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CALCULATION OF MULTIPLICITY OF STEADY STATES IN A CATALYST PELLET BY HOMOTOPIC CONTINUATION METHOD

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Abstract

Many exothermic reactions, such that the oxidation of CO in a catalyst pellet may present multiplicity of steady states. Experimental results suggest this behavior in a copper ceria catalyst, and this in turn would indicate that the kinetics should be non-monotonic with respect to reactants’ compositions.

The model for the reaction is described by a two-point boundary value problem that is hard to solve with direct methods, even when seeking a single solution.

The aim of this work is to implement a homotopic method in order to find all the steady states of this kind of problems.

The search for solutions is driven by a pseudo-arc length continuation. Homotopic curves that passes through all possible solutions are obtained. Also, a study of the dependence of the initial point upon the curve is performed.
Keywords: homotopy; CO oxidation; multiplicity; non-monotonic kinetics

Introduction

Steady states multiplicity in chemical engineering takes place when some feedback process (e.g. diffusion, heat conduction or counter-current contact) occurs, in addition to a non-monotonic behavior of the reaction rate with respect to composition or temperature\(^1\). These two conditions must occur simultaneously. Thus, multiplicity shall not be observed, for instance, in a single phase plug flow reactor or an isothermal pellet with a simple power – law kinetics of the form \(k c_A^n\).

The non–monotonic behavior could be due to:

a) thermal effects: when dealing with an exothermic reaction, temperature rises as reactants depletion advances; the non–monotonic effect lies on the fact that temperature tends to increase the rate of reaction, whereas reactants depletion has the opposite effect.

b) concentration effects: this situation happens in catalysis when reactants compete for the same active site, thus obtaining a non–monotonic kinetics (e.g. Langmuir); besides this non–monotonicity, the dependence must be sharp enough.

The steady state multiplicity was first studied about 50 years ago, in the work of Bilous and Amundson\(^2\). Then, Aris and Amundson\(^3-5\) developed a systematic analysis of the dynamic behavior of CRST, where an exothermic reaction takes place. Jorgensen et al.\(^6\) extended these studies to a reaction system in series. Moreover, Balakotaiah and Luss\(^7\) applied catastrophe theory to analyze the influence of residence time and temperature in a CRST where more than one reaction takes place simultaneously. On the other hand,
Lee et al. examined steady states multiplicity in a plug flow tubular reactor with axial dispersion and non-uniform catalyst activity.

Numerous works studied the porous catalyst pellet dynamics. The existence of multiple steady states in a catalyst pellet was proved by Weisz and Hicks and by Amundson and Raymond. Further, Van den Bosch and Luss studied multiplicity and uniqueness criteria for positive order reactions; Hu et al. analyzed the dependence of the multiplicity on the order of reaction and the geometry in a catalyst pellet. Besides, Nielsen and Villadsen considered the dynamic behavior in a catalyst pellet when diffusion, reaction and absorption take place simultaneously, and they found that up to five steady states may occur. Likewise, Tsotsis and Schmitz and Tsotsis studied the dynamic behavior in catalysts. They analyzed the instabilities in catalyst systems for both exothermic and endothermic reactions.

More recently, Botero et al. proved the existence of multiplicity and dynamic bifurcation phenomena in an enzymatic process, where diffusion and reaction occur simultaneously.

The present work arises from experimental evidence observed in the CO oxidation reaction, using a Cu/CeO₂ catalyst. In a lab-scale reactor, working in the absence of diffusion effects, a decrease of the reaction rate was observed, when the catalyst pellet size decreased. This fact leads us to study diffusion-reaction phenomena inside the pellet with a mathematical model. The model allows predicting that, for certain pellet sizes not only the reaction rate (or more precisely, the effectiveness factor) increases, but also steady state multiplicity takes place. Experimental results are shown in Table 1.

| Table 1. Variation of reaction rate with pellet size |

| Table 1. Variation of reaction rate with pellet size |
The aim of this work is to analyze the multiplicity of steady states in a catalyst pellet where the CO oxidation reaction occurs, using a mathematical model. The diffusion – reaction problem is associated to a two-point boundary value problem. If multiplicity occurs, the nonlinear mathematical model generated has more than one solution. Therefore, a homotopy continuation method, adapted to find all of the solutions of two-point boundary value problems, was used.

Homotopy continuation methods have the advantage of reaching the solution by tracing a path from a fairly arbitrary initial point\(^ {19}\). It is a global method that can calculate all solutions in a nonlinear model. Examples of homotopy continuation to find all solutions of algebraic nonlinear systems of equations can be found in chemical engineering literature\(^ {19,20}\).

The beginning of the practical use of homotopy methods in solving system of equations is attributed to Davidenko\(^ {21}\), and this topic has received contributions by several researchers\(^ {22-26}\). Allgower and Georg\(^ {26}\) played an essential role in popularizing the method.

The homotopy continuation method was widely used to calculate all solutions of a system of algebraic equations \(F(\theta) = 0\), with \(\theta \in \mathbb{R}^{n}\) and \(F: D \subseteq \mathbb{R}^{n} \rightarrow \mathbb{R}^{n}\). A homotopy function is defined with a homotopy parameter \(t\), \(H(\theta; t) = 0\), \(H: D \times R\subseteq \mathbb{R}^{n+1} \rightarrow \mathbb{R}^{n}\), such that \(H(\theta; 0) = G(\theta)\) and \(H(\theta; 1) = F(\theta)\), where \(G(\theta)\) is an “easy” function. The idea is to numerically follow the path determined by the equation \(H(\theta; t) = 0\) in \(D \times R\).

