitting of the Critical Biot Number Scaling

This script fits the collapse-boundary data to the power-law relation $Bi_{m,crit} = C\Phi^\alpha$ used in Equation (A.50). It supports Figures 4-9 through 4-13 and generates the multi-tolerance overlay, residual plots, and fitted scaling curves.

MATLAB Code

```

clear; close all; clc;

Phi_min_fit = 1;
Phi_max_fit = Inf;

set(groot,'defaultTextInterpreter','latex');
set(groot,'defaultAxesTickLabelInterpreter','latex');
set(groot,'defaultLegendInterpreter','latex');

figPos = [100 100 900 650];
lwData = 1.75;
lwFit = 2.25;
msData = 7;

```

```

doSaveFigures = true;
doPrintSummary = true;

csvPattern = 'Bi_crit_vs_Phi_tol_*.csv';
csvFiles = dir(csvPattern);

matCandidates =
{'boundary_data.mat','regime_artifacts.mat','ch4_boundary_exports.mat','ch4_r
egime_exports.mat'};

matFile = '';
for k = 1:numel(matCandidates)
    if exist(matCandidates{k},'file') == 2
        matFile = matCandidates{k};
        break;
    end
end

haveCSV = ~isempty(csvFiles);
haveMAT = ~isempty(matFile);

if ~haveCSV && ~haveMAT
    error('Missing required regime artifacts.');
```

end

```

if haveCSV
    datasets = loadDatasetsFromCSVs(csvFiles);
else
    datasets = loadDatasetsFromMAT(matFile);
end

fitRows = cell(numel(datasets),1);
nFits = 0;

for i = 1:numel(datasets)
    tolVal = datasets(i).tol;
    Phi = datasets(i).Phi(:);
    Bi = datasets(i).Bi(:);
```

```

    mask = isfinite(Phi) & isfinite(Bi) & (Phi > 0) & (Bi > 0) & (Phi >=
Phi_min_fit) & (Phi <= Phi_max_fit);

    PhiFit = Phi(mask);
    BiFit = Bi(mask);

    if numel(PhiFit) < 3
        continue;
    end

    x = log10(PhiFit);
    y = log10(BiFit);

    pfit = polyfit(x,y,1);
    alpha = pfit(1);
    a = pfit(2);
    C = 10^a;

    yhat = polyval(pfit,x);
    resid = y - yhat;

    SSres = sum((y - yhat).^2);
    SStot = sum((y - mean(y)).^2);

    if SStot > 0
        R2 = 1 - SSres/SStot;
    else
        R2 = NaN;
    end

    nPts = numel(PhiFit);
    PhiMinUsed = min(PhiFit);
    PhiMaxUsed = max(PhiFit);

    nFits = nFits + 1;
    fitRows{nFits} = {tolVal,PhiMinUsed,PhiMaxUsed,alpha,C,R2,nPts};

```

```

if doPrintSummary
    fprintf('tol=%s | Phi=[%.4g, %.4g] | alpha=%.6g | C=%.6g | R2=%.6g |
n=%d\n', ...
        tolToString(tolVal), PhiMinUsed, PhiMaxUsed, alpha, C, R2, nPts);
end

fig1 = figure('Color','w','Position',figPos);
ax1 = axes(fig1);
ax1.Toolbar.Visible = 'off';
hold(ax1,'on'); grid(ax1,'on'); box(ax1,'on');

maskPos = isfinite(Phi) & isfinite(Bi) & (Phi > 0) & (Bi > 0);
PhiAll = Phi(maskPos);
BiAll = Bi(maskPos);

loglog(ax1,PhiAll,BiAll,'o','LineWidth',lwData,'MarkerSize',msData);

PhiCurve = logspace(log10(PhiMinUsed),log10(PhiMaxUsed),400).';
BiCurve = C .* (PhiCurve.^ alpha);
loglog(ax1,PhiCurve,BiCurve,'-','LineWidth',lwFit);

xlabel(ax1,'$\Phi$');
ylabel(ax1,'$Bi_{\mathrm{crit}}$');
title(ax1,sprintf('$Bi_{\mathrm{crit}} = C \backslash \backslash \Phi^{\backslash \backslash \alpha}$ fit,
tol=%s',tolToString(tolVal)));

lg = legend(ax1,{'Data',sprintf('Fit: $C=%.3g$, $\alpha=%.3g$,
$R^2=%.3g$',C,alpha,R2)}, ...
    'Location','best');
lg.Box = 'off';

if doSaveFigures
    flname =
sprintf('ch4_Bicrit_scaling_tol_%s_loglog.png',tolToFileString(tolVal));
    exportgraphics(fig1,flname,'Resolution',300);
end

fig2 = figure('Color','w','Position',figPos);

