ANALYSIS OF THE DYNAMICS FOR THE SYSTEM OF NONLINEAR DIFFERENTIAL EQUATIONS DESCRIBING A TUBULAR REACTOR

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by

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The undersigned, appointed by the dean of the Graduate School have examined the thesis entitled

ANALYSIS OF THE DYNAMICS FOR THE SYSTEM OF NONLINEAR DIFFERENTIAL EQUATIONS DESCRIBING A TUBULAR REACTOR

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NOMENCLATURE

$(\overline{y_1}, \overline{y_2})$ and $(\underline{y_1}, \underline{y_2})$	Upper and Lower solutions, respectively
$(\overline{Y_1}, \overline{Y_2})$ and $(\underline{Y_1}, \underline{Y_2})$	Maximal and Minimal solutions, respectively
L	Length of the reactor
z	Spatial variable
D	Domain of z
D	Diffusion Coefficient
$R_1 \times R_2$	Range of (y_1, y_2)
TR	Tubular Reactor
CTR	Continuous Tubular Reactor
PFR	Plug Flow Reactor
CSTR	Continuous Stirred Tank Reactor
BVPs	Boundary Value Problems
ODEs	Ordinary Differential Equations
PDEs	Partial Differential Equations
k	Reaction rate constant
k_0	Pre-exponential factor
k_T	Fluid's thermal conductivity
C_P	Fluid's specific heat capacity
C_A	Reactant (A) concentration
C_{A_0}	Reactant (A) concentration before entering the reactor
$(-\Delta H_A)$	Heat of reaction relative to reactant (A)
$-r_A$	Rate of decomposition of reactant (A)
v	Fluid's superficial velocity
ρ	Fluid'sdensity
E	Reaction activation energy

R	Universal gas constant
T	Reaction absolute temperature
T_0	Reactant temperature before entering the reactor
T_{max}	Reaction maximum temperature
i	Subscript for 1,2 e.g., x_1, x_2, y_1, y_2
α	A constant known as the Hölder's exponent
δ	A number defined as $\frac{T_0}{T_{max}}$
γ	The activation energy parameter, defined as $\frac{E}{RT_{max}}$
β_1	Mass Péclet number
β_2	Thermal Péclet number
μ_1	The Damköhler number, defined as $\frac{k_0 L^2}{D}$
μ_2	The quantity defined as $\frac{(-\Delta H_A) k_0 L^2}{k_T T_{max}} C_{A_0}$
N_{Pr}	The Prater number, defined as $\frac{(-\mu_2)}{\mu_1}$
x_1	The dimensionless concentration, defined as $\frac{C_A}{C_{A_0}}$
x_2	The dimensionless temperature, defined as $\frac{T}{T_{max}}$
a_1, a_2, b_1, b_2, k_1 and k_2	The cofficients used to defined the pairs of upper and lower solutions
f_1 and f_2	The nonlinear functions of C_A and T in the original BVP [Equations (1.4) and (1.2b)]
F_1 and F_2	The nonlinear functions of z, y_1 and y_2 after nondimensionalization followed by transformation to self-adjoint BVP

ANALYSIS OF THE DYNAMICS OF THE SYSTEM OF NONLINEAR DIFFERENTIAL EQUATIONS DESCRIBING A TUBULAR REACTOR

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ABSTRACT

A characterization of the solution(s) of nonlinear boundary value problems (BVPs) arising from a class of chemical reactions occurring in a tubular reactor is performed. The system in this study is an adiabatic tubular reactor with different mass and thermal Péclet numbers. Bounds (lower and upper) on the number of solution(s) for the steady state behavior are obtained. The effect of the system parameters–Péclet numbers, Damköhler number, activation energy, etc.–on the number of steady-state solution(s) exhibited by the tubular reactor is investigated by applying the mathematical method of upper and lower solutions. The method was first used to show existence of at least one solution to the BVP for two sets of parameters. Uniqueness of the solution was also proved using this method combined with a theorem, Theorem 2.1. Based on restrictions on the parameters of the BVP, the existence of multiple solutions was proved as well. Results show that for large Péclet numbers and activation energy, and for sufficiently small Damköhler number and reactor length, the solution to the boundary value problem is unique. For small Péclet numbers and activation energy, and for large Damköhler number and reactor length, there exist at least three solutions for the BVP. The conclusion of all this is that the adiabatic tubular reactor is an intermediate model between the adiabatic plug flow reactor model and the adiabatic continuous stirred tank reactor model.

CHAPTER 1: INTRODUCTION

The tubular reactor (TR) model is used to describe chemical reactions in continuous, flowing systems of cylindrical geometry. This is the reason why the TR is sometimes called the continuous tubular reactor (CTR). In a TR, the feed typically enters at one end of a cylindrical tube and the product stream leaves at the other end. The 'long' tube and the lack of provision for stirring prevent complete mixing of the fluid in the tube. Hence, the properties of the flowing stream will vary from one point to another, namely in both radial and axial directions. The tubular reactor considered in this research is the non-ideal plug flow reactor (PFR); that is, no radial variation of properties, with the non-ideality from axial dispersion.

The dynamics of a tubular reactor give rise to one or more differential equations (partial differential equations (PDEs) if operating in an unsteady/transient state or ordinary differential equations (ODEs) if operating at a steady state). For non-isothermal tubular reactors in particular, the dynamics are described by coupled nonlinear PDEs or ODEs. The main sources of nonlinearities in the dynamics are concentrated in the kinetic terms of the constitutive equations. The existence of Arrhenius-type nonlinearities in the kinetics can generate multiple steady states, either stable or unstable, and in practical applications, the unstable steady states may correspond to the operating points of interest [1,2].

Our task is to find solution(s) to the equations and discuss the existence, uniqueness, and/or multiplicity of the solution(s) of the equations. Recent experimental, numerical, and theoretical results show that an adiabatic tubular reactor, in which occurs a simple first-order irreversible exothermic chemical reaction, can exhibit multiple steady-states. The study of the steady-state multiplicity and stability was the object of intense research in the 1960s and 1970s: most of the pertinent chemical engineering literature and results are reviewed by Varma and Aris [3], by Aris [4], and by Luss [5]. Multiple steady states have been observed experimentally, for example, in adiabatic tubular reactors [6,7]. However, a numerical method will work only if the solution of the problem exists [8]. With this in mind, many authors devoted their time to studying the existence of solutions.

1.1 RESEARCH BACKGROUND AND MOTIVATION

Many researchers (in the fields of chemical engineering, mathematics, and others) have worked extensively on the solution(s) to the nonadiabatic tubular reactor with both identical and differing mass and thermal Péclet numbers and the adiabatic tubular reactor with identical mass and thermal Péclet numbers [9–12]. However, very little has been done on or is known about the uniqueness and/or multiplicity of solution(s) to the adiabatic tubular reactor when the mass and thermal Péclet numbers are different.

For the nonadiabatic tubular reactor when the mass and thermal Péclet numbers are equal, tremendous achievements have been made: Donald S. Cohen and Theodore W. Laetsch [11], D. Luss and N.R. Amundson [5], D. Dochain [1], etc. have shown that multiple steady-states exist if the diffusion coefficient is sufficiently large, while for the nonadiabatic tubular reactor when the mass and thermal Péclet numbers are different, research by Retzloff et al [12], Laabissi et al [2], and A. Varma & R. Aris [3] have shown that multiple steady-state solutions are possible for various values of the system parameters values, e.g. the activation energy.

For the adiabatic tubular reactor when the mass and thermal Péclet numbers are equal, D. Cohen and T.W. Laetsch [11] has shown that multiple solutions can exist for certain values of the system parameters, especially when the activation is large. In fact, for this case, the original coupled boundary value problem (BVP) easily reduces to a scalar BVP, which is easily analyzed. However, for the case in this work, that is, the adiabatic tubular reactor when the mass and thermal Péclet numbers are different, the existence, uniqueness and/or multiplicity remains of solutions to the BVP remains an open question. Here, the mass and energy balances cannot be decoupled, making the analysis more difficult. Determining the existence, uniqueness, and/or multiplicity of solution(s) when the two Péclet numbers differ for specific parameter sets is the goal of this work.

1.2 STEADY-STATE EQUATIONS FOR AN ADIABATICALLY OPERATED TUBULAR REACTOR

The tubular reactor, as considered in this research, is defined as a non-ideal PFR; that is, no radial variation of properties, with the non-ideality being from axial dispersion; thus, the name axial-dispersion model tubular reactor. A schematic of an adiabatic tubular reactor is shown in Figure 1.

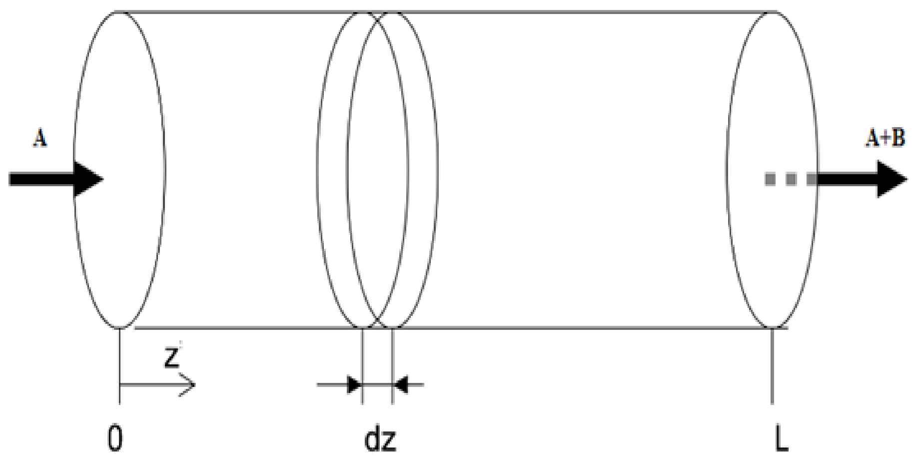


Figure 1: Schematic of an adiabatic tubular reactor. The reactant, A, forms the product, B, in an isomerization.

In this research, we considered the case of a single irreversible, first order, exothermic isomerization reaction in an adiabatic tubular reactor.

The reaction is

$$A \longrightarrow B,$$

And the rate of consumption of A is

$$-r_A = kC_A, \tag{1.1}$$

where $k = k_0 \exp\left(-\frac{E}{RT}\right)$.

The dynamics of the system are derived from material and energy balance considerations. The steady-state dynamics of an adiabatic tubular reactor with axially-dispersed plug flow for the simple irreversible exothermic reaction described by Equation (1.1) result in the following set of ODEs:

$$D\frac{d^2C_A}{dz^2} - v\frac{dC_A}{dz} = -r_A \tag{1.2a}$$

and

$$k_T\frac{d^2C_A}{dz^2} - v\rho C_p\frac{dC_A}{dz} = (-\Delta H_A)(-r_A), \tag{1.2b}$$

The boundary conditions are

$$\text{B.C. 1:} \ -D\frac{dC_A}{dz}(0) + vC_A(0) = vC_{A_0} \tag{1.3a}$$

$$-k_T\frac{dT}{dz}(0) + v\rho C_pT(0) = v\rho C_pT_0 \tag{1.3b}$$

$$\text{B.C. 2:} \quad \frac{dC_A}{dz}(L) = 0 \tag{1.3c}$$

$$\frac{dT}{dz}(L) = 0 \tag{1.3d}$$

Note that C_{A_0} is the concentration of A before the inlet of the reactor and T_0 is the inlet temperature just before the reaction starts, and they are assumed to be given/known.

In the above equations, z is the spatial variable in meter [m]; L [m] is the length of the reactor, where $0 \leq z \leq L$; v is the fluid's superficial velocity [m s^{-1}]; $T > 0$ is the process component temperature in Kelvins [K]; $C_A > 0$ is the reactant A concentration [kg m^{-3}]; $(-\Delta H_A)$ is the heat of reaction with respect to A [kJ kg^{-1}], where $(-\Delta H_A) < 0$ for exothermic reactions, and > 0 for endothermic reactions; ρ is the fluid's density [$kg\ m^{-3}$]; and C_p is the specific heat capacity [$kJ\ kg^{-1}\ K^{-1}$].

Note:

(1) Diffusion terms (i.e., dispersion) in Equations (1.2a) are based on the Fick's second law and the heat diffusion equation, but they also include contributions from fluid flow in the axial direction [13].

(2) In Equations (1.2), the reaction/kinetic term corresponds to the kinetics of a non-isothermal reaction with first order kinetics with respect to the reactant concentration C_A and Arrhenius-type dependence with respect to the temperature T. The term indeed closely couples the mass and energy balance equations.

(3) The boundary conditions in Equations (1.3) are known as the Danckwerts' conditions [14].

In deriving/formulating these equations, the following assumptions have been implicitly made:

(1) The fluid thermal (C_P) and physical parameters (ρ, k_T, D) are independent of temperature and composition.

(2) The heat of reaction, that is, the reaction enthalpy change $(-\Delta H_A)$, is independent of temperature.

(3) Radial gradients of the temperature and concentration are negligible.

(4) The fluid spatial velocity is constant in the axial direction.

(5) Kinetic and potential energy changes are negligible with respect to internal energy changes.

(6) There is no shaft work involved, that is, the only work is flow work.

(7) The dispersive fluxes of mass and heat can be described through Fick's and Fourier's law, respectively, with effective/overall mass and heat diffusion coefficients.