In this work the capabilities of the homotopy method of finding all solutions, which are generally used in algebraic systems, are exploited in order to handle the BVP problem.

**Problem statement**
The present work deals with a catalyst pellet of slab geometry \((a = 1)\) in which an exothermic reaction takes place. The following hypotheses were considered to simplify the model:

- negligible pressure drop inside the pellet
- constant thermodynamic properties (heat capacity and reaction enthalpy)
- constant thermal conductivity
- Dusty Gas Model (DGM) for mass flow\(^{27,28}\)
- no external film effects, i.e. \(Sh, Nu \to \infty\)
- unidimensional problem

When these hypotheses hold, the problem can be described by the following model\(^{29}\)

\[
\frac{dp_j}{dz} = R_p R T \sum_k B_{jk} N_k
\]

\[
\frac{dT}{dz} = R_p \frac{q}{\kappa}
\]

\[
\frac{dN_j}{dz} = \begin{cases} 
-R_p \sum_i \alpha_{ij} r_i + \frac{a-1}{1-z} N_j & z \neq 1 \\
-\frac{1}{a} R_p \sum_i \alpha_{ij} r_i & z = 1 
\end{cases}
\]

\[
\frac{dq}{dz} = \begin{cases} 
-\sum_k C_p N_k \frac{dT}{dz} + R_p \sum_i \Delta H_i r_i + \frac{a-1}{1-z} q & z \neq 1 \\
\frac{1}{a} R_p \sum_i \Delta H_i r_i & z = 1 
\end{cases}
\]

\[
\begin{align*}
p_j &= p_j^{sup}, T = T^{sup} \quad z = 0 \\
N_j &= 0, q = 0 \quad z = 1
\end{align*}
\]

where \(z = 0\) is the catalyst surface and \(z = 1\) is the catalyst centre. The definition of the DGM matrix \(B\) can be found in Krishna et al.\(^{27,28,30}\). Equations (1) to (4) can be rewritten in matrix notation.
\[
\frac{dp}{dz} = Rp \cdot R \cdot T \cdot B \cdot N
\]  
(6)

\[
\frac{dT}{dz} = \frac{g}{\kappa}
\]  
(7)

\[
\frac{dN}{dz} = \begin{cases} 
-\frac{Rp \cdot r \cdot \alpha}{1-z} + \frac{a-1}{1-z} N & z \neq 1 \\
-\frac{1}{a} & z = 1
\end{cases}
\]  
(8)

\[
\frac{dq}{dz} = \begin{cases} 
-Cp \cdot N \frac{dT}{dz} + \frac{Rp \cdot r \cdot \Delta H + a-1}{1-z} q & z \neq 1 \\
\frac{1}{a} & z = 1
\end{cases}
\]  
(9)

After solving this system, the effectiveness factor is calculated by

\[
\eta_j = \frac{a \cdot N_j^{sup}}{Rp \cdot r_j^{sup}}
\]  
(10)

The system so defined represents mathematically a boundary value problem with essential conditions on \( z = 0 \) (partial pressures and temperature) and natural conditions on \( z = 1 \) (mass and energy fluxes). Next section deals with this issue.

**Homotopy continuation method**

**Homotopy function**

The problem to solve is a two-point boundary value problem. The goal is to find all solutions of the problem, i.e. all steady states of the system. It is known that usual methods for solving this kind of problems (collocation, discretization, shooting, etc.) can find only one solution at a time. Moreover, all these methods will eventually lead to a nonlinear system of equations, which has to be solved with an iterative method. Therefore, initial values close to the solution are required in order to converge. If all
solutions are sought, a large set of initial values over the entire feasible domain should
be tried.

The homotopy method can find all solutions of a system of algebraic equations in a
fairly automatic way, and (almost) no care should be taken in selecting a good initial
point. As it was mentioned in the Introduction, the method consists on tracing a curve
described by the zeros of an homotopy function \( H(\theta; t) = 0 \). For \( t = 0 \), all solutions of
\( H(\theta; 0) = 0 \) are known, and when \( t = 1 \), \( H(\theta; 1) = 0 \) coincides with the original problem
whose solutions are sought.

In order to use homotopy continuation in our problem, the BVP is transformed into an
algebraic equation. By means of the shooting method, the BVP may be solved as a zero-
finding problem. Watson\textsuperscript{31} describes a homotopy-type algorithm for certain BVP
problems and proves that under certain hypotheses, it converges to a solution for almost
all initial point within a bounded set.

In this work the pseudo-arclength algorithm is used to follow the homotopy curve
defined by \( H(\theta; t) = 0 \). Since all solutions of the problem are sought, the homotopy
parameter \( t \) shall not be limited to be in the interval \([0,1]\), but we let it go beyond these
limits. In that way, the homotopy curve may cross several times the level \( t = 1 \), passing
by several solutions of the problem.

Following Hlavacek\textsuperscript{32}, the problem of finding steady states of a reaction in a catalyst
pellet can be stated as follows: a vectorial function \( F : \mathbb{R}^{Nn} \rightarrow \mathbb{R}^{Nn} \), which represents the
boundary conditions in \( z = 1 \), i.e. mass and heat fluxes at the center of the pellet
calculated with a trial value \( \theta \) of the fluxes in \( z = 0 \).

\[
E(\theta) = \begin{bmatrix}
N(\theta, z = 1) \\
q(\theta, z = 1)
\end{bmatrix}^{\text{calc}}
\]  \quad (11)
where $\theta$ is conveniently scaled and made dimensionless, $\theta_1 = \frac{N_{CO}}{10^4 \text{mol m}^{-2} \text{s}^{-1}}$ and $\theta_2 = \frac{q}{10^8 \text{J m}^{-2} \text{s}^{-1}}$. In this way, both elements of $\theta$ are in a similar order of magnitude (about $10^0 - 10^1$). For each value of $\theta$, $F$ can be computed by a numerical integration.