```

```

ax2 = axes(fig2);
ax2.Toolbar.Visible = 'off';
hold(ax2,'on'); grid(ax2,'on'); box(ax2,'on');

plot(ax2,x,resid,'o','LineWidth',lwData,'MarkerSize',msData);
yline(ax2,0,'-','LineWidth',1.25);

xlabel(ax2,'$\log_{10}(\Phi)$');
ylabel(ax2,'$\log_{10}(\text{Bi}_{\text{crit}})-\widehat{\log_{10}(\text{Bi}_{\text{crit}})}$');
title(ax2,sprintf('Residuals in log space, tol=%s',tolToString(tolVal)));

if doSaveFigures
    f2name =
sprintf('ch4_Bicrit_scaling_tol_%s_residuals.png',tolToFileString(tolVal));
    exportgraphics(fig2,f2name,'Resolution',300);
end
end

fitRows = fitRows(1:nFits);
outHeader =
{'tolerance','Phi_min_fit','Phi_max_fit','alpha','C','R2','n_points'};
fitMat = vertcat(fitRows{:});
outCell = [outHeader; fitMat];
writecell(outCell,'Bicrit_scaling_fits.csv');

if nFits > 1
    figM = figure('Color','w','Position',figPos);
    axM = axes(figM);
    axM.Toolbar.Visible = 'off';
    hold(axM,'on'); grid(axM,'on'); box(axM,'on');

    for i = 1:numel(datasets)
        tolVal = datasets(i).tol;
        Phi = datasets(i).Phi(:);
        Bi = datasets(i).Bi(:);

        maskPos = isfinite(Phi) & isfinite(Bi) & (Phi > 0) & (Bi > 0);

```

```

PhiAll = Phi(maskPos);
BiAll = Bi(maskPos);

[alpha,C,PhiMinUsed,PhiMaxUsed,ok] = lookupFitForTol(fitRows,tolVal);
if ~ok
    continue
end

loglog(axM,PhiAll,BiAll,'o','LineWidth',1.25,'MarkerSize',5);

PhiCurve = logspace(log10(PhiMinUsed),log10(PhiMaxUsed),300).';
BiCurve = C .* (PhiCurve.^ alpha);
loglog(axM,PhiCurve,BiCurve,'-','LineWidth',2.0);
end

xlabel(axM,'$\Phi$');
ylabel(axM,'$Bi_{\mathrm{crit}}$');
title(axM,'Multi-tolerance overlay: $Bi_{\mathrm{crit}}$ vs $\Phi$ with
fits');

if doSaveFigures

exportgraphics(figM,'ch4_Bicrit_scaling_multiTol_loglog.png','Resolution',300
);
end
end

```

B.18 Chapter 5 Stability Map from Growth–Detachment Competition

This script generates the Chapter 5 stability map by classifying granule behavior as growth, neutral stability, or shrinkage over the (U, R) space. It implements the growth–detachment competition represented by Equations (A.47–A.49) and supports Figure 5-1.

MATLAB Code

```

clear; clc; close all;

p.De = 1.0e-9;
p.mu_max = 1.0e-5;

```

```

p.X0      = 10.0;
p.Y       = 0.1;
p.Ks      = 1.0;
p.Sb      = 1.0;
p.kL      = 1.0e-5;
p.b       = 1.0e-6;

rho = 1000;
f    = 0.02;
k_d  = 1e-6;

p.N = 201;
p.newton.maxit = 80;
p.newton.tolF = 1e-12;
p.newton.tolS = 1e-14;
p.newton.lambda0 = 1.0;

R_list = logspace(-4,-2.5,30);
U_list = logspace(-3,0.5,30);

stability = zeros(length(R_list),length(U_list));

for i = 1:length(R_list)
    for j = 1:length(U_list)
        p.R = R_list(i);

        out = solve_RD_sphere_monod_newton(p);
        if ~out.info.converged
            stability(i,j) = NaN;
            continue
        end

        G = compute_growth_integral(p,out);
        tau = 0.5 * rho * U_list(j)^2 * f;
        J_det = k_d * tau;
        A = 4*pi*p.R^2;
        dMdt = G - J_det*A;
    end
end