We next establish specific upper and lower bounds for the dependent variables C_A and T by assuming that they are solutions of Equations (1.2) and (1.3) and show that C_A is a decreasing function of z while (for the exothermic case) T is an increasing function of z. The upper bounds will identify the scaling factors used to obtain dimensionless dependent variables.

1.3 A PRIORI BOUNDS ON $C_A(z)$ AND $T(z)$

Lemma 3.1 $C_A(z)$ is a decreasing function of z, and the maximum value of $C_A(z)$ is C_{A_0}.

Proof First, observe that r_A is negative for $C_A(z) > 0$ and rewrite Equation (1.2a) as:

$$\frac{d^2C_A}{dz^2} - \frac{v}{D}\frac{dC_A}{dz} = \frac{-r_A}{D} = f_1 \geq 0 \qquad (1.4)$$

Integrating the inequality in Equation (1.4) with respect to z from 0 to L and using the boundary conditions [Equations (1.3)] yields

$$-\frac{v}{D}C_A(L) + \frac{v}{D}C_{A_0} \geq 0,$$

from which it follows that

$$C_{A_0} \geq C_A(L). \tag{1.5}$$

As C_A is $C^2(0, L)$, that is, C_A is twice continuously differentiable on $(0, L)$, there exists a segment of $(0, L)$ for which $\frac{dC_A}{dz} \leq 0$. Assuming $C_A(0) > C_{A_0}$, then $\frac{dC_A}{dz}(0) > 0$. Thus there exists $z_1 \in (0, L)$ where $\frac{dC_A}{dz}(z_1) = 0$ and $C_A(z_2)$ is a maximum. Therefore, $\frac{d^2C_A}{dz^2}(z_1) < 0$. This a contradiction: it contradicts Equation (1.4) leading to the conclusion that $\frac{dC_A}{dz}(0) < 0$. In addition, $C_A(z)$ is a monotonically decreasing function of z, otherwise it would achieve a maximum value in $(0, L)$ and result in a contradiction of Equation (1.4). Hence, $C_A(z) < C_{A_0}$.

Lemma 3.2 For an exothermic reaction, $T(z)$ is an increasing function of z, and the maximum and minimum values of $T(z)$ are $T(L)$ and $T_0 > 0$, respectively.

Proof We observe that $(-\Delta H_A)(-r_A)$ is negative for an exothermic forward reaction and repeat Equation (1.2b) here for convenience:

$$k_T \frac{d^2C_A}{dz^2} - v\rho C_p \frac{dC_A}{dz} = (-\Delta H_A)(-r_A) = f_2 \leq 0. \tag{1.2b}$$

Integrating the inequality [Equation (1.2b)] with respect to z from 0 to L and using the boundary conditions [Equations (1.3)] yields

$$-\frac{v\rho C_P T(L)}{k_T} + \frac{v\rho C_p T_0}{k_T} \leq 0, \tag{1.6}$$

from which it follows that:

$$T_0 \leq T(L). \tag{1.7}$$

Now assume $T(0) < T_0$ which yields $\frac{dT}{dz}(0) < 0$. It follows that there exists a

$z_1 \in (0, L)$ where $\frac{dT}{dz}(z_3) = 0$, $T(L)$ is a minimum at z_1, and $\frac{d^2T}{dz^2} > 0$. This contradicts Equation (1.2b). Hence, $T_0 \leq T(0)$. It follows that $T(z)$ is an increasing function of z in the interval $[0, L]$, otherwise it contradicts Equation (1.2b). Hence, T_0 is the minimum temperature.

To determine the maximum temperature, T_{max}, combine Equation (1.4) and Equation (1.2b) to obtain:

$$\frac{d^2T}{dz^2} - \frac{v\rho C_p}{k_T}\frac{dT}{dz} = \frac{(-\Delta H_A)D}{k_T}\left(\frac{d^2C_A}{dz^2} - \frac{v}{D}\frac{dC_A}{dz}\right). \tag{1.8}$$

Integrating Equation (1.8) from $z = 0$ to $z = L$ yields

$$T(L) = T_0 - \frac{(-\Delta H_A)}{\rho C_p}\left[C_{A_0} - C_A(L)\right]. \tag{1.9}$$

Therefore, defining T_{max} as

$$T_{max} = T_0 - \frac{(-\Delta H_A)}{\rho C_p}C_{A_0}, \tag{1.10}$$

then $T(L) \leq T_{max}$.

1.4 CHANGE OF VARIABLES

We now do a change of variables, $(C_A, T) \longrightarrow (x_1, x_2)$ so that $(x_1, x_2) \in [0,1] \times [\delta, 1]$.

To accomplish this, let

$$x_1 = \frac{C_A}{C_{A_0}},\ x_2 = \frac{T}{T_{max}},\ z \to \frac{z}{L},\ \delta = \frac{T_0}{T_{max}},\ \gamma = \frac{E}{RT_{max}},\ \beta_1 = \frac{vL}{D},\ \beta_2 = \frac{v\rho C_p L}{k_T},$$

$$\mu_1 = \frac{k_0 L^2}{D} \equiv \left(\frac{k_0 L}{v}\right)\left(\frac{vL}{D}\right), \text{ and } \mu_2 = \frac{(-\Delta H_A) k_0 L^2}{k_T T_{max}} C_{A_0},$$

where C_{A_0} is the initial concentration, T_{max} is the reference temperature, $k_T/\rho C_p$ is the thermal diffusion coefficient $[\mathrm{m}^2\ \mathrm{s}^{-1}]$, and D is the mass diffusion coefficient $[\mathrm{m}^2\ \mathrm{s}^{-1}]$. Note that β_1 and β_2 are the mass and thermal Péclet numbers, respectively, and μ_1 is the Damköhler number.

The quantity

$$(-\mu_2)/\mu_1 = \frac{-(-\Delta H_A) k_0 L^2 C_{A_0}}{k_T T_{max}} \Big/ \frac{k_0 L^2}{D} = \frac{-(-\Delta H_A) D}{k_T} \frac{C_{A_0}}{T_{max}} = N_{Pr}$$

is the maximum fractional temperature difference or simply the Prater number (N_{Pr}), where $-(-\Delta H_A)D/k_T$ is the maximum temperature difference.

It was reported by Boglaev [15] that the Damköhler number, μ_1, can vary over a wide range, while the Prater number, N_{Pr} varies in the range $0.01 \leq N_{Pr} \leq 1$. Therefore, we choose the restriction that

$$0.01 \leq N_{Pr} \equiv (-\mu_2)/\mu_1 \leq 1. \tag{1.11}$$

With this change of variables, Equations (1.2) become

$$-\left(\frac{d^2x_1}{dz^2}-\beta_1\frac{dx_1}{dz}\right)=-\mu_1\exp\left(-\frac{\gamma}{x_2}\right)x_1 \tag{1.12a}$$

and

$$-\left(\frac{d^2x_2}{dz^2}-\beta_2\frac{dx_2}{dz}\right)=(-\mu_2)\exp\left(-\frac{\gamma}{x_2}\right)x_1 \tag{1.12b}$$

for $z \in D = (0,1)$.

Using the same scaling, Equations (1.3) become

$$-\frac{dx_1}{dz}(0)+\beta_1 x_1(0)=\beta_1 \tag{1.13a}$$

$$-\frac{dx_2}{dz}(0)+\beta_2 x_2(0)=\beta_2\delta \tag{1.13b}$$

$$\frac{dx_1}{dz}(1)=0 \tag{1.13c}$$

$$\frac{dx_2}{dz}(1)=0 \tag{1.13d}$$

Note: D is the domain of the existence of solutions of the elliptic boundary value problem (BVP) described by Equations (1.12) and (1.13) and let ∂D denotes the boundary of D and $\overline{D}$ the closure of D. Since $D=(0,1)$, then $\partial D = 0$ and 1 and $\overline{D} \equiv D \cup \partial D = [0,1]$.

The a-priori bounds for the steady-state reactant concentration and temperature are obvious from the system chemistry and physical arguments: x_1 is non-negative with $0 \le x_1(z) < 1$, while x_2 is positive with $0 < \delta < x_2(z) \le 1$, where $z \in [0,1]$.

REMARK 1.1 Since $\delta < x_2 \leq 1$, it must be that the following equation holds:

$$\text{min temperature} + \text{ max fractional temperature rise} \leq \text{max temperature} \quad (1.14)$$

where:

minimum (min) dimensionless temperature $= \delta$

maximum (max) fractional temperature rise $= N_{Pr} \equiv (-\mu_2)/\mu_1$

maximum (max) dimensionless temperature$=1$

Hence, we have that

$$\delta + N_{Pr} \leq 1 \Leftrightarrow \delta + (-\mu_2)/\mu_1 \leq 1$$

Therefore, knowing/choosing δ, we get $(-\mu_2)/\mu_1 \leq 1 - \delta$.

Therefore, we choose the restriction that

$$(-\mu_2)/\mu_1 \leq 1 - \delta. \quad (1.15)$$

Note: Equation (1.15) is a refinement of Equation (1.11). And this restriction will be enforced in Chapter 2 where the upper and lower solutions conditions for the BVP are proven.

CHAPTER 2: METHODOLOGY

The mathematical method adopted in this research is the method of upper and lower solutions together with its associated monotone sequence iteration. The first steps in the method of upper and lower solutions have been given by Picard in 1890 [16] for PDEs and three years later [17] for ODEs. In both cases, the existence of a solution is guaranteed from a monotone iterative technique. The existence of solutions for Cauchy equations was proved by Perron in 1915 [18]. In 1927, Müller extended Perron's results to initial value systems in [19]. In 1931, Dragoni [20] introduced the notion of the method of upper and lower solutions for ODEs with Dirichlet boundary value conditions.

It is well known that the upper and lower solutions method is a powerful tool for proving the existence of a solution to a boundary value problem. It has been used to deal with many two-point and multipoint boundary value problem ODEs (see, e.g., [21–23] and references therein). Many people pay attention to the existence, uniqueness, and/or multiplicity of solutions or positive solutions for boundary value problems of nonlinear differential equations by means of some fixed-point theorems, such as the Krasnosel'skii fixed-point theorem, the Leggett-Williams fixed-point theorem, and the Schauder fixed-point theorem [24–28].

Before using the method of upper and lower solutions to discuss and prove the existence, uniqueness, and/or multiplicity of solution(s), let us first transform the non-self-adjoint BVP to a corresponding self-adjoint BVP and also discuss the method of upper and lower solutions because these, as shown by Pao [29], are critical tools in order to establish the uniqueness and/or multiplicity of solutions of the BVP.

2.1 TRANSFORMATION OF THE COUPLED SYSTEM

Let us transform the system using the following equations:

$$x_1 = 1 - e^{\frac{\beta_1}{2}z} y_1 \tag{2.1a}$$

$$x_2 = \delta + e^{\frac{\beta_2}{2}z} y_2 \tag{2.1b}$$

Substituting Equations (2.1) into the two Equations (1.2) and the boundary conditions [Equations (1.3)] gives

$$-\frac{d^2y_1}{dz^2} = -\left(\frac{\beta_1}{2}\right)^2 y_1 + \mu_1 e^{\frac{-\beta_1}{2}z}\left(1 - e^{\frac{\beta_1}{2}z} y_1\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z} y_2}\right)} \equiv F_1(z, y_1, y_2) \tag{2.2a}$$

$$-\frac{d^2y_2}{dz^2} = -\left(\frac{\beta_2}{2}\right)^2 y_2 + (-\mu_2) e^{\frac{-\beta_2}{2}z}\left(1 - e^{\frac{\beta_1}{2}z} y_1\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z} y_2}\right)} \equiv F_2(z, y_1, y_2) \tag{2.2b}$$

in *D*,

and the transformed boundary conditions

$$-\frac{dy_1}{dz}(0) + \frac{\beta_1}{2} y_1(0) = 0 = h_1 \tag{2.3a}$$

$$\frac{dy_1}{dz}(1) + \frac{\beta_1}{2} y_1(1) = 0 = h_2 \tag{2.3b}$$

$$-\frac{dy_2}{dz}(0) + \frac{\beta_2}{2}\, y_2(0) = \ 0 = h_3 \tag{2.3c}$$

$$\frac{dy_2}{dz}(1) + \frac{\beta_2}{2}\, y_2(1) = \ 0 = h_4. \tag{2.3d}$$

The transformed BVP operators are now

$L_i \equiv \frac{d^2}{dz^2}$, and $B_i \equiv -\frac{d}{dz} + \frac{\beta_i}{2}$ at the boundary $z = 0$, and $\frac{d}{dz} + \frac{\beta_i}{2}$ at the boundary $z = 1$.

The transformed system with differential operators (L_i) and boundary operators (B_i) forms a self-adjoint system as shown in the following section.

2.1.1 SELF-ADJOINT DIFFERENTIAL AND BOUNDARY OPERATORS

Given an arbitrary operator L, then the adjoint of L is an operator denoted here by L^* such that

$$\langle v, Lu \rangle = \langle u, L^* v \rangle \tag{2.4a}$$

where $\langle .\, , . \rangle$ represents the inner product defined by:

$$\langle v, Lu \rangle \equiv \int_D v\, Lu\, dD \tag{2.4b}$$

for real-valued functions u and v.

If $L^* = L$, then the operator L is said to be self-adjoint.

