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Structural Identifiability Analysis of the Dynamic Gas–Liquid Film Model

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A structural identification analysis of the dynamic gas–liquid film model is applied to identify its theoretically accessible parameters. The analysis was performed considering the different experimental situations found in nonstationary bubble-column reactors. The system has been modeled considering both the liquid and the gas phases in a well-mixed flow regime with a global second-order irreversible chemical reaction. To describe the mass-transfer phenomenon at the gas–liquid interface level, chemical reactions and diffusive mass transport were considered simultaneously in the liquid film. The identifiability analysis shows that the simultaneous measurement of concentrations in the liquid and the gas phases is required to determine the parameters. Furthermore, model parameters such as the diffusion coefficients, the specific interfacial area, or the film thickness cannot be uncoupled from other parameters, although the kinetic rate constants could be identified in the fast or slow chemical regimes. It is demonstrated that the specific interfacial area cannot be measured from chemical data coming from a nonstationary bubble-column reactor. This result is discussed with respect to the classical Danckwerts' method for determination of the interfacial area in gas–liquid equipment. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 2851–2863, 2006
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Introduction

The mathematical models used in gas–liquid reaction modeling make use of a large number of physical and chemical parameters. Accurate knowledge of these parameters is one of the main concerns on the experimental study of these processes to confirm the theories, to model the processes, to design, scale-up the chemical reactors, and, finally, to control the reactor operation conditions. Because the number of parameters to be determined in such models is high and the number of observable magnitudes in gas–liquid reactors is limited, it is advisable to design accurate experiments to obtain the maximum number of parameters of the system. On the other hand, structural identifiability analysis is a mathematical tool that enables a preliminary study of models oriented to the design of experiments, to discern between different candidate mathematical models and to design computational programs for optimization and parameter estimation. Through the structural identifiability analysis of the dynamical film model we seek to obtain some a priori information about the input–output structure of the model that can help us to design experiments oriented toward parameter determination in gas–liquid systems such as bubble-column reactors.

The problem of structural identifiability is related to the uniqueness of the solution of an input–output system and can be stated as follows: given a mathematical model describing our physical system with an unknown vector parameter $\boldsymbol{p}$ and a vector of observable magnitudes $\boldsymbol{x}$, is there only a single vector of parameters $\boldsymbol{p}$ related to the observable vector $\boldsymbol{x}$? In other words, given two different parameter vectors $\boldsymbol{p}$ and $\boldsymbol{q}$ for the same mathematical model, is it possible to obtain identical observable response $\boldsymbol{x}$ for both vectors? The structural identi-

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fiability analysis tries to answer this question by considering just the mathematical structure of the model. In fact, the identifiability analysis does not give any information about how accurately a parameter can be determined from experiments, but which one or which combination of them can be achievable from a given mathematical model.

Structural identifiability is widely used in biomedical sciences and there is an extensive bibliography about the subject for the study of pharmacokinetic models.[1,2] Furthermore, because of the similarity between their model structures, its application to parameter identification in the modeling of the kinetics of the biological processes given in wastewaters[3-7] is also well known. Berthier et al.[8-11] treated the problem of the parameter identifiability to some extent in the field of electrochemistry. These authors analyzed different electrode processes with complex chemical mechanisms including homogeneous and heterogeneous steps. Assuming that the instrumental technique used to obtain the experimental data is electrochemical impedance spectroscopy, they deduced which parameters of the models could be accessible. Applications of structural identifiability on chemical engineering are less frequent, but some problems have been treated. Walter and Pronzato[12] analyzed the chemical mechanism of catalytic reduction of CO, concluding that different models will lead to the same input–output response of the system, making both models indistinguishable. Recently, Tayakout-Fayolle et al.[13] analyzed the structural identifiabililty of the classical model describing the dynamics of a chromatographic column. This paper shows how this analysis can help to identify the combination of parameters in the model that are accessible, depending on the mathematical model used to describe it, and how the analysis directs the experimental design, depending on the parameters that should be determined.

The aim of our work is to know which macroscopic state variables of the model, or their combination, must be measured to determine the maximum possible number of physical parameters in a bubble-column reactor. The mathematical representation of our system is based on the dynamic gas–liquid film model in a continuously stirred tank reactor (CSTR). The simplest representation of this model could imply up to ten thermodynamic, hydrodynamic, kinetic, and other physicochemical or operational parameters. To the best of our knowledge, this kind of analysis has never been applied to gas–liquid mass transfer problems. Because the analysis is always carried out with respect to a set of observable magnitudes, the model is restricted to a completely mixed gas-flowing/batch-liquid reactor or semibatch bubble-column reactor. In the first section of the paper we have sketched some basic concepts and the methodology used to carry out the identifiability analysis of the model. The next section describes the mathematical model used to describe the system that it is based on the dynamic gas–liquid film theory. Finally, the results are shown considering some appropriate limiting cases such as fast, slow, or no chemical reaction.