```

```

        if dMdt > 0
            stability(i,j) = 1;
        elseif abs(dMdt) < 1e-14
            stability(i,j) = 0;
        else
            stability(i,j) = -1;
        end
    end
end

figure;
imagesc(log10(U_list),log10(R_list),stability);
set(gca,'YDir','normal');
colorbar;
xlabel('$\log_{10}(U)$ (m/s)','Interpreter','latex');
ylabel('$\log_{10}(R)$ (m)','Interpreter','latex');
title('Granule stability map (1=growth, 0=neutral, -1=shrink)','Interpreter','latex');
grid on;

```

B.19 Chapter 5 Stability Boundary Extraction and Lambda Collapse Analysis

This script computes the critical superficial velocity $U_{\text{crit}}(R)$ by solving $dM_X/dt = 0$ using bisection, evaluates Λ along the neutral-stability boundary, and constructs the $\log_{10}(\Lambda)$ contour field. It supports Figures 5-2 through 5-4 and implements the stability framework of Equations (A.47–A.49).

MATLAB Code

```

clear; clc; close all;

p.De      = 1.0e-9;
p.mu_max  = 1.0e-5;
p.X0      = 10.0;
p.Y       = 0.1;
p.Ks      = 1.0;
p.Sb      = 1.0;
p.kL      = 1.0e-5;

```

```

p.b      = 1.0e-6;

p.N = 201;
p.newton.maxit = 80;
p.newton.tolF = 1e-12;
p.newton.tolS = 1e-14;
p.newton.lambda0 = 1.0;

rho = 1000;
f    = 0.02;
k_d = 1e-6;

Umin0 = 1e-8;
Umax0 = 10.0;

tolU_rel = 1e-8;
tolU_abs = 1e-10;

tolRel_dMdt = 1e-8;
Gfloor = 1e-22;

max_bisect_it = 120;
max_expand_it = 40;

R_list = logspace(-4,-2.5,60);
Ucrit_list = NaN(size(R_list));
Lambda_at_Ucrit = NaN(size(R_list));
G_list = NaN(size(R_list));

tau_of_U = @(U) 0.5*rho*(U.^2)*f;
A_of_R    = @(R) 4*pi*(R.^2);
det_loss  = @(R,U) k_d*tau_of_U(U).*A_of_R(R);

dMdt_of = @(G,R,U) G - det_loss(R,U);
Lambda_of = @(G,R,U) G ./ max(det_loss(R,U),realmin);

fprintf('\n--- Computing Ucrit(R) by bisection (relative tolerance) ---\n');

```

```

for i = 1:numel(R_list)
    p.R = R_list(i);

    out = solve_RD_sphere_monod_newton(p);
    if ~out.info.converged
        warning('RD solver failed at R=%g. Skipping.',p.R);
        continue;
    end

    G = compute_growth_integral(p,out);
    G_list(i) = G;
    dMdt_target = tolRel_dMdt * max(abs(G),Gfloor);

    Ulo = Umin0;
    Uhi = Umax0;

    Flo = dMdt_of(G,p.R,Ulo);
    Fhi = dMdt_of(G,p.R,Uhi);

    expand_it = 0;
    while sign(Flo) == sign(Fhi) && expand_it < max_expand_it
        if Flo > 0 && Fhi > 0
            Uhi = Uhi * 2;
        elseif Flo < 0 && Fhi < 0
            Ulo = Ulo / 2;
        end
        Flo = dMdt_of(G,p.R,Ulo);
        Fhi = dMdt_of(G,p.R,Uhi);
        expand_it = expand_it + 1;
    end

    if sign(Flo) == sign(Fhi)
        warning('Could not bracket root at R=%g. Flo=%.3e,
Fhi=%.3e',p.R,Flo,Fhi);
        continue;
    end

    for it = 1:max_bisect_it