A solution of the problem is such that mass and heat fluxes at the center of the pellet are zero, i.e. $F = 0$. Then, the solution procedure is constituted by two steps: integration and zero-finding schemes.

The zeros of $F$ may be obtained by means of Newton’s method

$$\theta^{(r+1)} = \theta^{(r)} - E^{-1}(\theta^{(r)}) \cdot F(\theta^{(r)})$$  \hspace{1cm} (12)

performing the integration in each step. A drawback of this method, as it is well known, is that the initial trial value must be close to the real value and it can find only one solution at the most. To overcome this problem, a continuation method consisting on embedding the function $F$ in a homotopy function $H : R^{Nn+1} \rightarrow R^{Nn}$ is used. In general, the function $H$ has the form

$$H(\theta; t) = t \cdot F(\theta) + (1-t) \cdot G(\theta)$$  \hspace{1cm} (13)

where $t$ is a new parameter in the problem called homotopy parameter. It must be said that in this work the homotopy parameter $t$ has no physical meaning but the method needs it to guide the homotopy curve towards the physical solutions. Clearly, a vector value $\theta_0$ such that $H(\theta_0; 0) = 0$ is a root of $G$, whereas a vector value $\theta^*$ such that $H(\theta^*; 1) = 0$ is a root of $F$.

Under certain differentiability conditions on $F$ and $G^{24,33}$, the Implicit Function Theorem shows that the set of points $(\theta, t)$ in $R^{Nn+1}$, such that $H(\theta; t) = 0$ is a smooth one-dimensional curve.
The key idea of the method is to trace numerically the solution curve of \( H(\theta; t) = 0 \) from \((\theta_0; 0)\). The function \( G \) is chosen so that the solution of \( G(\theta) = 0 \) is easy to compute. Two of the possible choices for this function are \( G(\theta) = \theta - \theta_0 \) (fixed point homotopy) or \( G(\theta) = F(\theta) - F(\theta_0) \) (Newton homotopy), for a proper value \( \theta_0 \).

In this work, the “easy” function \( G \) chosen was \( \theta - \theta_0 \). \( \theta_0 \) is the initial value (at \( t = 0 \)), and remains unchanged along the curve. The elements of both \( F \) and \( G \) are conveniently scaled, since their values are very different in order of magnitude.

The simplest way to trace the zero-curve is using a predictor-corrector method\(^{26}\), parametrizing the with \( t \), i.e.

\[
H(\theta(t); t) = 0
\]  

(14)

Given a point \( (\theta_u; t_u) \) on the curve, and the tangent vector \( \frac{d\theta}{dt} \), a new point in the curve for \( t_{u+1} = t_u + \Delta t_u \) is approximated in the predictor step by

\[
\theta_{u+1}^{(0)} = \theta_u + \frac{d\theta}{dt} \Delta t_u
\]  

(15)

and then corrected back to the curve \( H = 0 \) using the point \( (\theta_{u+1}^{(0)}; t_{u+1}) \) as the initial guess for the corrector step. The correction is made by means of Newton’s method,

\[
H_{\theta} \left( \theta_{u+1}^{(r)}; t_{u+1} \right) \cdot \Delta \theta_{u+1}^{(r)} = -H \left( \theta_{u+1}^{(r)}; t_{u+1} \right)
\]  

(16)

Once the method converge, the last value of \( \Delta \theta_{u+1} \) is employed to compute the next point on the curve

\[
\theta_{u+1} = \theta_u + \Delta \theta_{u+1}
\]  

(17)

If \( H_{\theta} \left( \theta_{u+1}; t_{u+1} \right) \) is nonsingular, the Newton iterations converge for a sufficiently small \( \Delta t_u \). Finally, the new tangent vector can be calculated with
\[ H_\theta(\theta_{w1};t_{w1}) \frac{d\theta_{w1}}{dt} = -H_\theta(\theta_{w1};t_{w1}) \]  \hspace{1cm} (18)

Eq. (18) is obtained differentiating Eq. (14) w.r.t. \( t \).

When multiplicity occurs, there may be more than one \( \theta \) at \( t = 1 \) that makes \( H = 0 \), namely, the zero curve crosses \( t = 1 \) more than once. This is possible if

a. the curve turns backwards after crossing \( t = 1 \)

b. the curve bifurcates

When case (a) occurs, the point in which the curve turns is called turning point. Let \( X = [\theta \ t] \). Mathematically, turning points arise in points where \( \text{rank} \left( H_x \right) = Nn \) and \( \text{rank} \left( H_\theta \right) = Nn - 1 \). That is, the null space of \( H_\theta \) has dimension 1 and \( H_\theta \) does not belong to its range. Therefore, \( H_\theta \) has to be zero in Eq. (18) and \( \frac{d\theta}{dt} \), if nonzero, generates the null space of \( H_\theta \). The important point is that \( H_\theta \) is singular and the Newton’s iterations, Eqs. (15) to (17), fails to converge.