For the case of the transformed differential and boundary operators L_i and B_i above, we have

$$\langle \mathrm{v}, L\mathrm{u}\rangle \equiv \int_D \mathrm{v}\, L\mathrm{u}\; \mathrm{d}D = \int_0^1 \mathrm{v}\frac{\mathrm{d}^2\mathrm{u}}{\mathrm{d}\mathrm{z}^2}\mathrm{d}\mathrm{z} = \int_0^1 \mathrm{v}\frac{\mathrm{d}}{\mathrm{d}\mathrm{z}}\left(\frac{\mathrm{d}\mathrm{u}}{\mathrm{d}\mathrm{z}}\right)\mathrm{d}\mathrm{z}$$

$$= \mathrm{v}\frac{\mathrm{d}\mathrm{u}}{\mathrm{d}\mathrm{z}}\bigg|_0^1 - \int_0^1 \frac{\mathrm{d}\mathrm{u}}{\mathrm{d}\mathrm{z}}\mathrm{d}\mathrm{v} \equiv \mathrm{v}\frac{\mathrm{d}\mathrm{u}}{\mathrm{d}\mathrm{z}}\bigg|_0^1 - \int_0^1 \frac{\mathrm{d}\mathrm{u}}{\mathrm{d}\mathrm{z}}\frac{\mathrm{d}\mathrm{v}}{\mathrm{d}\mathrm{z}}\mathrm{d}\mathrm{z} \equiv \mathrm{v}\frac{\mathrm{d}\mathrm{u}}{\mathrm{d}\mathrm{z}}\bigg|_0^1 - \int_0^1 \frac{\mathrm{d}\mathrm{v}}{\mathrm{d}\mathrm{z}}\frac{\mathrm{d}\mathrm{u}}{\mathrm{d}\mathrm{z}}\mathrm{d}\mathrm{z}$$

$$= \left(\mathrm{v}\frac{\mathrm{d}\mathrm{u}}{\mathrm{d}\mathrm{z}} - \mathrm{u}\frac{\mathrm{d}\mathrm{v}}{\mathrm{d}\mathrm{z}}\right)\bigg|_0^1 + \int_0^1 \mathrm{u}\frac{\mathrm{d}^2\mathrm{v}}{\mathrm{d}\mathrm{z}^2}\mathrm{d}\mathrm{z}$$

From the boundary conditions [Equations (1.3)], the expression

$$\left(\mathrm{v}\frac{\mathrm{d}\mathrm{u}}{\mathrm{d}\mathrm{z}} - \mathrm{u}\frac{\mathrm{d}\mathrm{v}}{\mathrm{d}\mathrm{z}}\right)\bigg|_0^1 = 0.$$

Hence, we have

$$\langle \mathrm{v}, L\mathrm{u}\rangle \equiv \int_0^1 \mathrm{v}\frac{\mathrm{d}^2\mathrm{u}}{\mathrm{d}\mathrm{z}^2}\mathrm{d}\mathrm{z} = \int_0^1 \mathrm{u}\frac{\mathrm{d}^2\mathrm{v}}{\mathrm{d}\mathrm{z}^2}\mathrm{d}\mathrm{z} \equiv \langle \mathrm{u}, L^*\mathrm{v}\rangle \qquad (2.5)$$

Therefore, we conclude that the differential operators L_i in Equations (2.2) together with the boundary conditions operator B_i in Equations (2.3) form a self-adjoint system. Other features brought about by this choice of transformation are:

(1) preservation of the positivity of the solutions,

(2) homogeneity of the boundary conditions, which results from the self-adjointness of the operators.

Note: Self-adjointness of the differential and boundary condtions operators is a requirement to apply Theorem 2.1 in section 2.2.2.1 to the BVP, thus the reason for the transformation of our non-self-adjoint BVP to self-adjoint BVP.

2.1.2 QUASIMONOTONICITY OF AN ARBITRARY FUNCTION $\mathbf{F} = (\mathbf{F_1}, \mathbf{F_2})$

Definition 2.1 A function $F = (F_1, F_2)$ is called quasimonotonically nondecreasing (resp., nonincreasing) in $R_1 \times R_2$ if both F_1 and F_2 are quasimonotonically nondecreasing (resp., nonincreasing) for $(y_1, y_2) \in R_1 \times R_2$. When F_1 is quasimonotonically nondecreasing and F_2 is quasimonotonically nonincreasing (or vice versa), then F is called mixed quasimonotone, where $R_1 \times R_2$ is the range of (y_1, y_2).

Note: The prefix 'quasi' as used here means that the function $F = (F_1, F_2)$ or F_i is a multivariable function, that is, at least two independent variables. Hence, if we know the monotonicity with respect to one variable, then the monotonicity with respect to other variables is left open.

The function F is said to be quasimonotone in $R_1 \times R_2$ if it has any one of the quasimonotone properties in Definition 2.1. As usual, we call F a C^1-function in $R_1 \times R_2$ if both F_1 and F_2 are continuously differentiable in (y_1, y_2) for all functions $(y_1, y_2) \in R_1 \times R_2$. F is called a quasi C^1-function in $R_1 \times R_2$ if F_1 is continuously differentiable in y_2 and F_2 is continuously differentiable in y_1 for all functions $(y_1, y_2) \in R_1 \times R_2$. It is clear that every C^1-function is a quasi C^1-function, but the converse is not necessarily true. Hence, if F is a C^1-function or a quasi C^1-function then three types of quasimonotone functions in Definition 2.1 are reduced to the form

$$\frac{\partial F_1}{\partial y_2} \geq 0, \qquad \frac{\partial F_2}{\partial y_1} \geq 0 \tag{2.6a}$$

$$\frac{\partial F_1}{\partial y_2} \leq 0, \qquad \frac{\partial F_2}{\partial y_1} \leq 0 \tag{2.6b}$$

$$\frac{\partial F_1}{\partial y_2} \geq 0, \qquad \frac{\partial F_2}{\partial y_1} \leq 0 \tag{2.6c}$$

for $(y_1, y_2) \in R_1 \times R_2$.

2.1.2.1 MIXED QUASIMONOTONICITY OF $\mathbf{F} = (\mathbf{F_1}, \mathbf{F_2})$ DEFINED IN THE BVP

For the function F_1 defined in Equation (2.2a), that is,

$$F_1(z, y_1, y_2) = -\left(\frac{\beta_1}{2}\right)^2 y_1 + \mu_1 e^{\frac{-\beta_1}{2}z}\left(1 - e^{\frac{\beta_1}{2}z} y_1\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z} y_2}\right)},$$

we have,

$$\frac{\partial F_1(z, y_1, y_2)}{\partial y_2} = \gamma \mu_1 e^{\frac{-(\beta_1 - \beta_2)}{2}z}\left(\delta + e^{\frac{\beta_2}{2}z} y_2\right)^{-2}\left(1 - e^{\frac{\beta_1}{2}z} y_1\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z} y_2}\right)}$$

for $(z, y_1, y_2) \in D \times \langle \underline{\mathbf{y}}, \overline{\mathbf{y}} \rangle$, since γ and μ_1 are positive constants.

To prove that

$$\frac{\partial F_1(z, y_1, y_2)}{\partial y_2} \geq 0, \tag{2.7a}$$

it suffices to show that

$$1-e^{\frac{\beta_1}{2}z}y_1 \geq 0 \text{ for } (z, y_1, y_2) \in D \times \langle \underline{\mathbf{y}}, \overline{\mathbf{y}} \rangle, \tag{2.7b}$$

where $D \times \langle \underline{\mathbf{y}}, \overline{\mathbf{y}} \rangle$ is the domain of (z, y_1, y_2); $\overline{\mathbf{y}} = (\overline{y_1}, \overline{y_2})$ and $\underline{\mathbf{y}} = (\underline{y_1}, \underline{y_2})$ are the upper and lower solutions vector respectively, that will define in the next section. One way to prove Equation (2.7b) is that if $1-e^{\frac{\beta_1}{2}z}\overline{y_1} \geq 0$ and $1-e^{\frac{\beta_1}{2}z}\underline{y_1} \geq 0$, then we have that $1-e^{\frac{\beta_1}{2}z}y_1 \geq 0$ for $(z, y_1, y_2) \in D \times \langle \underline{\mathbf{y}}, \overline{\mathbf{y}} \rangle$. However, because Equation (2.7b) depends on our choice of $\overline{y_1}$ and $\underline{y_1}$ (upper and lower solutions to the BVP), which are not yet available, an alternative is to consider the bounds on x_1 and then the corresponding transformation to y_1.

We note that since $1-e^{\frac{\beta_1}{2}z}y_1 = x_1 : 0 \leq x_1 < 1$, then we have that $1-e^{\frac{\beta_1}{2}z}y_1 \geq 0$ for $(z, y_1, y_2) \in D \times \langle \underline{\mathbf{y}}, \overline{\mathbf{y}} \rangle$.

For the function F_2 defined in Equation (2.2b), that is,

$$F_2(z, y_1, y_2) = -\left(\frac{\beta_2}{2}\right)^2 y_2 + (-\mu_2)e^{\frac{-\beta_2}{2}z}\left(1-e^{\frac{\beta_1}{2}z}y_1\right)e^{\left(\frac{-\gamma}{\delta+e^{\frac{\beta_2}{2}z}y_2}\right)},$$

we have

$$\frac{\partial F_2(z, y_1, y_2)}{\partial y_1} = -(-\mu_2)e^{\frac{\beta_1-\beta_2}{2}z}e^{\left(\frac{-\gamma}{\delta+e^{\frac{\beta_2}{2}z}y_2}\right)}.$$

Clearly,

$$\frac{\partial F_2(z, y_1, y_2)}{\partial y_1} < 0 \tag{2.8}$$

for all $(z, y_1, y_2) \in D \times \langle \underline{\mathbf{y}}, \overline{\mathbf{y}} \rangle$, since $(-\mu_2)$ is a positive constant for our exothermic isomerization.

Thus, we conclude that $F_1(z, y_1, y_2)$ is quasimonotonically nondecreasing and $F_2(z, y_1, y_2)$ quasimonotonically nonincreasing, and thus complete the proof that the function $F = (F_1, F_2)$ is **mixed quasimonotone**.

Note: Knowing the type of quasimonotonicity the function $F = (F_1, F_2)$ is allows us to define an accurate iterative scheme for the solution to the BVP. For the case when the function $F = (F_1, F_2)$ is either quasimonotonically nondecreasing or nonincreasing, the iterative scheme normally converges to the BVP true solutions depending on the choice of upper and lower solutions chosen to start the iteration with. But for the mixed quasimonotonocity, the iterative scheme either converges to the true solution or just gives us the closest region where the true solution lies. Then, for this case of mixed quasimonotonicity, there is a mathematical condition to check to know if the iteration actually converges to the true solution or otherwise. Moreover, the iterative scheme for each type of quasimonotonicity defers in one way or another [29].

2.2 UPPER AND LOWER SOLUTIONS FOR THE COUPLED SYSTEM

The method of upper and lower solutions is a useful mathematical tool that one uses when trying to prove the existence of a solution to a differential equation or system of differential equations [29–32]. In fact, it can also be used to prove multiplicity of solutions, provided there exist more than one disjoint pair of upper and lower solutions [29]. First, we define upper and lower solutions for the coupled system, give one or two theorems about the properties pertaining to them, and then apply them to the BVP of interest, specifically the transformed one [Equations (2.2) and (2.3)].

Definition (2.2) Suppose that for the mixed quasimonotonic function $\mathrm{F} = (\mathrm{F}_1, \mathrm{F}_2)$: F_1 quasimonotonically nondecreasing and F_2 quasimonotonically nonincreasing, there exists a pair of functions $\bar{\mathbf{y}} = (\overline{y_1}, \overline{y_2})$ and $\underline{\mathbf{y}} = (\underline{y_1}, \underline{y_2})$ which satisfies the boundary inequalities

$$-\frac{d\overline{y_1}}{dz}(0) + \frac{\beta_1}{2}\,\overline{y_1}(0) \geq 0 \qquad (2.9a) \qquad \frac{d\overline{y_1}}{dz}(1) + \frac{\beta_1}{2}\,\overline{y_1}(1) \geq 0 \qquad (2.9b)$$

$$-\frac{d\underline{y_1}}{dz}(0) + \frac{\beta_1}{2}\,\underline{y_1}(0) \leq 0 \qquad (2.9c) \qquad \frac{d\underline{y_1}}{dz}(1) + \frac{\beta_1}{2}\,\underline{y_1}(1) \leq 0 \qquad (2.9d)$$

$$-\frac{d\overline{y_2}}{dz}(0) + \frac{\beta_2}{2}\,\overline{y_2}(0) \geq 0 \qquad (2.9e) \qquad \frac{d\overline{y_2}}{dz}(1) + \frac{\beta_2}{2}\,\overline{y_2}(1) \geq 0 \qquad (2.9f)$$

$$-\frac{d\underline{y_2}}{dz}(0) + \frac{\beta_2}{2}\,\underline{y_2}(0) \leq 0 \qquad (2.9g) \qquad \frac{d\underline{y_2}}{dz}(1) + \frac{\beta_2}{2}\,\underline{y_2}(1) \leq 0 \qquad (2.9h)$$

The pair of functions $\bar{\mathbf{y}} = (\overline{y_1}, \overline{y_2})$ and $\underline{\mathbf{y}} = (\underline{y_1}, \underline{y_2}) \in C^{\alpha}(\overline{D}) \cap C^2(D)$ are called ordered upper and lower solutions of Equations (2.2) and (2.3) if they satisfy the following conditions:

(i) The boundary inequalities [Equations (2.9)],

(ii) $L_1\overline{y_1} + \mathrm{F}_1(z, \overline{y_1}, \overline{y_2}) \leq 0 \leq L_1\underline{y_1} + \mathrm{F}_1(z, \underline{y_1}, \underline{y_2})$, (2.10)

(iii) $L_2\overline{y_2} + \mathrm{F}_2(z, \underline{y_1}, \overline{y_2}) \leq 0 \leq L_2\underline{y_2} + \mathrm{F}_2(z, \overline{y_1}, \underline{y_2})$, (2.11)

(iv) $\overline{\mathbf{y}}$ and $\underline{\mathbf{y}}$ are ordered, that is, $\overline{\mathbf{y}} \geq \underline{\mathbf{y}}$, where $\overline{\mathbf{y}} = (\overline{y_1}, \overline{y_2})$ and $\underline{\mathbf{y}} = (\underline{y_1}, \underline{y_2})$. This is equivalent to $\overline{y_1} \geq \underline{y_1}$ and $\overline{y_2} \geq \underline{y_2}$. (2.12)

$\overline{D}$ is the closure of D.