```

```

    Umid = 0.5*(Ulo + Uhi);
    Fmid = dMdt_of(G,p.R,Umid);

    if abs(Fmid) <= dMdt_target
        break;
    end

    if abs(Uhi - Ulo) <= max(tolU_abs,tolU_rel*abs(Umid))
        break;
    end

    if sign(Fmid) == sign(Flo)
        Ulo = Umid;
        Flo = Fmid;
    else
        Uhi = Umid;
        Fhi = Fmid;
    end
end

Ucrit = 0.5*(Ulo + Uhi);
Ucrit_list(i) = Ucrit;

Lam = Lambda_of(G,p.R,Ucrit);
Lambda_at_Ucrit(i) = Lam;

fprintf('R=%.3e m: G=%.3e kgX/s, Ucrit=%.6e m/s, |dMdt|/|G|=%.3e,
Lambda=%.6f\n', ...
    p.R,G,Ucrit,abs(dMdt_of(G,p.R,Ucrit))/max(abs(G),Gfloor),Lam);
end

mask_ok = isfinite(Ucrit_list) & isfinite(Lambda_at_Ucrit) &
isfinite(G_list);
R_ok = R_list(mask_ok);
Ucrit_ok = Ucrit_list(mask_ok);
Lam_ok = Lambda_at_Ucrit(mask_ok);
G_ok = G_list(mask_ok);

```

```

figure;
loglog(R_ok,Ucrit_ok,'o-','LineWidth',2);
xlabel('$R$ (m)','Interpreter','latex');
ylabel('$U_{\mathrm{crit}}$ (m/s)','Interpreter','latex');
title('Stability boundary: $U_{\mathrm{crit}}(R)$ from $dM/dt=0$ (bisection,
relative tol)','Interpreter','latex');
grid on;

figure;
semilogx(R_ok,Lam_ok,'o-','LineWidth',2); hold on;
yline(1,'--','LineWidth',1.5);
xlabel('$R$ (m)','Interpreter','latex');
ylabel('$\Lambda(R,U_{\mathrm{crit}})$','Interpreter','latex');
title('$\Lambda$ evaluated on stability boundary (should be $\approx
1$)','Interpreter','latex');
grid on;

fprintf('\nBoundary Lambda stats: min=%.6f, max=%.6f, mean=%.6f\n', ...
        min(Lam_ok),max(Lam_ok),mean(Lam_ok));

U_grid = logspace(-3,0.5,80);
R_grid = logspace(-4,-2.5,80);

[UU,RR] = meshgrid(U_grid,R_grid);

G_interp = interp1(log10(R_ok),G_ok,log10(R_grid),'linear','extrap');
G_interp = G_interp(:);

Lambda_field = NaN(size(UU));
for iR = 1:numel(R_grid)
    G_here = G_interp(iR);
    R_here = R_grid(iR);
    Lambda_field(iR,:) = Lambda_of(G_here,R_here,U_grid);
end

figure;
contourf(log10(U_grid),log10(R_grid),log10(Lambda_field),30,'LineColor','none
');
```

```

colorbar;
xlabel('$\log_{10}(U)$ (m/s)', 'Interpreter', 'latex');
ylabel('$\log_{10}(R)$ (m)', 'Interpreter', 'latex');
title('$\log_{10}(\Lambda)$ contour map with  

$\Lambda=1$ boundary', 'Interpreter', 'latex');
grid on; hold on;

[C,h] = contour(log10(U_grid),log10(R_grid),log10(Lambda_field),[0
0], 'k', 'LineWidth', 2);
clabel(C,h);

plot(log10(Ucrit_ok),log10(R_ok), 'w.', 'MarkerSize', 14);
plot(log10(Ucrit_ok),log10(R_ok), 'w--', 'LineWidth', 1.5);

fprintf('\nDone.\n');