Case (b) occurs when \( \text{rank} \left( H_\theta \right) = Nn - 2 \) and \( H_\theta \notin \text{range}(H_\theta) \) or when \( \text{rank} \left( H_\theta \right) = Nn - 1 \) and \( H_\theta \in \text{range}(H_\theta) \). In both cases, there are two directions to follow in the curve. In the problem presented here, no bifurcation was detected.

In both cases, the simple tracking-curve method described above, Eqs. (15) – (18), fails since it implies calculating a unique solution for each value of \( t \), that increases monotonically. Then, as proposed by Keller\textsuperscript{37}, the zero-curve of \( H \) is calculated by a pseudo-arclength homotopy.

\textit{Pseudo-arclength homotopy continuation}
To trace the curve beyond turning and bifurcation points, both $t$ and $\theta$ are reparametrized with the arclength $s$. By definition of the arclength

\[ \|\dot{\theta}\|^2 + (i)^2 = 1 \]  

(19)

where $\dot{\theta} = \frac{d\theta}{ds}$ and $i = \frac{dt}{ds}$. Eq. (19) can be approximated and rearranged in the following form\(^{38}\)

\[ \Delta s \approx \Delta \theta^T \cdot \dot{\theta} + \Delta t \cdot i \]  

(20)

The Keller’s pseudo-arclength method traces the zero-curve of the function $\varepsilon: \mathbb{R}^{n+1} \to \mathbb{R}^{n+1}$, defined as

\[ \varepsilon(X) = \begin{bmatrix} H \\ \varphi \end{bmatrix} \]  

(21)

where $X = \begin{bmatrix} \theta \\ t \end{bmatrix}$. The new function added is

\[ \varphi = (\theta - \theta^{(0)})^T \cdot \dot{\theta} + (t - t^{(0)})i - \Delta s \]  

(22)

where $\theta^{(0)}$ and $t^{(0)}$ are reasonable starting values of the corrector step.

If $X^0$ is such that $\varepsilon(X^0) = 0$ and $\text{rank}(\varepsilon_X(X^0)) = Nn$, the Implicit Function Theorem states that there exist a unique zero-curve of Eq. (21) through $X^0$, which is called the solution branch.

Note that

\[ \varepsilon_X = \begin{bmatrix} H_{\theta} & H_t \\ \dot{\theta} & i \end{bmatrix} \]  

(23)

from what it is clear that $\varepsilon_X$ is nonsingular in turning points, even when $H_{\theta}$ is singular.

The Newton’s method is applied to $\varepsilon$, to find the root $X$ with

\[ X^{(r+1)} = X^{(r)} - \varepsilon^{-1}_X(\dot{X}^{(r)}) \cdot \varepsilon(\dot{X}^{(r)}) \]  

(24)
Iterations stop when \( \|X^{(r+1)} - X^{(r)}\| < tol \), for a given tolerance \( tol \). Each point in the curve is calculated iteratively by Eq. (24).

Partial derivatives of \( H \) and \( \varphi \) are needed to obtain \( \xi_x \). Like \( F \) in Eq. (11), \( H_\theta \) in Eq. (23) must somehow be the result of the integration inside the catalyst pellet. Therefore, the corresponding differential equations must be found. Some new variables are defined by

\[
\begin{align*}
\pi_n &= \frac{\partial p_j}{\partial \theta_n}, \quad \tau_n = \frac{\partial T}{\partial \theta_n}, \\
\nu_n &= \frac{\partial N_j}{\partial \theta_n}, \quad \lambda_n = \frac{\partial q}{\partial \theta_n},
\end{align*}
\]

where \( \pi = p_o, \quad \tau = T_o, \quad \nu = N_o, \quad \lambda = q_o \). It will also be convenient to introduce the variables \( \xi = \begin{bmatrix} p \\ T \end{bmatrix} \) and \( \psi = \begin{bmatrix} \pi \\ \tau \end{bmatrix} \).

From Eqs. (1) to (5), the differential equations to be solved together with Eqs. (6) to (9) are (see APPENDIX A)

\[
\begin{align*}
\frac{d\pi}{dz} &= Rp \left[ \tau B \cdot N + T \psi \cdot B \cdot N + T \psi \cdot B^T \right] \\
\frac{d\tau}{dz} &= \frac{Rp}{\kappa} \lambda
\end{align*}
\]

\[
\frac{d\nu}{dz} = \begin{cases} \\
-\frac{Rp}{\xi} \psi \cdot r_\epsilon \cdot \alpha + \frac{a-1}{1-\xi} \nu & z \neq 1 \\
-\frac{1}{a} \frac{Rp}{\xi} \psi \cdot r_\epsilon \cdot \alpha & z = 1
\end{cases}
\]

\[
\frac{d\lambda}{dz} = \begin{cases} \\
- \left[ \frac{dT}{dz} \psi \cdot C_d + \frac{d\tau}{dz} \cdot N \cdot C_d \right] + Rp \psi \cdot r_\epsilon \cdot \Delta H + \frac{a-1}{1-\xi} \frac{\lambda}{a} & z \neq 1 \\
\frac{1}{a} \frac{1}{a} \frac{Rp}{\xi} \psi \cdot r_\epsilon \cdot \Delta H & z = 1
\end{cases}
\]

with boundary conditions
\[ \pi = 0, \tau = 0 \quad z = 0 \]
\[ \nu = 1, \lambda = e_{\nu+1} \quad z = 1 \]  
(29)

Note that juxtaposition (e.g. \( \tau B \)) denote tensor product, whereas the dot (\( B \cdot N \)) denotes inner product. The gradients of \( B \) in Eq. (25) and \( r \) in Eqs. (27) and (28) are calculated numerically.