Remark 2.1 By $\overline{\mathbf{y}}$ and $\underline{\mathbf{y}} \in C^{\alpha}(\overline{D})$, we mean $\overline{\mathbf{y}}$ and $\underline{\mathbf{y}}$ are $\alpha -$ Hölder continuous in $\overline{D}$, and by $\overline{\mathbf{y}}$ and $\underline{\mathbf{y}} \in C^2(D)$, we mean $\overline{\mathbf{y}}$ and $\underline{\mathbf{y}}$ are at least twice continuously differentiable in D. Thus, $\overline{\mathbf{y}}$ and $\underline{\mathbf{y}} \in C^{\alpha}(\overline{D}) \cap C^2(D)$ meant $\overline{\mathbf{y}}$ and $\underline{\mathbf{y}}$ are both $\alpha -$ Hölder continuous in $\overline{D}$ and at least twice continuously differentiable in D. And the number α is called the Hölder's exponent.

In summary, the method of upper and lower solutions allows us to ensure the existence of a solution of the considered problem lying between the lower and the upper solutions, that is, we have information about the existence and location of the solutions. So, the problem of finding a solution of the considered problem is replaced by that of finding two well-ordered functions that satisfy some suitable inequalities. Following these results, there have been a large number of works in which the method has been developed for different kinds of boundary value problems; first-, second- and higher-order ordinary differential equations with different types of boundary conditions such as, among others, periodic, mixed, Dirichlet, or Neumann conditions, have been considered [32]. Also, PDEs of first and second-order, have been treated in the literature [33–35].

2.2.1 EXISTENCE OF A SOLUTION FOR THE COUPLED SYSTEM

The results in this section will guarantee the existence of at least one solution to the coupled BVP. Here, existence of a solution (at least one) will be proven by construction of a pair of upper and lower solutions for the transformed BVP, and its dependence on the system parameters. Though there is no hard rule on how to construct upper and lower solutions for ODEs or PDEs, a brief guide on how to construct for ODEs is discussed by Tam [36].

The proposed pair of upper and lower solutions is as shown below.

$$\begin{cases} \overline{y_1} = k_1 e^{-a_1 \frac{\beta_1}{2} z} \\ \underline{y_1} = \frac{b_1}{\pi^2} \sin(\pi z) \end{cases} \qquad \begin{cases} \overline{y_2} = k_2 e^{-a_2 \frac{\beta_2}{2} z} \\ \underline{y_2} = \frac{b_2}{\pi^2} \sin(\pi z) \end{cases} \tag{2.13}$$

This pair was defined so that it covers any/some part (i.e., not necessarily the entire solution range) of the solution range for all $z \in [0,1]$. Every solution range is bounded by upper and lower solutions.

Based on the two parameters values sets (i) $\beta_1/2 = 100$, $\beta_2/2 = 75$ and (ii) $\beta_1/2 = 75$, $\beta_2/2 = 50$ together with $\mu_1 = 0.35$, $\mu_2 = -0.1$, $\delta = 0.0025$, $\gamma = 1.5$, and the constants $a_1 = a_2 = 0.5$, $b_1 = b_2 = 5 \times 10^{-10}$, $k_1 = 0.5, k_2 = 0.5 - \delta$, the upper and lower solution' conditions (i-iv) [Equations (2.9-2.12)] are proved as follows.

Proof of condition i [Equations (2.9)]:

From Equation (2.9a),

$$-\frac{d\overline{y_1}}{dz}(0) + \frac{\beta_1}{2}\,\overline{y_1}(0) \geq 0, \text{we have}$$

$$-\frac{d\left(k_1 e^{-a_1\frac{\beta_1}{2}z}\right)}{dz}(0) + \frac{\beta_1}{2}\left(k_1 e^{-a_1\frac{\beta_1}{2}z}\right)(0) = a_1\frac{k_1\beta_1}{2} + \frac{k_1\beta_1}{2} = \frac{k_1\beta_1}{2}(1 + a_1) \geq 0,$$

$$\Longrightarrow 1 + a_1 \geq 0 \Rightarrow a_1 \geq -1.$$

Hence, we have

$$\frac{d\overline{y_1}}{dz}(0) + \frac{\beta_1}{2}\,\overline{y_1}(0) \geq 0 \text{ for } a_1 \geq -1.$$

From Equation (2.9b),

$$\frac{d\overline{y_1}}{dz}(1) + \frac{\beta_1}{2}\,\overline{y_1}(1) \geq 0, \text{we have}$$

$$\frac{d\left(k_1 e^{-a_1\frac{\beta_1}{2}z}\right)}{dz}(1) + \frac{\beta_1}{2}\left(k_1 e^{-a_1\frac{\beta_1}{2}z}\right)(1) = -a_1\frac{k_1\beta_1}{2}e^{-a_1\frac{\beta_1}{2}} + \frac{k_1\beta_1}{2}e^{-a_1\frac{\beta_1}{2}}$$

$$= \frac{k_1\beta_1}{2}e^{-a_1\frac{\beta_1}{2}}(1 - a_1) \geq 0,$$

$$\Longrightarrow 1 - a_1 \geq 0 \Longrightarrow -a_1 \geq -1 \Rightarrow a_1 \leq 1.$$

Hence, we have

$$\frac{d\overline{y_1}}{dz}(1) + \frac{\beta_1}{2}\,\overline{y_1}(1) \geq 0 \text{ for } a_1 \leq 1.$$

Therefore, we conclude that for Equations (2.9a) and (2.9b) to hold simultaneously,

$-1 \leq a_1 \leq 1.$

From Equation (2.9c),

$$-\frac{d\underline{y_1}}{dz}(0) + \frac{\beta_1}{2}\,\underline{y_1}(0) \le 0, \text{we have}$$

$$-\frac{d\left(\frac{b_1}{\pi^2}\sin(\pi z)\right)}{dz}(0) + \frac{\beta_1}{2}\frac{b_1}{\pi^2}\sin(\pi z)\,(0) = -\frac{b_1}{\pi}\cos(0) + \frac{\beta_1}{2}\frac{b_1}{\pi^2}\sin(0) = -\frac{b_1}{\pi}.$$

$$\text{Clearly}, -\frac{d\overline{y_1}}{dz}(0) + \frac{\beta_1}{2}\,\overline{y_1}(0) = -\frac{b_1}{\pi} < 0 \Longrightarrow -b_1 < 0 \Longrightarrow b_1 > 0.$$

This implies that Equation (2.9c) holds for $b_1 > 0$.

From Equation (2.9d),

$$\frac{d\underline{y_1}}{dz}(1) + \frac{\beta_1}{2}\,\underline{y_1}(1) \le 0, \text{we have}$$

$$\frac{d\left(\frac{b_1}{\pi^2}\sin(\pi z)\right)}{dz}(1) + \frac{\beta_1}{2}\frac{b_1}{\pi^2}\sin(\pi z)\,(1) = \frac{b_1}{\pi}\cos(\pi) + \frac{\beta_1}{2}\frac{b_1}{\pi^2}\sin(\pi) = -\frac{b_1}{\pi}.$$

$$\text{Clearly}, -\frac{d\overline{y_1}}{dz}(1) + \frac{\beta_1}{2}\,\overline{y_1}(1) = -\frac{b_1}{\pi} < 0 \Longrightarrow -b_1 < 0 \Longrightarrow b_1 > 0.$$

This implies that Equation (2.9d) holds for $b_1 > 0$.

For Equation (2.9e),

$$-\frac{d\overline{y_2}}{dz}(0) + \frac{\beta_2}{2}\,\overline{y_2}(0) \ge 0, \text{we have}$$

$$-\frac{d\left(k_2 e^{-a_2\frac{\beta_2}{2}z}\right)}{dz}(0) + \frac{\beta_2}{2}\left(k_2 e^{-a_2\frac{\beta_2}{2}z}\right)(0) = a_2\frac{k_2\beta_2}{2} + \frac{k_2\beta_2}{2} = \frac{k_2\beta_2}{2}(1 + a_2) \ge 0$$

$$\Longrightarrow 1 + a_2 \ge 0 \Rightarrow a_2 \ge -1$$

Hence, we have $\quad -\frac{d\overline{y_2}}{dz}(0) + \frac{\beta_2}{2}\,\overline{y_2}(0) \ge\ 0$

For Equation (2.9f),

$$\frac{d\overline{y_2}}{dz}(1) + \frac{\beta_2}{2}\,\overline{y_2}(1) \geq\; 0, \text{we have}$$

$$\frac{d\left(k_2 e^{-a_2\frac{\beta_2}{2}z}\right)}{dz}(1) + \frac{\beta_2}{2}\left(k_2 e^{-a_2\frac{\beta_2}{2}z}\right)(1) = -a_2\frac{k_2\beta_2}{2}e^{-a_2\frac{\beta_2}{2}} + \frac{k_2\beta_2}{2}e^{-a_2\frac{\beta_2}{2}}$$

$$= \frac{k_2\beta_2}{2}e^{-a_2\frac{\beta_2}{2}}(1 - a_2) \geq 0$$

$$\Longrightarrow 1 - a_2 \geq 0 \Longrightarrow -a_2 \geq -1 \Rightarrow a_2 \leq 1.$$

Therefore, we conclude that for Equations (2.9e) and (2.9f) to hold simultaneously, $-1 \leq a_1 \leq 1$.

From Equations (2.9e) and (2.9f) above, we have that $-1 \leq a_2 \leq 1$, but likewise, let us restrict to $-1 < a_2 < 1$.

$$\text{Hence, we have:}\quad \frac{d\overline{y_2}}{dz}(1) + \frac{\beta_2}{2}\,\overline{y_2}(1) \geq\; 0$$

From Equation (2.9g),

$$-\frac{d\underline{y_2}}{dz}(0) + \frac{\beta_2}{2}\,\underline{y_2}(0) \leq\; 0, \text{we have}$$

$$-\frac{d\left(\frac{b_2}{\pi^2}\sin(\pi z)\right)}{dz}(0) + \frac{\beta_2}{2}\frac{b_2}{\pi^2}\sin(\pi z)(0) = -\frac{b_2}{\pi}\cos(0) + \frac{\beta_2}{2}\frac{b_2}{\pi^2}\sin(0) = -\frac{b_2}{\pi}$$

$$\text{In fact,} -\frac{d\overline{y_2}}{dz}(0) + \frac{\beta_2}{2}\,\overline{y_2}(0) = -\frac{b_2}{\pi} < 0 \Longrightarrow -b_2 < 0 \Longrightarrow b_2 > 0$$

From Equation (2.9h),

$$\frac{d\underline{y_2}}{dz}(1) + \frac{\beta_2}{2}\ \underline{y_2}(1) \leq\ 0, \text{we have}$$

$$\frac{d\left(\frac{b_2}{\pi^2}\sin(\pi z)\right)}{dz}(1) + \frac{\beta_2}{2}\frac{b_2}{\pi^2}\sin(\pi z)(1) = \frac{b_2}{\pi}\cos(\pi) + \frac{\beta_2}{2}\frac{b_2}{\pi^2}\sin(\pi) = -\frac{b_2}{\pi}$$

Likewise, $-\frac{d\overline{y_2}}{dz}(1) + \frac{\beta_2}{2}\ \overline{y_2}(1) = -\frac{b_2}{\pi} < 0 \Longrightarrow -b_2 < 0 \Longrightarrow b_2 > 0$

Proof of condition ii [Equation (2.10)]:

$$L_1\overline{y_1} + F_1(z, \overline{y_1}, \overline{y_2}) \leq 0 \leq L_1\underline{y_1} + F_1(z, \underline{y_1}, \underline{y_2})$$

The left hand side (L. H. S.) inequality: $L_1\overline{y_1} + F_1(z, \overline{y_1}, \overline{y_2}) \leq 0$

$$\text{L. H. S.} = \frac{d^2\overline{y_1}}{dz^2} - \left(\frac{\beta_1}{2}\right)^2 \overline{y_1} + \mu_1 e^{\frac{-\beta_1}{2}z}\left(1 - e^{\frac{\beta_1}{2}z}\,\overline{y_1}\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z}\,\overline{y_2}}\right)}$$

$$= \frac{d^2\left(k_1 e^{-a_1\frac{\beta_1}{2}z}\right)}{dz^2} - \left(\frac{\beta_1}{2}\right)^2 k_1 e^{-a_1\frac{\beta_1}{2}z}$$

$$+\mu_1 e^{-\frac{\beta_1}{2}z}\left(1 - e^{\frac{\beta_1}{2}z}\, k_1 e^{-a_1\frac{\beta_1}{2}z}\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z}\, k_2 e^{-a_2\frac{\beta_2}{2}z}}\right)}$$

$$= -\left(\frac{\beta_1}{2}\right)^2 k_1 e^{-a_1\frac{\beta_1}{2}z}\left(1 - {a_1}^2\right)$$