Basic Concepts on Structural Identifiability and on the Linear/Nonlinear Splitting Method

Several methods have been proposed to perform the structural identifiability of dynamical systems. Although for linear state-space models the identifiability problem has been solved with general analytical and computational algorithms based on Gröbner bases,[14,15] the problem for nonlinear state-space models is far from being solved. The proposed methods for these systems are based on a Taylor series expansion[4,6,16] or on the generating series expansion[1,12,13] (which amounts to the Laplace transform method for linear state-space models), on methods based on local state-space isomorphism theorem[17-19] (also known as the local isomorphism transformation), and, finally, on methods derived from differential algebra.[2,20] None of these methodologies is better than any other because the success of such analysis depends on the structure of the model itself and its complexity; moreover, there are no general rules to decide the best methodology for a particular system. For example, the Taylor series method could be easily outlined for complex dynamical systems with a large number of observable state variables, but there are no general rules to solve the final set of algebraic equations giving the identifiable parameters. Conversely, the local isomorphism transformation gives a general procedure for the analysis of dynamical systems with any level of complexity (together with linear system), although the initial stages of the procedure could give a set of nonlinear algebraic equations that are difficult to solve either analytically or computationally.

The methodology used in this work was recently proposed by Chapman et al.[21,22] and we refer the reader to these papers and references therein for a detailed description of the proofs of the method. This proposed procedure is an extension of the local state isomorphism theorem applied to a particular class of nonlinear state-space dynamical systems. It is based on the splitting of the linear and the nonlinear parts of the state-space model and doing the analysis of both parts separately.

Consider that the process under study could be described by the nonlinear state-space model of the form:

$$\dot{\mathbf{x}}(t, \mathbf{p}) = \mathbf{A}(\mathbf{p})\mathbf{x}(t, \mathbf{p}) + \mathbf{B}(\mathbf{p})\mathbf{u}(t) + \sum_{i=1}^{s} f_i[\mathbf{x}(t, \mathbf{p}), \mathbf{p}]\boldsymbol{\nu}_i(\mathbf{p}) \tag{1a}$$

$$\mathbf{z}(t, \mathbf{p}) = \mathbf{C}(\mathbf{p})\mathbf{x}(t, \mathbf{p}) \tag{1b}$$

$$\mathbf{x}(0, \mathbf{p}) = \mathbf{0} \tag{1c}$$

with the additional properties:

$$\left.\begin{aligned} f_i(0, \mathbf{p}) &= 0 \\ \frac{\partial f_i}{\partial \mathbf{x}_i}(0, \mathbf{p}) &= 0 \end{aligned}\right\} \tag{2}$$

where $\mathbf{x}(t, \mathbf{p}) \in \mathbb{R}^n$ is the state variable vector, $\dot{\mathbf{x}}(t, \mathbf{p})$ stands for the time derivative of $\mathbf{x}(t, \mathbf{p})$, and $\mathbf{p}$ is a vector containing the constants and parameters that would be determined from the observable (measurable) vector $\mathbf{z}(t, \mathbf{p})$. Notice that the observable magnitudes $\mathbf{z}(t, \mathbf{p})$ are linearly related with the state variables $\mathbf{x}(t, \mathbf{p})$, but could be nonlinearly related with the parameters $\mathbf{p}$ of the model through the observation matrix $\mathbf{C}(\mathbf{p})$. The input vector $\mathbf{u}(t) \in \mathbb{R}^r$ is also considered bounded and measurable and represents the perturbation applied to the system from its outward bounds. On the other hand, $f_i[\mathbf{x}(t, \mathbf{p})$,

$\mathbf{p}$] ($i = 1, \ldots, s$) represents the nonlinear functions in $\mathbf{x}$ and $\mathbf{p}$ of the equation system. Finally, $\mathbf{A}(\mathbf{p})$, $\mathbf{B}(\mathbf{p})$, $\mathbf{C}(\mathbf{p})$, and $\mathbf{v_i}(\mathbf{p})$ are matrices that define the system and describe the relationship between the state vector $\mathbf{x}(t, \mathbf{p})$, the perturbation applied to the system $\mathbf{u}(t)$, and the physically observed response $\mathbf{z}(t, \mathbf{p})$. Thus, after Eqs. 1 and 2 the system is described by a set of first-order ordinary differential equations (ODEs) that have linear and nonlinear components. Moreover, the additional conditions (Eq. 2) ensure that the system is initially in a stationary state and there is no contribution of the nonlinear part to the linear part.