Integrating Eqs. (25) to (28) together with (6) to (9) throughout the catalyst pellet by means of a 4th order Runge – Kutta routine, \( F, G, H \) and \( H_\theta \) are obtained for \( z = 1 \), and thus Eq. (24) can be computed. In particular, \( H_\theta = \begin{bmatrix} \nu & \lambda \end{bmatrix}^T \) at \( z = 1 \).

**Homotopy continuation algorithm**

The algorithm traces the solution branch of Eq. (21). The steps of the algorithm are as follows:

0. Initialization: select initial values \( X_0 = [\theta_0, 0] \), and initial tangent vector \( \dot{X}_0 = \left[ \dot{\theta}_0, \dot{t}_0 \right] \), and a length step \( \Delta s \). Set iteration counter \( u = 1 \).

1. Solve \( \varepsilon (X) = 0 \) with the Newton’s method,

\[ X_u^{(r+1)} = X_u^{(r)} - \varepsilon^{-1} (X_u^{(r)}) \cdot \varepsilon (X_u^{(r)}) \]

using the initial point

\[ X_u^{(0)} = X_u^{(r-1)} + X_u^{(r-1)} \Delta s \]. Call \( X_u \) the solution found.

2. Calculate the next tangent vector \( \dot{X}_u \) from \( \varepsilon (X_u) \cdot \dot{X}_u = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \), then scale it to take unit length.

3. If all the desired solutions at \( t = 1 \) have been found, stop. Otherwise, set \( u = u + 1 \) and go to step 1.
This method is implemented in Matlab®, taking advantages of its user-friendly matrix manipulation.

Remarks:

- If $\xi_x$ is nonsingular and $\Delta s$ is small enough, convergence of Newton is assured.
- $\xi_x$ is singular in branching points. In such a case, it is desired to follow the two branches emanating from the branching point. Doedel\textsuperscript{38} shows how to calculate these branches. However, branching does not occur in this problem.
- The algorithm has step controls on $\Delta s$ to prevent divergence in Newton’s method where the curvature is large and to increase the speed of the algorithm when the curvature is small.

It should be pointed out that the proposed algorithm finds all solutions of Eq. (1) - (4) for a fixed $Rp$. All the physical solutions are found at $t = 1$, and the desired profiles are straightforwardly obtained.

Continuation algorithms implemented in tools like AUTO\textsuperscript{39} or MatCont\textsuperscript{40} can be used to perform the continuation in Eq. (11), using $Rp$ (or other physical parameter) as continuation parameter. However, good initial values of $(\Omega, Rp)$ should be provided in order to find the first solution of Eq. (11).

Furthermore, if only solutions for specific values of operating conditions are searched, it seems more advantageous using Eq. (13), since it is almost independent of the initial point.

The methodology proposed here always starts with a point in the solution curve of Eq. (13). The drawback, as it is shown in the following section, is that for certain initial points the curve does not pass for all physical solutions in $t = 1$. However Kuno and
Seader\textsuperscript{19} give some criteria for choosing $X_0$ so that all solutions belong to the curve $H = 0$.

**Results and discussion**

Experimental results in Table 1 showed that the rate of reaction increased for increasing pellet sizes. Since in this case the value of thermal conductivity was large enough to handle the heat flux evolved, temperature can be considered constant in the range of pellet sizes analyzed (this assumption was confirmed in the simulations). This induces to think that the source of non-monotonicity comes from the concentration. Thus, the rate expression employed in this work is taken from Carberry\textsuperscript{41}.

$$
 r = \frac{k p_{co}}{(1 + K_{co} p_{co})^2} \quad (30)
$$

Although in the CO oxidation reaction it is usual to employ a Mars – van Krevelen type kinetics, recently Vannice\textsuperscript{42} has criticized its use, suggesting in turn a Langmuir – Hinshelwood type kinetics like that in Eq. (30).

Since the homotopy curves have intermediate solutions that do not have physical meaning, negative $p_{co}$ may occur. Thus, the denominator of Eq. (30) may become zero in the algorithm. In order to avoid division by zero, the expression

$$
 r = \frac{k p_{co}}{(1 + K_{co} |p_{co}|)^2} \quad (31)
$$

is used instead of Eq. (30).

Reference conditions at the catalyst surface and kinetic parameters are listed in Table 2 and Table 3.

**Table 2. Reference conditions at the catalyst surface**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Temperature</td>
<td>800 K</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 bar</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Pt</td>
</tr>
<tr>
<td>Reaction</td>
<td>CO oxidation</td>
</tr>
</tbody>
</table>

Reference conditions at the catalyst surface and kinetic parameters are listed in Table 2 and Table 3.
Table 3. Kinetic parameters

Parameter sensitivity

The sharp non-monotonic dependence of $r$ w.r.t. CO introduces a strong sensitivity.

Figure 1. Dependence of the rate of reaction w.r.t. CO partial pressure

Numerical problems arise when CO is near depletion, where the maximum of $r$ occurs. Therefore, this kind of sensitivity shall be expected when conversion is high.

Homotopy curves

Homotopy curves are constructed departing from an initial value of $\theta$. Since curves can be tracked for both negative and positive values of $t$, the sign of $i_0$ must be chosen positive so as to track the curve in the direction of interest. The initial predicting direction was chosen $\dot{X}_0 = [0\ 1]$.