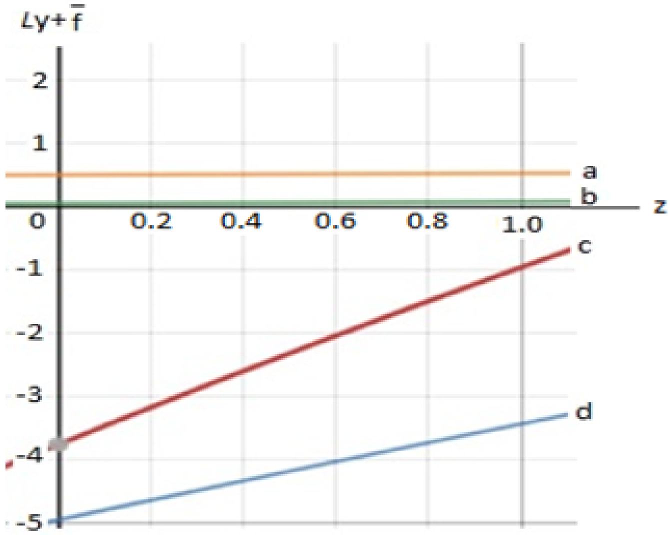
$$+\mu_1 e^{\frac{-\beta_1}{2}z}\left(1 - k_1 e^{(1-a_1)\frac{\beta_1}{2}z}\right) e^{\left(\frac{-\gamma}{\delta + k_2 e^{(1-a_2)\frac{\beta_2}{2}z}}\right)}$$

For values of μ_1, we need $1 - {a_1}^2 = (1 - a_1)(1 + a_1) \geq 0$ for the L. H. S. to be ≤ 0.

An easy way to show that the L. H. S. ≤ 0 for all values of $z \in [0,1]$ is the graphical method; this is shown in Figure 2 for $\beta_1/2 = 100$ and $\beta_2/2 = 75$ and Figure 3 for $\beta_1/2 = 75$ and $\beta_2/2 = 50$.

Note: We can refine the limit on a_i as $1 < a_i < 1$, instead of $1 \leq a_i \leq 1$ to avoid any possibility of trivial solution.

For the first parameter set where $\beta_1 = 200$ and $\beta_2 = 150$, we have Figure 2.



<u>Notation</u>

Graph a: $L_1\underline{y_1} + F_1(z, \underline{y_1}, \underline{y_2}) \geq 0$

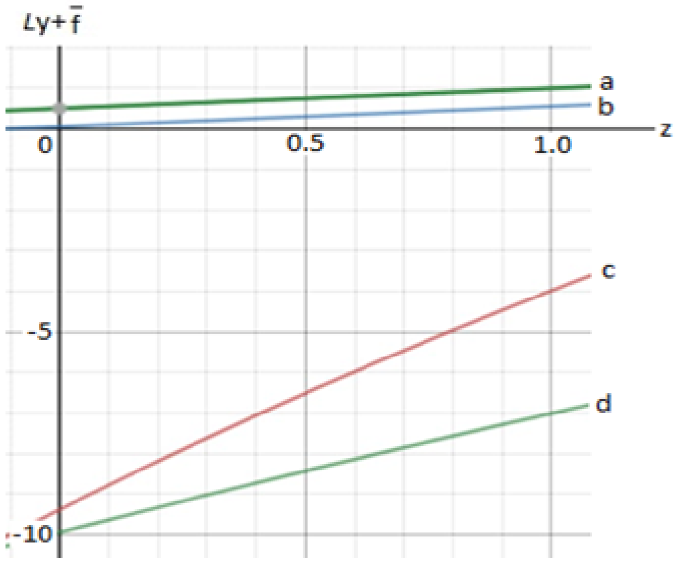
Graph b: $L_2\underline{y_2} + F_2(z, \overline{y_1}, \underline{y_2}) \geq 0$

Graph c: $L_1\overline{y_1} + F_1(z, \overline{y_1}, \overline{y_2}) \leq 0$

Graph d: $L_2\overline{y_2} + F_2(z, \underline{y_1}, \overline{y_2}) \leq 0$

Figure 2: Graphs of conditions (ii) and (iii) for Equation (2.13) for $z \in [0,1]$ using parameters $\beta_1 = 200$, $\beta_1 = 150$, $\mu_1 = 0.35$, $\mu_2 = -0.1$, $\delta = 0.0025$, $\gamma = 1.5$; and constants $a_1 = a_2 = 0.5$, $b_1 = b_2 = 5 \times 10^{-10}$, $k_1 = 0.5$, $k_2 = 0.5 - \delta$.

And for the other parameter set where $\beta_1 = 150$ and $\beta_2 = 100$, we have Figure 3.



Notation

Graph a: $L_1\underline{y_1} + F_1(z,\underline{y_1},\underline{y_2}) \geq 0$

Graph b: $L_2\underline{y_2} + F_2(z,\overline{y_1},\underline{y_2}) \geq 0$

Graph c: $L_1\overline{y_1} + F_1(z,\overline{y_1},\overline{y_2}) \leq 0$

Graph d: $L_2\overline{y_2} + F_2(z,\underline{y_1},\overline{y_2}) \leq 0$

Figure 3: Graphs of conditions (ii) and (iii) for Equation (2.13) for $z \in [0,1]$ using parameters $\beta_1/2 = 75$, $\beta_2/2 = 50$, $\mu_1 = 0.35$, $\mu_2 = -0.1$, $\delta = 0.0025$, $\gamma = 1.5$; and constants $a_1 = a_2 = 0.5$, $b_1 = b_2 = 5 \times 10^{-10}$, $k_1 = 0.5$, $k_2 = 0.5 - \delta$.

The right hand side inequality, $0 \leq L_1\underline{y_1} + F_1(z,\underline{y_1},\underline{y_2})$, is equivalent to

$$L_1\underline{y_1} + F_1(z,\underline{y_1},\underline{y_2}) \geq 0$$

$$\text{L.H.S.} = \frac{d^2\underline{y_1}}{dz^2} - \left(\frac{\beta_1}{2}\right)^2 \underline{y_1} + \mu_1 e^{\frac{-\beta_1}{2}z}\left(1 - e^{\frac{\beta_1}{2}z}\underline{y_1}\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z}\underline{y_2}}\right)}$$

$$= \frac{d^2\left(\frac{b_1}{\pi^2}\sin(\pi z)\right)}{dz^2} - \left(\frac{\beta_1}{2}\right)^2 \frac{b_1}{\pi^2}\sin(\pi z)$$

$$+ \mu_1 e^{\frac{-\beta_1}{2}z}\left(1 - e^{\frac{\beta_1}{2}z}\frac{b_1}{\pi^2}\sin(\pi z)\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z}\frac{b_2}{\pi^2}\sin(\pi z)}\right)}$$

$$= -b_1\left(1+\left(\frac{\beta_1/2}{\pi}\right)^2\right)\sin(\pi z)$$

$$+\mu_1 e^{\frac{-\beta_1}{2}z}\left(1-\frac{b_1}{\pi^2}e^{\frac{\beta_1}{2}z}\sin(\pi z)\right)e^{\left(\frac{-\gamma}{\delta+\frac{b_2}{\pi^2}e^{\frac{\beta_2}{2}z}\sin(\pi z)}\right)}$$

This is ≥ 0 as shown in Figures 2 and 3.

Proof of condition iii [Equation (2.11)]:

$$L_2\overline{y_2}+F_2(z,\underline{y_1},\overline{y_2})\leq 0\leq L_2\underline{y_2}+F_2(z,\overline{y_1},\underline{y_2})$$

The left hand side (L.H.S.) inequality: $L_2\overline{y_2}+F_2(z,\underline{y_1},\overline{y_2})\leq 0$

$$\text{L. H. S.}=\frac{d^2\overline{y_2}}{dz^2}-\left(\frac{\beta_2}{2}\right)^2\overline{y_2}+(-\mu_2)e^{\frac{-\beta_2}{2}z}\left(1-e^{\frac{\beta_1}{2}z}\underline{y_1}\right)e^{\left(\frac{-\gamma}{\delta+e^{\frac{\beta_2}{2}z}\overline{y_2}}\right)}$$

$$=\frac{d^2\left(k_2e^{-a_2\frac{\beta_2}{2}z}\right)}{dz^2}-\left(\frac{\beta_2}{2}\right)^2e^{-a_2\frac{\beta_2}{2}z}$$

$$+(-\mu_2)e^{\frac{-\beta_2}{2}z}\left(1-e^{\frac{\beta_1}{2}z}\frac{b_1}{\pi^2}\sin(\pi z)\right)e^{\left(\frac{-\gamma}{\delta+e^{\frac{\beta_2}{2}z}k_2e^{-a_2\frac{\beta_2}{2}z}}\right)}$$

$$\text{L. H. S.}=-\left(\frac{\beta_2}{2}\right)^2k_2e^{-a_2\frac{\beta_2}{2}z}\left(1-{a_2}^2\right)$$

$$+(-\mu_2)e^{\frac{-\beta_2}{2}z}\left(1-\frac{b_1}{\pi^2}e^{\frac{\beta_1}{2}z}\sin(\pi z)\right)e^{\left(\frac{-\gamma}{\delta+k_2e^{(1-a_2)\frac{\beta_2}{2}z}}\right)}$$

For the chosen parameter values, this is ≥ 0 as shown in Figures 2 and 3.

The right hand side inequality: $0 \leq L_2\underline{y_2} + F_2(z, \overline{y_1}, \underline{y_2})$; this is equivalent to

$$L_2\underline{y_2} + F_2(z, \overline{y_1}, \underline{y_2}) \geq 0$$

$$\text{L.H.S.} = \frac{d^2\underline{y_2}}{dz^2} - \left(\frac{\beta_2}{2}\right)^2 \underline{y_2} + (-\mu_2)e^{\frac{-\beta_2}{2}z}\left(1 - e^{\frac{\beta_1}{2}z}\overline{y_1}\right)e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z}\underline{y_2}}\right)}$$

$$= \frac{d^2\left(\frac{b_2}{\pi^2}\sin(\pi z)\right)}{dz^2} - \left(\frac{\beta_2}{2}\right)^2 \frac{b_2}{\pi^2}\sin(\pi z)$$

$$+(-\mu_2)e^{\frac{-\beta_2}{2}z}\left(1 - e^{\frac{\beta_1}{2}z}k_1 e^{-a_1\frac{\beta_1}{2}z}\right)e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z}\frac{b_2}{\pi^2}\sin(\pi z)}\right)}$$

$$\text{L.H.S.} = -b_2\left(1 + \left(\frac{\beta_2/2}{\pi}\right)^2\right)\sin(\pi z)$$

$$+(-\mu_2)e^{\frac{-\beta_2}{2}z}\left(1 - k_1 e^{(1-a_1)\frac{\beta_1}{2}z}\right)e^{\left(\frac{-\gamma}{\delta + \frac{b_2}{\pi^2}e^{\frac{\beta_2}{2}z}\sin(\pi z)}\right)}$$

For the indicated choice of parameters, this is ≥ 0 as shown in Figures 2 and 3.

Proof of condition iv [Equation (2.12)]: $\overline{\mathbf{y}}$ and $\underline{\mathbf{y}}$ are ordered, that is, $\overline{\mathbf{y}} \geq \underline{\mathbf{y}}$, where $\overline{\mathbf{y}} = (\overline{y_1}, \overline{y_2})$ and $\underline{\mathbf{y}} = \left(\underline{y_1}, \underline{y_2}\right)$. This implies that $\overline{y_1} \geq \underline{y_1}$ and $\overline{y_2} \geq \underline{y_2}$. This is shown in Figure 4.

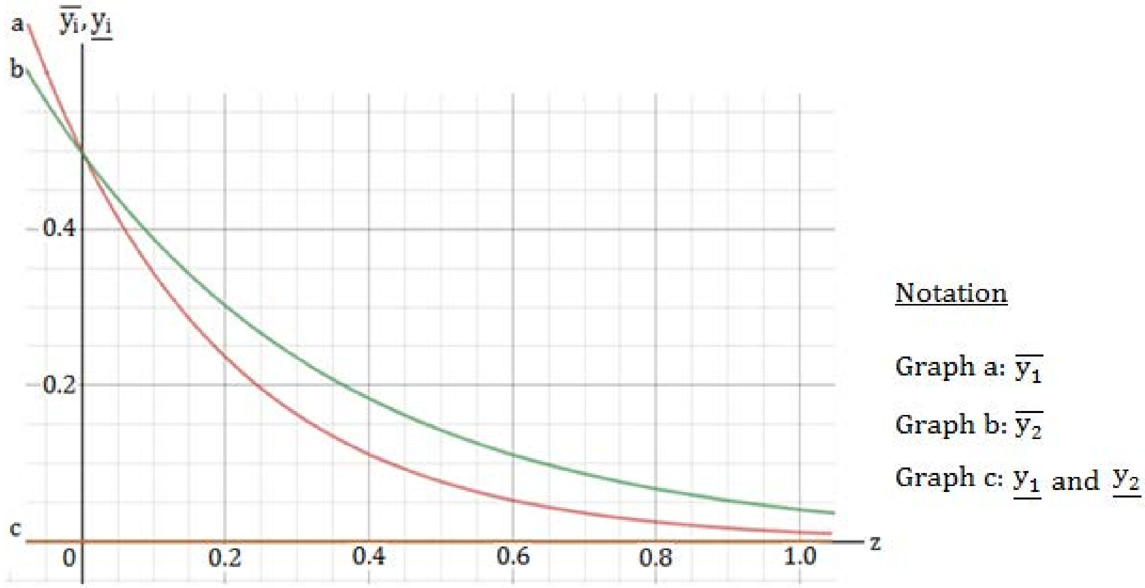


Figure 4: Graph of $\overline{y_i} \geq \underline{y_i}$ for the pair in Equation (2.13) for $z \in [0,1]$ using $\beta_1 = 200$, $\beta_2 = 150$, $a_1 = a_2 = 0.5$, $b_1 = b_2 = 5 \times 10^{-10}$, $k_1 = 0.5$, $k_2 = 0.5 - \delta$ and $\delta = 0.0025$.