```

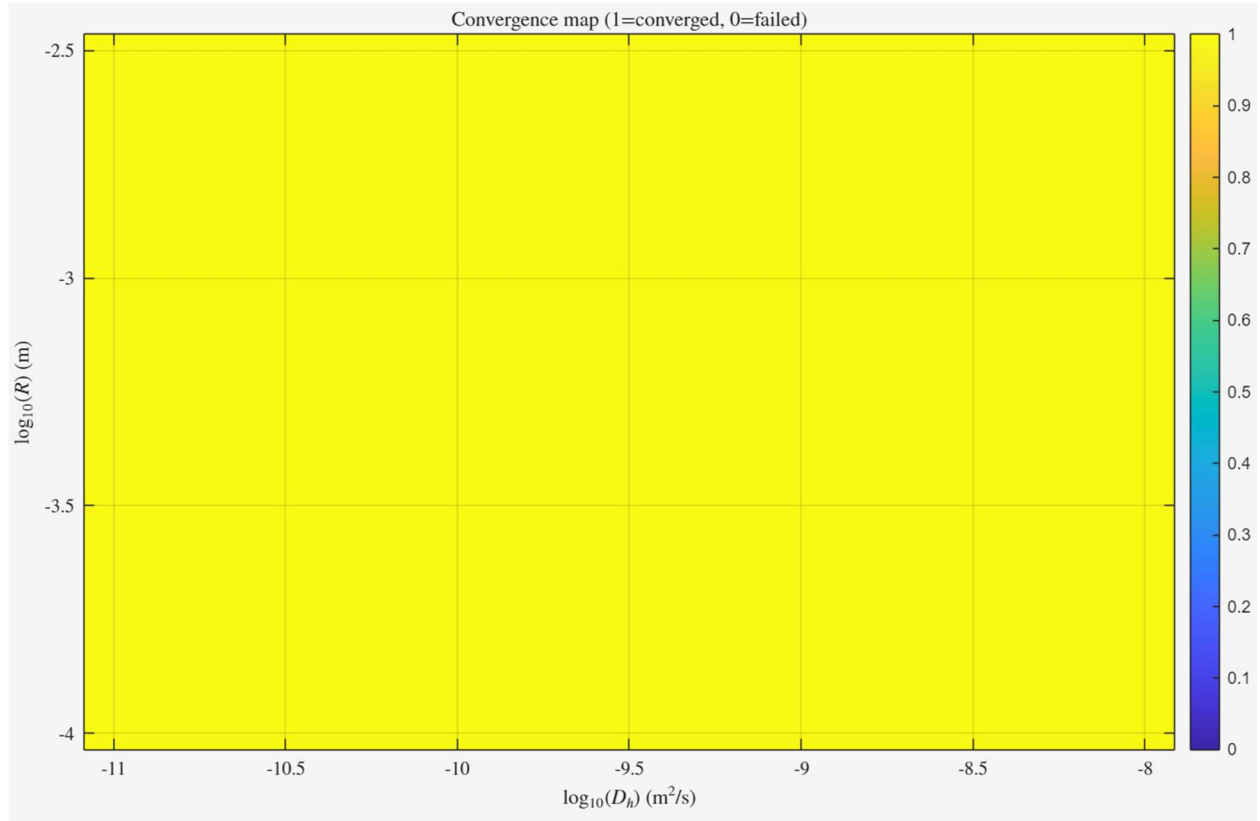
Appendix C - Numerical Solver Verification

The reaction–diffusion equations used throughout this work were solved numerically using a finite-difference discretization combined with a Newton iteration procedure, as described in Appendix B. Because the nonlinear transport–reaction equations must be solved repeatedly across wide parameter sweeps to generate the regime maps and stability analyses presented in the main text, it is important to verify that the numerical solution procedure converges reliably over the parameter ranges considered.