The method employed in this work obtains every possible steady state, i.e., the state vector which drives Eq. (11) to zero for different values of $Rp$. The only points of these curves which have a physical meaning are those obtained for $t = 1$, since in this case $H = 0$ becomes $F = 0$, which is the original problem. Thus, the homotopy method presented in this work must be run for different values of $Rp$, each time obtaining all available solutions for $t = 1$. Appendix B shows a validation of the method proposed in this work.

Figure 2 illustrates homotopy curves for different pellet sizes. The thicker lines correspond to the limits of the multiplicity region, i.e. the curves that cross $t = 1$ more than once.
Figure 2. Homotopy curves for different pellet sizes

When $t = 1$, $\theta_1$ is the molar flux of CO at the surface, value with which the effectiveness factor is computed by virtue of Eq. (10) and plotted in Figure 3.

Figure 3. Effectiveness factor vs. pellet size

This curve shows three regions: lower, middle and upper branches. Moreover, Figure 3 shows that in the region between $R_p = 5$ and $R_p = 8 \, \mu m$ (approximately), the three branches coexist and multiplicity takes place.

It can be seen in the upper branch in Figure 3 that $\eta$ depends inversely upon $R_p$. On the other hand, Figure 2 shows that the solution corresponding to the upper branch has the same value for different $R_p$. Analyzing Eq. (10), for constant surface temperature and reactants composition, the expression $\frac{N_{j}^{\text{sup}}}{r_{j}^{\text{sup}}}$ is constant, thus obtaining a constant value of the molar flux of any species at the surface, regardless of the pellet size. Therefore, the effectiveness factor is inversely proportional to $R_p$, in accordance to the asymptotic behavior when the catalyst operates at diffusive control (large values of Thiele modulus).

Dependence on initial conditions

Figure 4 shows typical curves $\theta_1$ vs. $t$ when (a) $R_p = 5 \, \mu m$, (b) $R_p = 7 \, \mu m$ and (c) $R_p = 12 \, \mu m$, for different initial values of $\theta_1$ and constant initial value of $\theta_2$. 
Figure 4. Homotopy curves for two different initial values of $\theta_1$ for (a) $R_p = 2 \, \mu m$, 
(b) $R_p = 7 \, \mu m$, (c) $R_p = 12 \, \mu m$

Figure 4 (a) shows the typical behavior for small pellet sizes of any homotopy curve to reach the single steady state condition. The solution for this case is readily obtained. On the other hand, Figure 4 (b) shows the dependence of the method on the initial value of $\theta_1$ in order to find the multiple steady states. It can be seen that initial values of $\theta_1$ above c. -9.5 (the upper steady state) allow the curve to find the three steady states. Any value within -9.5 and -23.8 (the middle steady state) allows the curve to find only the first steady state. Within the range of -23.8 and -33.2 (the lower steady state), the curve passes only through the third steady state. For initial values of $\theta_1$ lower than -33.2, numerical problems arise, although values lower but sufficiently close to -33.2 show that only the lower steady state is reached.

Figure 4 (b) also suggests that, when starting from a value in the neighborhood of the middle steady state, this steady state, which is known to be physically unstable\textsuperscript{1}, cannot be easily reached by the method unless a very accurate value is adopted, since small perturbations from the exact value lead to either the first or the third steady states.

Figure 4 (c) shows the typical behavior of the zero-curve for large pellet sizes. It must be said that the algorithm cannot always trace the zero-curve for $R_p$ greater than about 8 $\mu m$ up to $t = 1$. Numerical difficulties arise when integrating in condition of total depletion inside the pellet. When this case occurs, step controls must be applied, and thus the algorithm becomes slower in traversing this zone.

The dependence of the number of steady states achievable upon the initial $\theta$, shown in Figure 4 (b), agrees with the result of Kuno and Seader\textsuperscript{19}, for whom $\theta_0$ should be selected such that $F(\theta) - \theta + \theta_0 = 0$ has a minimum number of solutions. Since $F(\theta)$
is assumed to be bounded in the domain of interest, extreme values of $\theta_1$ should satisfy the condition.

**Figure 5. Curves $H(\theta_1, t) = 0$ for $R_p = 7 \mu m$ in the $\theta_1 - \theta_2$ space**

Figure 5 depicts the homotopy curves in the $(\theta_1, \theta_2)$-space. Initial values $\theta_0$ are shown with hollow circles and steady states with solid circles. It can be seen that only initial values in the region of $\theta_1 > -9.5$ (regardless of the value of $\theta_2$) reach the three steady states, as already mentioned.

As regards $\theta_2$, when $t = 1$ it represents the heat flux at the surface. It was observed that temperature remained constant throughout the pellet. Therefore, the system is rather insensitive to heat flux, so initial conditions of $\theta_2$ are not critical. This was verified by numerical results not shown. If the thermal conductivity was such that temperature gradients existed, initial values of $\theta_2$ may have analogous impact as $\theta_1$.

**Conclusions**

In this work, an algorithm that allows finding multiple steady states in a catalyst pellet with a non-monotonic kinetics is presented. The equation system that arises when simulating the pellet is highly nonlinear and traditional solver packages fail either to converge or to find all possible steady states. The method proposed in this work, based on homotopy continuation, finds every steady state by tracking a curve from a fairly arbitrary initial point.

A sensitivity study of the homotopy curves w.r.t. $\theta_1$ was performed. Although homotopy curves can be tracked from any starting point, it was observed that there is a region of $\theta_1$ for which curves pass through the three solutions and other regions


departing from which only one of the three solutions is achieved. The limits of these regions are determined by the values of $\theta_i$ in the three solutions. These regions are independent of the initial value of $\theta_2$ (which represents the heat flux) since the thermal conductivity is high enough to guarantee constant temperature within the pellet.