2.2.2 UNIQUE SOLUTION AND/OR MULTIPLE SOLUTIONS TO THE COUPLED BVP USING THE UPPER AND LOWER SOLUTIONS METHOD

As a direct consequence of the transformed Danckwerts BCs [Equations (2.3)], the TR model reduces to the continous stirred tank reactor (CSTR) and the plug flow reactor (PFR) models for very large and very small axial dispersion coefficients (equivalent to very small and very large Péclet numbers, β_i, $i = 1,2$), respectively. The multiplicity of solutions to the CSTR has been well established, at least for simple reacting systems [1,43,44]. On the other hand, the PFR model does not admit any multiple steady states, since it is constituted by initial-value first-order ordinary differential equations (ODEs) [43,44].

2.2.2.1 UNIQUE SOLUTION FOR THE COUPLED BVP USING UPPER AND LOWER SOLUTIONS METHOD

Since only a positive real solution is of interest here, and if the maximal $(\overline{Y_1}, \overline{Y_2})$ and the minimal $(\underline{Y_1}, \underline{Y_2})$ solutions are strictly positive, it is possible to impose a condition in order to ensure the uniqueness of a positive solution [29]. The existence and uniqueness of this positive solution is ensured if there exists a pair of ordered nonnegative upper and lower solutions $\overline{\mathbf{y}} = (\overline{y_1}, \overline{y_2})$, $\underline{\mathbf{y}} = (\underline{y_1}, \underline{y_2})$ with $\underline{y_i} \not\equiv 0$, that is, $\underline{y_i}$ not identically zero for all $z \in [0,1]$, where $i = 1,2$. In Theorem 2.1, we show that if $F = (F_1, F_2)$ satisfies either one of the conditions

$$\frac{\partial}{\partial y_1}\left(\frac{F_1(z, y_1, y_2)}{y_1}\right); \ (z, y_1, y_2) \in D \times \langle \underline{\mathbf{y}}, \overline{\mathbf{y}} \rangle > 0, \quad h_1 = 0, \quad h_2 \geq 0 \qquad (2.14a)$$

or

$$\frac{\partial}{\partial y_2}\left(\frac{F_2(z, y_1, y_2)}{y_2}\right); \ (z, y_1, y_2) \in D \times \langle \underline{\mathbf{y}}, \overline{\mathbf{y}} \rangle > 0, \quad h_1 \geq 0, \quad h_2 = 0 \qquad (2.14b)$$

then for the mixed quasimonotone functions the BVP has a unique positive solution in the sector $\langle \underline{\mathbf{y}}, \overline{\mathbf{y}} \rangle$.

Theorem 2.1 Let $\overline{\mathbf{y}} = (\overline{y_1}, \overline{y_2})$, $\underline{\mathbf{y}} = (\underline{y_1}, \underline{y_2})$ in $C^{\alpha}(\overline{D}) \cap C^2(D)$ be the ordered nonnegative upper and lower solutions of the given BVP with $\underline{y_i} \not\equiv 0, i = 1,2;$ and let L_i, B_i be self-adjoint. Assume that (F_1, F_2) is mixed quasimonotone and

either

$$\frac{\partial F_1(z, y_1, y_2)}{\partial y_2} > 0 \text{ and Equation (2.14a) holds}$$

or

$$\frac{\partial F_1(z, y_1, y_2)}{\partial y_2} < 0 \text{ and Equation (2.14b)holds.}$$

Then $(\overline{Y_1}, \overline{Y_2}) = (\underline{Y_1}, \underline{Y_2})$ and is the unique positive solution of the BVP in $\langle \underline{\mathbf{y}}, \overline{\mathbf{y}} \rangle$.

Proof The proof of Theorem 2.1 can be found in Pao [29].

Remark 2.1 Theorem 2.1 is a slightly modified version of Theorem 8.6.5 in Pao [29] in that the mixed quasimonotonicity is swapped. However, for $F = (F_1, F_2)$, the proof remains the same.

2.2.2.1.1 APPLICATION OF THEOREM 2.1 TO THE COUPLED BVP

For unique solution of the BVP, the same pair of functions [Equation(2.13)] as used to prove the existence of a solution is proposed for an upper and lower solution pair, y_1 and y_2, but with the following set of restrictions on parameters: $x_1(0) \leq k_1 < 1$, $k_2 \geq 1 - \delta$, a_i are constants whose limits are to be determined to satisfy the upper and lower solutions' conditions [Equations (2.9-2.12)], and $b_i \to 0^+$, i.e., the b_i parameters are vanishingly small and positive. We chose the two Peclet numbers, $\beta_1 = 150, \beta_2 = 10$; the Damkoler number, $\mu_1 = 0.35$; $\mu_2 = -0.1, \delta = 0.0025, \gamma = 1.5$; and the constants $a_1 = a_2 = 0.5$, $b_1 = b_2 = 5 \times 10^{-10}$, $k_1 = 0.975$, $k_2 = 1 - \delta$ considered for establishing uniqueness.

Remark 2.2: The proposed choice of the pair of upper and lower solutions here is such that it covers the entire solution range to be sure of uniqueness.

Note: This choice of the parameters of the upper and lower functions/solutions was made so that the entirety of the solution range of the BVP is covered by considering the upper and lower bounds on the varables y_1 and y_2. This was actually from my personal intuition.

Next, we prove the other hypotheses in the uniqueness Theorem 2.1.

$$\text{(i)}\;\; F_1(z, y_1, y_2) = -\left(\frac{\beta_1}{2}\right)^2 y_1 + \mu_1 e^{\frac{-\beta_1}{2}z}\left(1 - e^{\frac{\beta_1}{2}z} y_1\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z} y_2}\right)}$$

Therefore,

$$\frac{F_1(z, y_1, y_2)}{y_1} = -\left(\frac{\beta_1}{2}\right)^2 + \mu_1 e^{\frac{-\beta_1}{2}z}\left(\frac{1}{y_1} - e^{\frac{\beta_1}{2}z}\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z} y_2}\right)}$$

$$\frac{\partial}{\partial y_1}\left(\frac{F_1(z, y_1, y_2)}{y_1}\right) = -\frac{\mu_1}{{y_1}^2} e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z} y_2}\right)} < 0$$

Clearly, this does not satisfy Equation (2.22a).

$$\text{(ii)}\;\; F_2(z, y_1, y_2) = -\left(\frac{\beta_2}{2}\right)^2 y_2 + (-\mu_2) e^{\frac{-\beta_2}{2}z}\left(1 - e^{\frac{\beta_1}{2}z} y_1\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z} y_2}\right)}$$

Therefore,

$$\frac{F_2(z,y_1,y_2)}{y_2} = -\left(\frac{\beta_2}{2}\right)^2 + (-\mu_2)e^{\frac{-\beta_2}{2}z}\,\frac{\left(1-e^{\frac{\beta_1}{2}z}y_1\right)}{y_2}e^{\left(\frac{-\gamma}{\delta+e^{\frac{\beta_2}{2}z}y_2}\right)}$$

$$\frac{\partial}{\partial y_2}\left(\frac{F_2(z,y_1,y_2)}{y_2}\right) = (-\mu_2)e^{\frac{-\beta_2}{2}z}\,\frac{\left(1-e^{\frac{\beta_1}{2}z}y_1\right)}{y_2{}^2}\frac{\left(\gamma e^{\frac{\beta_2}{2}z}y_2\left(\delta+e^{\frac{\beta_2}{2}z}y_2\right)^{-2}-1\right)}{e^{\left(\frac{\gamma}{\delta+e^{\frac{\beta_2}{2}z}y_2}\right)}}$$

With $h_1 = 0$, $h_2 = 0$, and $1 - e^{\frac{\beta_1}{2}z}y_1 > 0$, then Equation (2.14b) holds, that is,

$$\frac{\partial}{\partial y_2}\left(\frac{F_2(z,y_1,y_2)}{y_2}\right) = (-\mu_2)e^{\frac{-\beta_2}{2}z}\,\frac{\left(1-e^{\frac{\beta_1}{2}z}y_1\right)}{y_2{}^2}\frac{\left(\gamma e^{\frac{\beta_2}{2}z}y_2\left(\delta+e^{\frac{\beta_2}{2}z}y_2\right)^{-2}-1\right)}{e^{\left(\frac{\gamma}{\delta+e^{\frac{\beta_2}{2}z}y_2}\right)}} > 0$$

$$= (-\mu_2)e^{\frac{-\beta_2}{2}z}\,\frac{\left(1-e^{\frac{\beta_1}{2}z}y_1\right)}{y_2{}^2}\frac{\left(\gamma e^{\frac{\beta_2}{2}z}y_2\left(\delta+e^{\frac{\beta_2}{2}z}y_2\right)^{-2}-1\right)}{e^{\left(\frac{\gamma}{\delta+e^{\frac{\beta_2}{2}z}y_2}\right)}} > 0$$

if and only if

$$\gamma e^{\frac{\beta_2}{2}z}y_2\left(\delta+e^{\frac{\beta_2}{2}z}y_2\right)^{-2}-1 > 0.$$

By recalling the substitution $x_2 = \delta + e^{\frac{\beta_2}{2}z}y_2$, then $\gamma e^{\frac{\beta_2}{2}z}y_2 - \left(\delta+e^{\frac{\beta_2}{2}z}y_2\right)^2 > 0$ is equivalent to

$$-\gamma\delta + \gamma x_2 - x_2{}^2 \equiv \gamma(x_2-\delta) - x_2{}^2 \equiv G(x_2) > 0 \tag{2.15}$$

Recall also that $0 < \delta < 1$ and $\delta < x_2 \leq 1 \Rightarrow x_2 - \delta > 0$. Also, since $\gamma > 0$, we know that γ must be sufficiently large and δ sufficiently small that Equation (2.14) hold.

Based on the parameter values above, we have Figure 5, which clearly satisfies Equation (2.14).

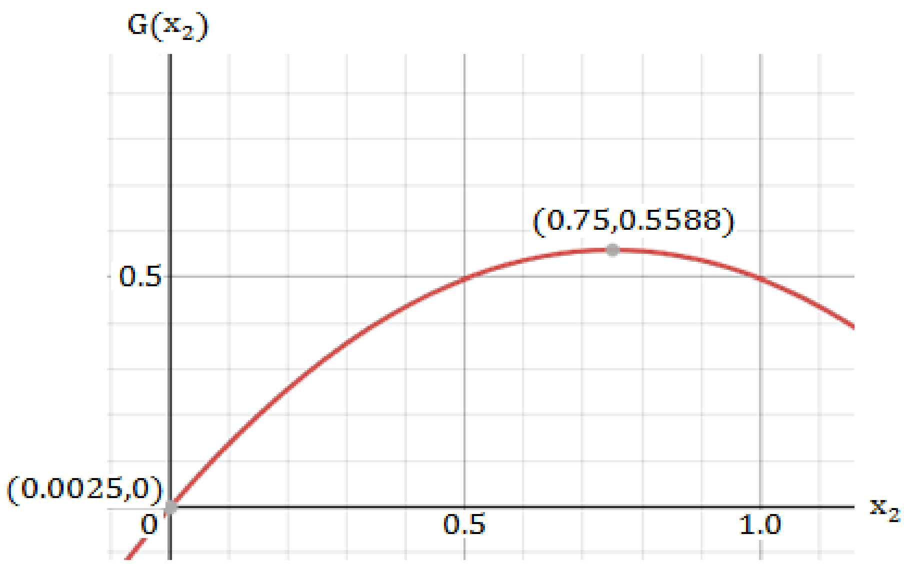


Figure 5: Graph of Equation (2.15), that is, $-\gamma\delta + \gamma x_2 - {x_2}^2 > 0$ for $\delta < x_2 \leq 1$ using $\delta = 0.0025$ and $\gamma = 1.5$.

2.2.2.2 MULTIPLE SOLUTIONS FOR THE COUPLED BVP USING UPPER AND LOWER SOLUTIONS METHOD

Some researchers working on multiplicity of ODEs and/or PDEs have used different analytical/mathematical methods to show multiplicity to ODEs or PDEs, the work of some of them are contained in [37–39]. Some have also used experimental study to also show multiplicity [40,41] to ODEs or PDEs. Unfortunately, no one that I know has used the method of upper and lower solutions to show multiplicity.