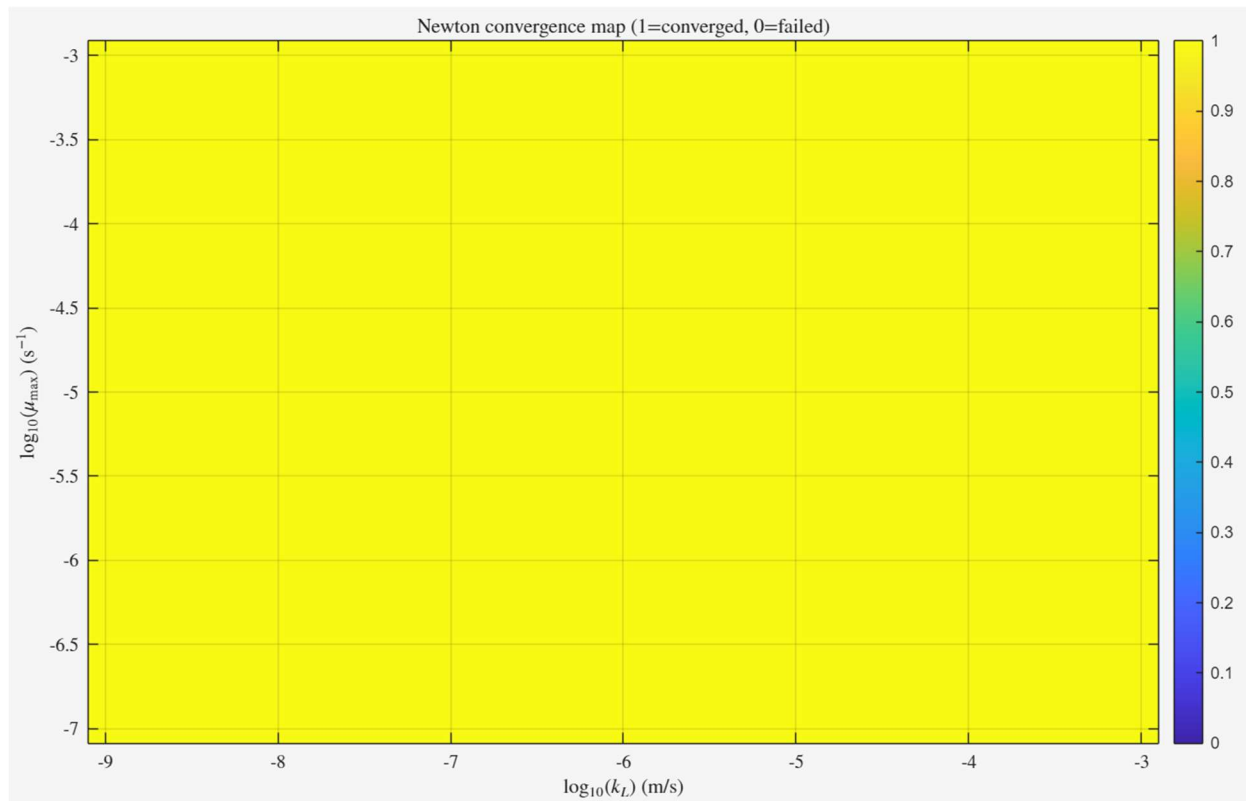
The convergence diagnostics presented in this appendix document the behavior of the Newton solver across the parameter domains explored in the computational studies. Each convergence map reports whether the solver successfully converged to a steady-state solution for a given combination of model parameters. A value of 1 indicates that the nonlinear system satisfied the solver convergence criteria, while a value of 0 indicates that the solver failed to converge within the specified tolerance or iteration limits.

These convergence diagnostics serve two purposes. First, they demonstrate that the parameter sweeps used to generate the figures in Chapters 3 and 4 lie within a numerically stable region of the model. Second, they provide transparency regarding the numerical behavior of the solution procedure used to compute the reaction–diffusion solutions.

Appendix Figure C.1 Convergence map of the Newton solver across the (D_h, R) parameter domain used in the selectivity analysis presented in Chapter 3. Each point represents a parameter combination evaluated in the numerical sweep. Values of 1 indicate successful convergence of the nonlinear reaction–diffusion system, while values of 0 indicate solver failure. The map shows that the solver converged for all parameter combinations examined in the selectivity regime analysis.



Appendix Figure C.2 Convergence map of the Newton solver across the (μ_{max}, k_L) parameter domain used in the regime analysis presented in Chapter 4. Each point represents a parameter combination evaluated during the numerical parameter sweep. Values of 1 indicate successful convergence of the nonlinear reaction–diffusion system, while values of 0 indicate solver failure



Glossary of Terms

Geometry

$R \equiv$ Granule radius [m]

$r \equiv$ Radial coordinate within spherical granule [m]

$V \equiv$ Granule volume, $V = \frac{4}{3}\pi R^3$ [m³]

$A \equiv$ Granule surface area, $A = 4\pi R^2$ [m²]

Transport Properties and Dimensionless Groups

$D_e \equiv$ Effective intragranular diffusivity [m²/s]

$D_b \equiv$ Bulk liquid diffusivity [m²/s]

$D_p \equiv$ Volatile fatty acid (VFA) diffusivity [m²/s]

$D_h \equiv$ Hydrogen diffusivity [m²/s]

$k_L \equiv$ External liquid-film mass transfer coefficient [m/s]

$k_{LP} \equiv$ Film mass transfer coefficient for VFA species [m/s]

$k_{LH} \equiv$ Film mass transfer coefficient for hydrogen [m/s]