Given two parameter vectors $\mathbf{p}, \mathbf{q} \in \mathbb{R}^m$ and the same input vector $\mathbf{u}(t)$, the observed outputs depend on the model structure $\mathbf{M}(\cdot)$; we write this relation as $\mathbf{z}(t, \mathbf{p}) = \mathbf{M}(t, \mathbf{p}, \mathbf{u})$ and $\mathbf{z}(t, \mathbf{q}) = \mathbf{M}(t, \mathbf{q}, \mathbf{u})$. We say that two parameter sets, $\mathbf{p}$ and $\mathbf{q}$, are *indistinguishable* if they give the same input–output behavior, that is, if $\mathbf{z}(t, \mathbf{p}) = \mathbf{z}(t, \mathbf{q})$ for all $\mathbf{u}(t)$. Concerning the relation between $\mathbf{M}(\cdot)$ and $\mathbf{p}$, we say that the model is:

- *structurally globally identifiable* if for any generic $\mathbf{q}$, the only solution for $\mathbf{p}$ of $\mathbf{M}(t, \mathbf{p}, \mathbf{u}) = \mathbf{M}(t, \mathbf{q}, \mathbf{u})$ is $\mathbf{p} = \mathbf{q}$. Here, the parameters of the model can be determined uniquely from the experimental data.
- *structurally locally identifiable* if for any generic $\mathbf{q}$, the only solution for $\mathbf{p}$ of $\mathbf{M}(t, \mathbf{p}, \mathbf{u}) = \mathbf{M}(t, \mathbf{q}, \mathbf{u})$ is $\mathbf{p} = \mathbf{q}$, provided that $\mathbf{q}$ belongs to a neighborhood of $\mathbf{p}$. In this case, from the experimental data it is possible to obtain a finite set of alternative values for the parameters.
- *unindentifiable* if the model is not structurally locally identifiable; otherwise, the number of alternatives to parameters obtained from experimental data is infinite.

Let us return to the work of Chapman et al.[21] about the structural identifiability of the particular nonlinear models described by Eqs. 1 and 2. Theorem 6 in this paper gives a procedure to demonstrate the indistinguishability between two parameters and, then, the identifiability of the model; a detailed demonstration is given in Chapman et al.[22] From a practical perspective let us reproduce this theorem here. The authors proceed to the demonstration of the structural identifiability of the model splitting the analysis into a linear stage and a nonlinear stage. Theorem 6 can be summarized as follows: two parameters, $\mathbf{p}$ and $\mathbf{q}$, are indistinguishable in the model structure represented by Eq. 1 if there exists a function $\boldsymbol{\lambda}(\mathbf{x}) = \mathbf{T}\mathbf{x} + \boldsymbol{\mu}(\mathbf{x})$, with $\mathbf{T} \in \mathbb{R}^{n\times n}$ and $\boldsymbol{\mu}(\mathbf{x}) \in \mathbb{R}^n$ where the linear part holds:

$$\mathbf{C}(\mathbf{q})\mathbf{T} = \mathbf{C}(\mathbf{p}) \tag{3a}$$

$$\mathbf{B}(\mathbf{q}) = \mathbf{T}\mathbf{B}(\mathbf{p}) \tag{3b}$$

$$\mathbf{A}(\mathbf{q})\mathbf{T} = \mathbf{T}\mathbf{A}(\mathbf{p}) \tag{3c}$$

together with the nonlinear equations:

$$\mathbf{C}(\mathbf{q}) \cdot \boldsymbol{\mu}(\mathbf{x}) = \mathbf{0} \tag{4a}$$

$$\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{x}}(\mathbf{x}) \cdot \mathbf{B}(\mathbf{p}) = \mathbf{0} \tag{4b}$$

$$\mathbf{A}(\mathbf{q}) \cdot \boldsymbol{\mu}(\mathbf{x}) + \sum_i f_i[\mathbf{x}(\mathbf{q}), \mathbf{q}] = \frac{\partial \boldsymbol{\mu}}{\partial \mathbf{x}}(\mathbf{x}) \cdot \mathbf{A}(\mathbf{p}) \cdot \mathbf{x} + \left[\mathbf{T} + \frac{\partial \boldsymbol{\mu}}{\partial \mathbf{x}}(\mathbf{x})\right] \sum_i f_i[\mathbf{x}(\mathbf{q}), \mathbf{q}] \tag{4c}$$

The system is *structurally globally identifiable* if $\mathbf{T} = \mathbf{I}$ and $\boldsymbol{\mu}(\mathbf{x}) = \mathbf{0}$, where $\mathbf{I}$ is the identity matrix.