Here, we seek to construct two pairs of upper and lower solutions for the transformed coupled system such that they divide the solution range into two disjoint regions for all $z \in [0,1]$. Successful construction of these two disjoint pairs of upper and lower solutions guarantees the existence of two solutions, and consequently proves existence of multiple solutions to the BVP.

2.2.2.1.1 CONSTRUCTION OF FIRST PAIR OF UPPER AND LOWER SOLUTIONS EACH FOR $\mathbf{y_1}$ AND $\mathbf{y_2}$

The following is a choice of upper and lower solutions pair, each for y_1 and y_2,

$$\begin{cases} \overline{y_1} = k_1 e^{-a_1 \frac{\beta_1}{2} z} \\ \underline{y_1} = \frac{b_1}{\pi^2} \sin(\pi z) \end{cases} \qquad \begin{cases} \overline{y_2} = (1-\delta) k_2 e^{-a_2 \frac{\beta_2}{2} z} \\ \underline{y_2} = \frac{b_2}{\pi^2} \sin(\pi z) \end{cases} \tag{2.16}$$

where a_i are constants whose limits are to be determined to satisfy the upper and lower solutions conditions (i)-(iv) [Equations (2.9-2.12)], $0 < b_i \ll 1$ and $0 < k_i < 1$.

This pair is chosen so that only the lower part of the solution range is covered as shown in Figures (7) and (8) is covered.

As for this choice, conditions (i) and (iv) [Equations (2.9) and (2.12)] are clearly satisfied, as shown in section 2.2.1. We now need to prove that the other conditions, (ii) and (iii) [Equations (2.10) and (2.11)] are satisfied.

Proof of condition (ii) [Equation (2.10)]:

$$L_1 \overline{y_1} + F_1(z, \overline{y_1}, \overline{y_2}) \leq 0 \leq L_1 \underline{y_1} + F_1(z, \underline{y_1}, \underline{y_2})$$

The left hand side (L. H. S.) inequality: $L_1\overline{y_1} + F_1(z, \overline{y_1}, \overline{y_2}) \leq 0$

$$\text{L. H. S.} = \frac{d^2\overline{y_1}}{dz^2} - \left(\frac{\beta_1}{2}\right)^2 \overline{y_1} + \mu_1 e^{-\frac{\beta_1}{2}z}\left(1 - e^{\frac{\beta_1}{2}z}\,\overline{y_1}\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z}\,\overline{y_2}}\right)}$$

$$= \frac{d^2\left(k_1 e^{-a_1\frac{\beta_1}{2}z}\right)}{dz^2} - \left(\frac{\beta_1}{2}\right)^2 k_1 e^{-a_1\frac{\beta_1}{2}z}$$

$$+\mu_1 e^{-\frac{\beta_1}{2}z}\left(1 - e^{\frac{\beta_1}{2}z} k_1 e^{-a_1\frac{\beta_1}{2}z}\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z}\,(1-\delta)k_2 e^{-a_2\frac{\beta_2}{2}z}}\right)}$$

$$\text{L. H. S.} = -\left(\frac{\beta_1}{2}\right)^2 k_1 e^{-a_1\frac{\beta_1}{2}z}\left(1 - {a_1}^2\right)$$

$$+\mu_1 e^{\frac{-\beta_1}{2}z}\left(1 - k_1 e^{(1-a_1)\frac{\beta_1}{2}z}\right) e^{\left(\frac{-\gamma}{\delta + (1-\delta)k_2 e^{(1-a_2)\frac{\beta_2}{2}z}}\right)}$$

For values of μ_1, we need $1 - {a_1}^2 = (1 - a_1)(1 + a_1) \geq 0$ for the L. H. S. to be ≤ 0.

An easy way to show that the L. H. S. ≤ 0 for all values of $z \in [0,1]$ is graphically, as shown in Figure 6.

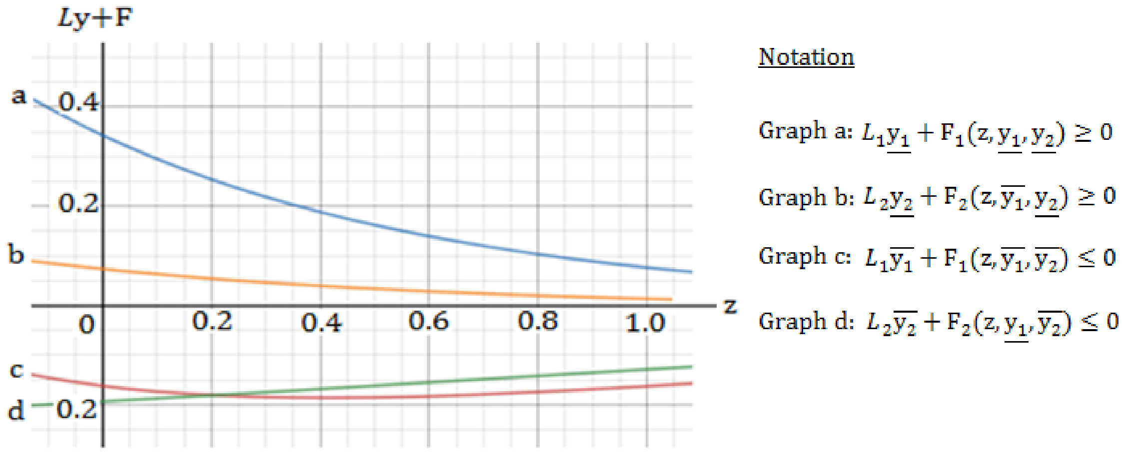


Figure 6: Graphs of conditions (ii) and (iii) [Equations (2.10) and (2.11)] for the pair in Equation (2.16) for $z \in [0,1]$ for parameters $\beta_1/2 = 1.5$, $\beta_2/2 = 1.25$, $\mu_1 = 0.35$, $\mu_2 = -0.1$, $\delta = 0.25$, $\gamma = 0.005$ and constants $a_1 = a_2 = 0.5$, $b_1 = b_2 = 5 \times 10^{-10}$, $k_1 = 0.2$, $(1-\delta)k_2 = 0.25$.

Next, we prove the right hand side of condition ii in Equation (2.10).

The right hand side inequality: $0 \leq L_1\underline{y_1} + F_1(z,\underline{y_1},\underline{y_2})$, is equivalent to

$$L_1\underline{y_1} + F_1(z,\underline{y_1},\underline{y_2}) \geq 0$$

$$\text{L. H. S.} = \frac{d^2\underline{y_1}}{dz^2} - \left(\frac{\beta_1}{2}\right)^2 \underline{y_1} + \mu_1 e^{-\frac{\beta_1}{2}z}\left(1 - e^{\frac{\beta_1}{2}z}\underline{y_1}\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z}\underline{y_2}}\right)}$$

$$= \frac{d^2\left(\frac{b_1}{\pi^2}\sin(\pi z)\right)}{dz^2} - \left(\frac{\beta_1}{2}\right)^2 \frac{b_1}{\pi^2}\sin(\pi z)$$

$$+ \mu_1 e^{-\frac{\beta_1}{2}z}\left(1 - e^{\frac{\beta_1}{2}z}\frac{b_1}{\pi^2}\sin(\pi z)\right) e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z}\frac{b_2}{\pi^2}\sin(\pi z)}\right)}$$

$$= -b_1\left(1+\left(\frac{\beta_1}{2\pi}\right)^2\right)\sin(\pi z)$$

$$+\mu_1 e^{-\frac{\beta_1}{2}z}\left(1-\frac{b_1}{\pi^2}e^{\frac{\beta_1}{2}z}\sin(\pi z)\right)e^{\left(\frac{-\gamma}{\delta+\frac{b_2}{\pi^2}e^{\frac{\beta_2}{2}z}\sin(\pi z)}\right)}$$

This is non-negative as shown in Figure 6.

Proof of condition (iii) [Equation (2.11)]:

$$L_2\overline{y_2}+F_2(z,\underline{y_1},\overline{y_2})\le 0\le L_2\underline{y_2}+F_2(z,\overline{y_1},\underline{y_2})$$

The left hand side inequality: $L_2\overline{y_2}+F_2(z,\underline{y_1},\overline{y_2})\le 0$

$$\text{L.H.S.}=\frac{d^2\overline{y_2}}{dz^2}-\left(\frac{\beta_2}{2}\right)^2\overline{y_2}+(-\mu_2)e^{\frac{-\beta_2}{2}z}\left(1-e^{\frac{\beta_1}{2}z}\underline{y_1}\right)e^{\left(\frac{-\gamma}{\delta+e^{\frac{\beta_2}{2}z}\overline{y_2}}\right)}$$

$$=\frac{d^2\left((1-\delta)k_2e^{-a_2\frac{\beta_2}{2}z}\right)}{dz^2}-\left(\frac{\beta_2}{2}\right)^2(1-\delta)e^{-a_2\frac{\beta_2}{2}z}$$

$$+(-\mu_2)e^{\frac{-\beta_2}{2}z}\left(1-e^{\frac{\beta_1}{2}z}\frac{b_1}{\pi^2}\sin(\pi z)\right)e^{\left(\frac{-\gamma}{\delta+e^{\frac{\beta_2}{2}z}(1-\delta)k_2e^{-a_2\frac{\beta_2}{2}z}}\right)}$$

$$\text{L.H.S.}=-\left(\frac{\beta_2}{2}\right)^2(1-\delta)k_2e^{-a_2\frac{\beta_2}{2}z}(1-{a_2}^2)$$

$$+(-\mu_2)e^{\frac{-\beta_2}{2}z}\left(1-\frac{b_1}{\pi^2}e^{\frac{\beta_1}{2}z}\sin(\pi z)\right)e^{\left(\frac{-\gamma}{\delta+(1-\delta)k_2e^{(1-a_2)\frac{\beta_2}{2}z}}\right)}$$

This is non-positive as shown in Figure 6.

The right hand side inequality: $0 \leq L_2\underline{y_2} + F_2(z, \overline{y_1}, \underline{y_2})$, is equivalent to

$$L_2\underline{y_2} + F_2(z, \overline{y_1}, \underline{y_2}) \geq 0$$

$$\text{L.H.S.} = \frac{d^2\underline{y_2}}{dz^2} - \left(\frac{\beta_2}{2}\right)^2 \underline{y_2} + (-\mu_2)e^{\frac{-\beta_2}{2}z}\left(1 - e^{\frac{\beta_1}{2}z}\overline{y_1}\right)e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z}\underline{y_2}}\right)}$$

$$= \frac{d^2\left(\frac{b_2}{\pi^2}\sin(\pi z)\right)}{dz^2} - \left(\frac{\beta_2}{2}\right)^2 \frac{b_2}{\pi^2}\sin(\pi z)$$

$$+(-\mu_2)e^{\frac{-\beta_2}{2}z}\left(1 - e^{\frac{\beta_1}{2}z}k_1 e^{-a_1\frac{\beta_1}{2}z}\right)e^{\left(\frac{-\gamma}{\delta + e^{\frac{\beta_2}{2}z}\frac{b_2}{\pi^2}\sin(\pi z)}\right)}$$

$$\text{L.H.S} = -b_2\left(1 + \left(\frac{\beta_2}{2\pi}\right)^2\right)\sin(\pi z)$$

$$+(-\mu_2)e^{\frac{-\beta_2}{2}z}\left(1 - k_1 e^{(1-a_1)\frac{\beta_1}{2}z}\right)e^{\left(\frac{-\gamma}{\delta + \frac{b_2}{\pi^2}e^{\frac{\beta_2}{2}z}\sin(\pi z)}\right)}$$

This is non-negative as shown in Figure 6.

2.2.2.2.2 CONSTRUCTION OF SECOND (AND DISJOINT) PAIR OF UPPER AND LOWER SOLUTIONS EACH FOR $\mathbf{y_1}$ AND $\mathbf{y_2}$

Here, the pair of upper and lower solutions chosen is

$$\begin{cases} \overline{y_1} = 0.5e^{-0.5\frac{\beta_1}{2}z} \\ \underline{y_1} = 0.35e^{-0.95\frac{\beta_1}{2}z} \end{cases} \qquad \begin{cases} \overline{y_2} = 0.75e^{-0.5\frac{\beta_2}{2}z} \\ \underline{y_2} = 0.35e^{-0.95\frac{\beta_2}{2}z} \end{cases} \tag{2.17}$$

This pair was chosen so that only the upper part of the solution range, as shown in Figures 8 and 9, is covered and that it is disjoint from the pair in Equation (2.16).

As for this choice, conditions (i) and (iv) [Equations (2.9) and (2.12)] are clearly satisfied as shown in section 2.2.1. We now need to prove the other conditions, (ii) and (iii) [Equations (2.10) and (2.11)].

Using the same parameters values as were used in constructing the upper and lower solutions in Equation (2.16), we have the graphs in Figure 7, which prove conditions (ii) and (iii) [Equations (2.10) and (2.11)].