$Sh \equiv$ Sherwood number, $Sh = \frac{k_L d_p}{D_b}$

$Bi_m \equiv$ Mass-transfer Biot number, $Bi_m = \frac{k_L R}{D_e}$

$\Phi \equiv$ Monod-based Thiele modulus (dimensionless transport–reaction group)

$\Phi^2 \equiv \Phi^2 = \frac{R^2}{D_e} \frac{\mu_{\max} X_0}{Y S_{\text{ref}}}$

$\phi_{\text{H}_2}^2 \equiv$ Hydrogen transport–reaction modulus (Chapter 3 selectivity analysis)

Substrate and Biomass Variables

$S \equiv$ Local substrate concentration within granule [kg_S/m³]

$S_b \equiv$ Bulk liquid substrate concentration [kg_S/m³]

$S_s \equiv$ Surface substrate concentration, $S(R)$ [kg_S/m³]

$X \equiv$ Local biomass concentration [kg_X/m^3]

$X_0 \equiv$ Uniform biomass concentration (pellet closure assumption) [kg_X/m^3]

$M_X \equiv$ Total biomass within granule [kg_X]

Intrinsic Kinetic Parameters

$\mu \equiv$ Specific microbial growth rate [s^{-1}]

$\mu_{\max} \equiv$ Maximum specific growth rate [s^{-1}]

$K_S \equiv$ Monod half-saturation constant [kg_S/m^3]

$Y \equiv Y_{X/S} \equiv$ Yield coefficient (biomass formed per substrate consumed) [kg_X/kg_S]

$b \equiv$ Biomass decay coefficient [s^{-1}]

$\alpha \equiv$ Reaction coefficient, $\alpha = \mu_{\max} X_0 / Y [\text{s}^{-1}]$

$r_S \equiv$ Growth-associated substrate consumption rate [$\text{kg}_S/(\text{m}^3 \cdot \text{s})$]

Apparent and Effectiveness Quantities

$R_{\text{obs}} \equiv$ Observed total substrate uptake rate [kg_S/s]

$R_{\text{no-diff}} \equiv$ Hypothetical uptake rate without internal diffusion limitation [kg_S/s]

$\mu_{\text{app}} \equiv$ Apparent specific growth rate inferred from bulk measurements [s^{-1}]

$K_{S,\text{app}} \equiv$ Apparent half-saturation constant under transport limitation [kg_S/m^3]

$\eta \equiv$ Internal effectiveness factor, $\eta = R_{\text{obs}}/R_{\text{no-diff}}$

$\eta_{\text{num}} \equiv$ Numerically computed effectiveness factor

$\Omega \equiv$ Overall effectiveness factor based on bulk concentration

Reaction Network and Selectivity (Chapter 3)

$\Sigma_{\text{int}} \equiv$ Intrinsic selectivity ratio (surface-referenced)

$\Sigma_{\text{app}} \equiv$ Apparent selectivity ratio (volume-averaged)

$\nu_{H1} \equiv$ Hydrogen stoichiometric coefficient from VFA oxidation

$\nu_{H3} \equiv$ Hydrogen consumption coefficient in methanogenesis

Stability and Detachment Parameters (Chapter 5)

$G(R) \equiv$ Volumetric net biomass growth rate

$$G(R) = \int_0^R (\mu(S) - b) X_0 4\pi r^2 dr \quad [\text{kg}_X/\text{s}]$$

$J_{\text{det}} \equiv$ Biomass detachment flux at granule surface $[\text{kg}_X/(\text{m}^2 \cdot \text{s})]$

$k_d \equiv$ Detachment proportionality constant $[(\text{kg}_X/(\text{m}^2 \cdot \text{s}))/\text{Pa}]$

$\tau \equiv$ Wall shear stress, $\tau = \frac{1}{2}\rho U^2 f [\text{Pa}]$

$U \equiv$ Characteristic bulk or approach velocity $[\text{m/s}]$

$U_{\text{crit}}(R) \equiv$ Critical velocity satisfying $dM_X/dt = 0 [\text{m/s}]$

$\Lambda \equiv$ Stability diagnostic ratio, $\Lambda = G/L$

Numerical Quantities

$F \equiv$ Nonlinear residual vector in Newton iteration

$J \equiv$ Jacobian matrix of residual system

$\| F \|_{\infty} \equiv$ Infinity norm of residual

$\lambda \equiv$ Newton damping parameter

$N \equiv$ Number of radial grid point