Numerical instabilities occur around the total depletion of the reactant, where the kinetics is strongly sensitive to this reactant composition. This happens for the solutions in the upper branch in Figure 3. In some cases, this difficulty is overcome applying step controls, but yet when the problem persists, an asymptotic behavior of the curve is observed, tending to the correct solution.

Even when in practice pellet sizes to be employed are far from the multiplicity region, experimental data to fit kinetic parameters fall in this range of multiplicity. Thus, it is important to take this effect into account when analyzing the experimental data.

This study also suggests that the kinetics of a reaction that produces in a certain range increasing effectiveness factors for increasing pellet sizes should behave non-monotonically, when no thermal effects are present. This would discard a Mars – van Krevelen type kinetics for the CO oxidation reaction catalyzed by copper/ceria catalysts.

**Acknowledgements**

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**APPENDIX A: Auxiliary differential equations**

Since $H_\theta = tE_\theta + (1-t)G_\theta$ and $G_\theta$ is a diagonal matrix with the scale factor in its diagonal, all the effort is focused on $E_\theta$. As regards $t$, it is constant for the integration in
It can also be said that $\theta_n$ are also independent from $z$. Thus, Eqs. (1) to (4) can be used in the following form \(^{36}\)

$$
\frac{\partial}{\partial \theta_n} \left( \frac{dp_j}{dz} \right) = \frac{d}{dz} \left( \frac{\partial p_j}{\partial \theta_n} \right) = \frac{d\pi_n}{dz} = Rp \frac{\partial}{\partial \theta_n} \left( T B_{jk} N_k \right) \quad (A.1)
$$

Analogously

$$
\frac{d\tau_n}{dz} = \frac{Rp}{\kappa} \frac{\partial q}{\partial \theta_n} \quad (A.2)
$$

$$
\frac{dV_{nj}}{dz} = \left\{ \begin{array}{l}
-Rp \alpha_i \frac{\partial r_i}{\partial \theta_n} + \frac{a-1}{1-z} \frac{\partial N_j}{\partial \theta_n} \quad z \neq 1 \\
-\frac{1}{a} Rp \alpha_i \frac{\partial r_i}{\partial \theta_n} \quad z = 1
\end{array} \right. \quad (A.3)
$$

$$
\frac{d\lambda_n}{dz} = \left\{ \begin{array}{l}
-Cp_j N_j \frac{d}{dz} \frac{\partial T}{\partial \theta_n} + Rp\Delta H_i \frac{\partial r_i}{\partial \theta_n} + \frac{a-1}{1-z} \frac{\partial q}{\partial \theta_n} \quad z \neq 1 \\
\frac{1}{a} Rp\Delta H_i \frac{\partial r_i}{\partial \theta_n} \quad z = 1
\end{array} \right. \quad (A.4)
$$

where repeated indexed indicate summation. In the same way, boundary conditions (5) are transformed into

$$
\frac{\partial p_j}{\partial \theta_n} = 0, \frac{\partial T}{\partial \theta_n} = 0 \quad z = 0 \quad (A.5)
$$

$$
\frac{\partial N_j}{\partial \theta_n} = \delta_{nj}, \frac{\partial q}{\partial \theta_n} = \delta_{nNc+1} \quad z = 1
$$

where $\delta$ is the Kronecker delta.

Eqs. (A.1) to (A.4) can be rewritten with these new variables introduced in tensorial form by means of adding bases and dot and tensorial products.

$$
\frac{d\pi_{nj}}{dz} e_n e_j = Rp \left[ \tau_n e_n B_{jk} e_j e_k \cdot N_j e_k + T \frac{\partial \xi'}{\partial \theta_n} e_n e_k \cdot \frac{\partial B_{jk}}{\partial \xi'} e_n e_k e_j e_k \cdot N_j e_k + T V_{nj} e_n e_k \cdot B_{jk} e_j e_k \right]
$$

$$
\frac{d\tau_n}{dz} e_n = \frac{Rp}{\kappa} \lambda_n e_n
$$
\[
\frac{d v_{nj}}{dz} e_j = \begin{cases} 
-R_p \frac{\partial z^{\prime \prime}}{\partial \theta_n} e_j e_j \cdot e_j + \frac{a-1}{1-z} v_{nj} e_j & z \neq 1 \\
-\frac{R_p}{a} \frac{\partial z^{\prime \prime}}{\partial \theta_n} e_j e_j \cdot e_j \cdot \alpha_j e_j & z = 1 
\end{cases}
\]

\[
\frac{d \lambda_n}{dz} e_n = \begin{cases} 
-\left[ \frac{dT}{dz} v_{nj} e_j e_j + \frac{d \tau_n}{dz} e_j \cdot N e_j \right] \cdot C_p e_j + \\
R_p \frac{\partial z^{\prime \prime}}{\partial \theta_n} e_j e_j \cdot e_j \cdot \alpha_j e_j \cdot \Delta H e_n e_n + \frac{a-1}{1-z} \lambda_n e_n & z \neq 1 \\
\frac{1}{a} R_p \frac{\partial z^{\prime \prime}}{\partial \theta_n} e_j e_j \cdot e_j \cdot \alpha_j e_j \cdot \Delta H e_n e_n & z = 1 
\end{cases}
\]