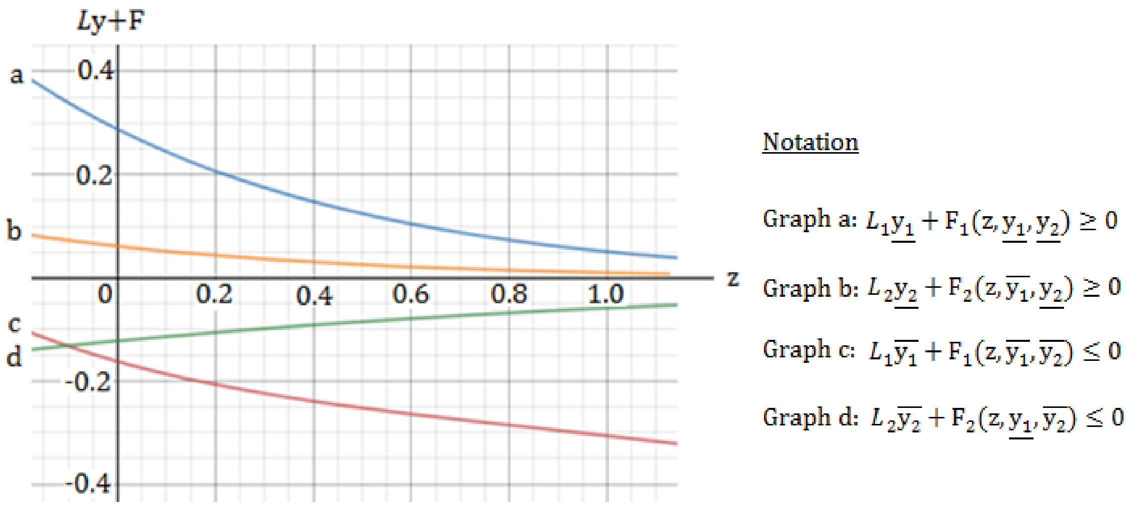


Figure 7: Graphs of conditions (ii) and (iii) [Equations (2.10) and (2.11)] for pair in Equation (2.17) for $z \in [0,1]$ for parameters $\beta_1/2 = 1.5$, $\beta_2/2 = 1.25$, $\mu_1 = 0.35$, $\mu_2 = -0.1$, $\delta = 0.25$, $\gamma = 0.005$ and constants $a_1 = a_2 = 0.5$, $b_1 = b_2 = 5 \times 10^{-10}$.

Next, we show, graphically, that pair defined in Equation (2.24) is disjoint from the one defined in Equation (2.15) each for y_1 and y_2.

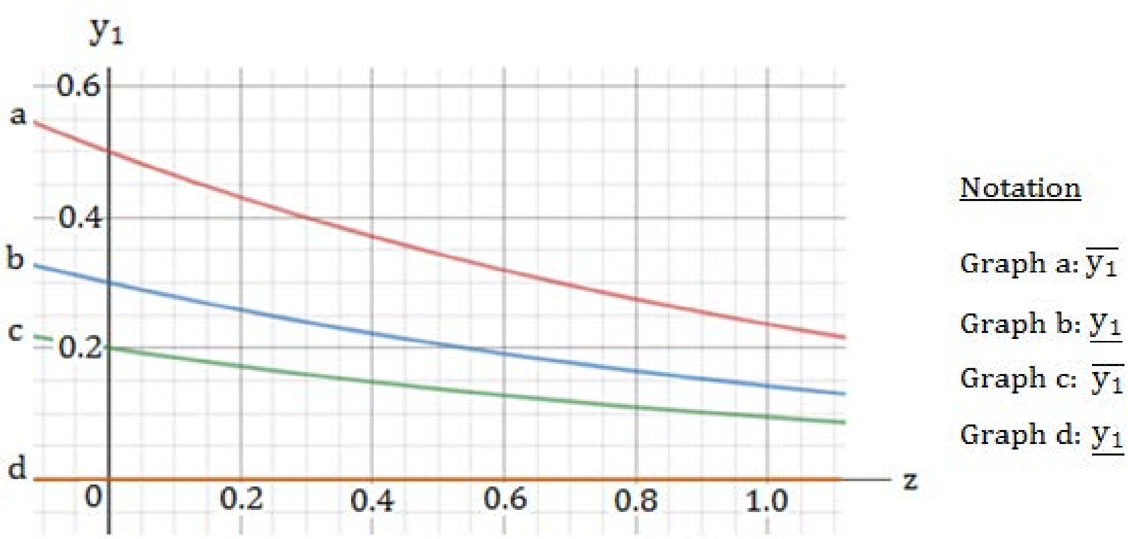


Figure 8: Graphs that show that the pair in Equation (2.16) is disjoint from the pair in Equation (2.17) for y_1 for all $z \in [0,1]$ for parameters $\beta_2/2 = 1.25$, and $\delta = 0.25$; constants $a_1 = 0.5$, $b_1 = 5 \times 10^{-10}$, and $(1 - \delta)k_2 = 0.25$. Graphs a and b are for the pair in Equation (2.25) and c and d for the one in Equation (2.24).

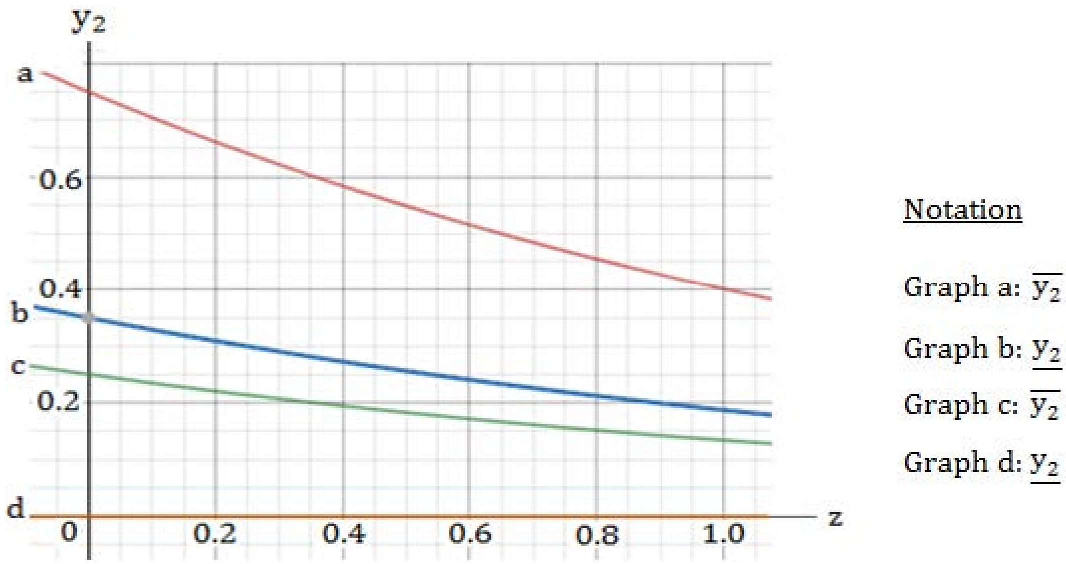


Figure 9: Graphs that show that the pair in Equation (2.16) is disjoint from the pair in Equation (2.17) for y_2 for all $z \in [0,1]$ for parameters $\beta_2/2 = 1.25$, and $\delta = 0.25$; constants $a_2 = 0.5$, $b_2 = 5 \times 10^{-10}$, and $(1-\delta)k_2 = 0.25$. Graphs a and b are for the pair in Equation (2.17) and c and d for the one in Equation (2.16).

Note: (1) In Figures 8 and 9, Graph d is not identically zero, but significantly positively close to zero. It is the 'sine' function defined in Equation (2.16) with infinitesimally small coefficient $b_i = 5 \times 10^{-10}$.

(2) The pair in Equation (2.16) is below the pair in Equation (2.17), no overlapping whatsoever for all $z \in [0,1]$.

Remark 2.2: Interesting thing about the Figures 8 and 9 is that we were able to construct two disjoint pairs of upper and lower solutions for all $z \in [0,1]$ for the transformed BVP. Since each of those pairs/regions has at least one solution [29], then, we conclude that at least two solutions exist for the BVP for the indicated choice of parameters. The region between Graphs a and b combined with the region between graphs c and d means that there exist at least two solutions to the BVP with the choice of parameter set. Hence, this gave us the possibility of existence of multiple solutions to the BVP.

2.3 RESULTS AND DISCUSSION

The results of this work are summarized and then discussed in this section.

2.3.1 RESULTS

The nonlinearities in this BVP are caused by Arrhenius-type dependencies of the rate coefficients. This implies that for every single solution x_2, there is a corresponding solution x_1. This is to say that if in the original BVP, x_2 is unique, then we can be sure that x_1 is also unique.

By successfully constructing a pair [Equation (2.13)] of upper and lower solutions to the coupled BVP such that Equations (2.9) through (2.12) are all satisfied for the set of parameters chosen, then we have that a solution (at least one) exists for the BVP for that particular set of parameters.

When the Péclet numbers and the activation energy are sufficiently large, and the Damköhler number and the reactor length are sufficiently small, a pair of upper and lower solutions was constructed for the BVP such that all the hypotheses in

Theorem 2.1 are satisfied, then we have that a unique solution exists for that set of parameters.

However, when the Péclet numbers and the activation energy are sufficiently small, and the Damköhler number and the reactor length are sufficiently large, at least for the parameter set chosen here, two disjoint pairs [Equations (2.16) and (2.17)] of upper and lower solutions were successfully constructed, and each one has a solution. This implies that at least two solutions exist for the BVP. By applying the Schauder fixed-point argument, we know that the number of solutions can only be odd, so we must have at least three solutions for the BVP in the case when the Péclet numbers and the activation energy are small and the Damköhler number and the reactor length are large. This existence of multiple solutions is discussed in [41].

2.3.2 DISCUSSION

For a uniquely predetermined/preset function x_2, the coupled BVP reduces to a scaler linear BVP in x_1. Thus, multiple solutions can never result.

However, for a uniquely predetermined/preset function x_1, the BVP reduces to a scalar nonlinear BVP in x_2, with Arrhenius-type nonlinearities. Because the nonlinearities still exist in this case, multiple solutions can exist for certain sets of parameters.

With large Péclet numbers and activation energy with small Damköhler number and reactor length, the nonlinearities in the coupled BVP vanish, and the coupled BVP reduces to two uncoupled linear BVPs, each of which gives a unique solution. This was ascertained using the method of upper and lower solutions. Because most of the previous research on this work concluded that multiple solutions only exist [25], then to have successfully established uniqueness here is a significant contribution of this work.

However, that does not mean no one else had ever shown uniqueness before. In fact, the work of Luss and Amundson [5] using comparison methods gave a condition on the Damköhler number for uniqueness of solution to occur. The result here is a concrete proof of uniqueness for a particular set of parameters with large Péclet numbers and activation energy and small Damköhler number and reactor length.

Likewise, using an alternative set of parameters including small Péclet numbers and activation energy and large Damköhler number and reactor length, the coupled BVP has increased nonlinearities. Hence, by the same method of upper and lower solutions, multiplicity of solutions is guaranteed. This is consistent with the school of thought of most previous researchers on this topic, though they all made one assumption or another in their research.

CHAPTER 3: CONCLUSIONS AND FUTURE WORK

3.1 CONCLUSIONS

This research has been concerned with the analysis of the tubular reactor model with an exothermic reaction and diffusion terms under adiabatic conditions with different Péclet numbers for mass and energy dispersion.

Using the method of upper and lower solutions, at least one solution exists for a specific choice of the parameters for the BVP. In fact, it is stated by Laabissi et al. [2] as well as by Achhab et al [42] that at least one solution exists for the BVP by using the Schauder fixed-point argument without any additional assumptions on its parameters, compactness being the main tool to establish this.

Likewise, by successfully constructing a pair of upper and lower solutions that covers the solution range of the transformed BVP, we were able to show that a unique solution exists when the Péclet numbers are sufficiently large (that is, diffusion coefficients are sufficiently small), the activation energy is sufficiently large, and the Damköhler number and the reactor length are sufficiently small, after having satisfied the constraints of Theorem 2.1.

The results also show that multiple steady-state solutions are possible if the Péclet numbers are sufficiently small (that is, diffusion coefficients are sufficiently large), the activation energy is sufficiently small, and the Damköhler number and the reactor length are sufficiently large. The existence of multiple steady-state solutions, specifically there, in an adiabatic tubular reactor was also proved in [43–45] for equal

Péclet numbers. However, when Péclet numbers are different, Deimling [45] also proved multiplicity but the analysis developed there was based on unfeasible assumptions on the model parameters, i.e., when the reactor temperature is lower than the inlet and cooling temperature in an exothermic reactor.

This is in line with the perception that the tubular reactor model with axial diffusion is an intermediate model between the PFR model (with no axial diffusion), for which only one steady-state solution is possible, and the CSTR model (effectively a reactor with an "infinite" diffusion coefficient), for which three equilibrium solutions have been proven to be possible.

However, in general, the steady-state solution is not unique. In fact, for a certain set of parameters (in the reaction function or in the boundary conditions) the BVP possesses multiple positive solutions, at least three of which have been shown here.

Hence, we also conclude that the lower bound on the number of solutions is one while the upper bound on the number of solutions is at least three.

3.2 FUTURE WORK

One possible follow-up to this study is to accurately, rigorously, and uniquely determine the upper bounds on the number of solutions of the BVP. However, in some special cases, an infinite number of solutions has already been reported to this BVP [1].

It also still remains to show multiplicity of steady-state for the tubular reactor in the non-adiabatic case with different mass and thermal Péclet numbers. Meanwhile, a promising way to address this issue is to consider the case of a perturbation to the one analyzed here. However, a detailed analysis using regular and/or singular perturbation theories is yet to be performed.

Another refinement is the consideration of the case when the velocity profile is not uniform, such as laminar flow with high mass and thermal Péclet numbers.

Confirming the existence, uniqueness, and/or multiplicity of solutions for higher order (greater than one), reversible, and complex reactions would be another possible area of future work.

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