These lead to

\[
\frac{d \pi}{dz} = R_p R \left[ \xi B \cdot N + T \psi \cdot B \cdot N + T \psi \cdot B^T \right]
\] (A.6)

\[
\frac{d \tau}{dz} = R_p \frac{\lambda}{\kappa}
\] (A.7)

\[
\frac{d v}{dz} = \begin{cases} 
-R_p \psi \cdot r \cdot \alpha + \frac{a-1}{1-z} v & z \neq 1 \\
-\frac{1}{a} R_p \psi \cdot r \cdot \alpha & z = 1 
\end{cases}
\] (A.8)

\[
\frac{d \lambda}{dz} = \begin{cases} 
-\left[ \frac{dT}{dz} + \frac{d \tau}{dz} \right] C_p + R_p \psi \cdot r \cdot \alpha \cdot \Delta H + \frac{a-1}{1-z} \lambda & z \neq 1 \\
\frac{1}{a} R_p \psi \cdot r \cdot \alpha \cdot \Delta H & z = 1 
\end{cases}
\] (A.9)

**APPENDIX B: Model validation**

The package MatCont\textsuperscript{40} was employed to validate the method presented in this work. This package is coded in Matlab as well as the algorithm employed in this work.

MatCont allows performing the continuation in \( Rp \) departing from a good initial point. It may calculates the Jacobian in Eq. (16) either analytically if the expression is available (which is not the case) or numerically running the integration of the system.
from $z = 0$ to $z = 1$, $(N_n + 1)$ times in order to compute all of the partial derivatives required, whereas the algorithm presented in this work computes the Jacobian integrating only once, although more equations need to be integrated.

In both MatCont and the method presented in this work, numerical difficulties arise when integrating in condition of total depletion inside the pellet. MatCont could not trace the curve beyond $R_p = 5 \mu m$ in the upper branch, either because an error occurs or the successive solutions do not follow a smooth curve. This takes place for solutions with high CO fluxes.

Effectiveness factors for different $R_p$ obtained by both methods are shown in Figure 6

**Figure 6. Comparison of the two methods**

Figure 6 shows that both methods agree in the results.

**NOMENCLATURE**

- $a$: Shape factor
- $B$: Dusty Gas Model matrix [s/m$^2$]
- $C_p$: Species heat capacities [J/mol·K]
- $\mathbf{e}$: Basis vector
- $F$: System of equations of the real problem
- $G$: System of equations for the “easy” problem
- $H$: Homotopy function
- $\Delta H$: Reaction enthalpies [J/mol]
- $I$: Identity matrix
\( k \)  Kinetic constant [mol/m\(^3\)s-Pa]

\( K_{CO} \)  Adsorption constant of CO [1/Pa]

\( N \)  Species molar fluxes [mol/m\(^2\)s]

\( N_c \)  Number of species

\( N_n \)  System dimension

\( Nu \)  Nusselt number

\( \rho \)  Species partial pressure [Pa]

\( q \)  Heat flux [J/m\(^2\)s]

\( R \)  Reaction rates [mol/m\(^3\)s]

\( R_p \)  Universal constant of gases [J/mol-K]

\( s \)  Arclength

\( S_h \)  Sherwood number

\( t \)  Homotopy parameter

\( T \)  Temperature [K]

\( X \)  Points of the homotopy curve

\( z \)  Dimensionless space coordinate

**Greek letters**

\( \alpha \)  Stoichiometric coefficients

\( \delta \)  Kronecker Delta

\( \phi_X \)  Jacobian matrix of the augmented system

\( \varphi \)  Additional equation for the augmented system

\( \eta \)  Effectiveness factor
\( \theta \) Homotopy variables

\( \kappa \) Thermal conductivity of the solid [J/m·K·s]

\( \lambda \) Gradient of \( q \) w.r.t. \( \theta \)

\( \nu \) Gradient of \( N \) w.r.t. \( \theta \)

\( \xi \) State variables (partial pressures and temperature)

\( \pi \) Gradient of \( p \) w.r.t. \( \theta \)

\( \tau \) Gradient of \( T \) w.r.t. \( \theta \)

\( \psi \) Gradient of \( \xi \) w.r.t. \( \theta \)

Subscripts and superscripts

\( \theta \) Starting value

\( j,k \) Species \( j, k \)

\( i \) Reaction \( i \)

\( n \) Element \( n \) of vector \( \theta \)

\( (r) \) Iteration \( r \)

\( sup \) Surface

\( T \) Transpose

\( u \) Point \( u \) on the zero-curve
References


Table 1. CO conversion for different temperatures and pellet sizes

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<th>$T$ [K]</th>
<th>$R_p &lt; 4.4$ µm</th>
<th>$4.4$ µm $&lt; R_p &lt; 6.2$ µm</th>
<th>$6.2$ µm $&lt; R_p &lt; 8.8$ µm</th>
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<tr>
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Table 2. Reference conditions at the catalyst surface

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Table 3. Kinetic parameters at 413 K

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<th>Parameter</th>
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<tr>
<td>$k$ [mol/Pa·m$^3$·s]</td>
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<tr>
<td>$K_{CO}$ [1/Pa]</td>
<td>$5.03 \times 10^{-2}$</td>
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Figure 1. Dependence of the rate of reaction w.r.t. CO partial pressure
Figure 2. Homotopy curves for different pellet sizes
Figure 3. Effectiveness factor vs. pellet size
Figure 4. Homotopy curves for different initial values of $\theta_1$ for (a) $R_p = 2 \ \mu m$, (b) $R_p = 7 \ \mu m$, (c) $R_p = 12 \ \mu m$
Figure 5. Curves $H(\theta; t) = 0$ for Rp = 7 μm in $\theta_1 - \theta_2$ space
Figure 6. Comparison of the two methods