The advantage of this procedure is that if the analysis of the linear part of the model (Eqs. 3a–3c) gives the parameters that are globally identifiable, analysis of the nonlinear part of this theorem (Eqs. 4a–4c), which usually is much more complicated, is not needed. Moreover, another advantage of this method is that Eqs. 3a–3c could be solved simultaneously using computer algebra as described elsewhere.[21,23] Nevertheless, the disadvantage of this method is that it is limited to models described by Eqs. 1a–1c subject to restrictions given by Eq. 2.

Given the inherent complexity of the dynamic gas–liquid film model, our work is focused on the recognition of the different alternative observation matrices $\mathbf{C}(\mathbf{p})$, by Eqs. 3a–3c, which makes the model structurally globally identifiable.

Model Description

The mathematical model described in this work was written keeping in mind the experiments that typically are carried out using a semibatch bubble-column reactor. Usually, a reactive gas A is bubbled through a liquid in which a nonvolatile solute B is present, reacting both substances together. The only physically measurable magnitudes of this kind of system are the concentration of both substances in the liquid or in the gas phase. Accordingly, the system has been modeled with consideration to the following assumptions: (1) the gas is considered as ideal; (2) the liquid and the gas phases are in a well-mixed flow regime (CSTR condition); (3) the gas-phase mass transfer resistance is considered negligible; (4) a global second-order irreversible chemical reaction of the type $A + B \rightarrow$ products is supposed, where A is the component transferred from the gas phase to the liquid phase, whereas B is present only in the liquid phase:

$$A(g \rightarrow l) + B(l) \xrightarrow{k_2} products(l) \tag{5}$$

To describe the mass-transfer phenomenon at the gas–liquid interface level, we have assumed the unsteady state gas–liquid film model where a rigid liquid film of thickness δ is next to the gas phase (see Figure 1) and where the chemical reactions and diffusive mass transport occur simultaneously.

By applying an unsteady state mass balance to the A component in the continuous gas phase, the following equation is obtained:

$$\frac{dy_A(t)}{dt} = \frac{RT}{PV}\frac{1-\varepsilon}{\varepsilon} F_i\left[\frac{y_{A0}}{1-y_{A0}} U(t) - \frac{y_A(t)}{1-y_A(t)}\right] + \frac{RT}{P}\frac{1-\varepsilon}{\varepsilon} D_A a\left[\frac{\partial C_A(x,t)}{\partial x}\right]_{x=0} \tag{6}$$

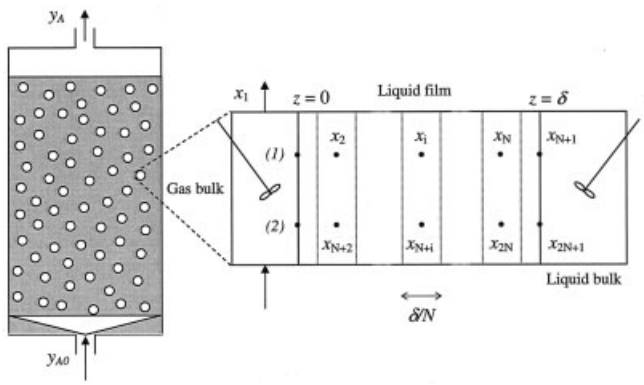

Figure 1. Discretization scheme for the liquid film at the bubble wall used in the modeling of the non-stationary bubble-column reactor.

The gas and liquid bulk are considered in complete mixing regime. The x values in the top row correspond to substance A and those in the bottom row to B. The dimensionless molar concentration of A at the interface (1) is in equilibrium with the gas phase. The dimensionless molar concentration of B at (2) is calculated using a backward-difference approximation of Eq. 8b.

with the initial condition $y_A(0) = 0$ and where y_A and y_{A0} are the molar fractions of component A in the gas phase at reactor outlet and inlet, respectively; F_i is the inert gas molar flow rate; ε is the gas fraction coefficient; R is the ideal gas constant; T is the reactor temperature; P is the total pressure; V is the volume of the liquid phase; $U(t)$ is the unit step function; a is the interfacial specific area; D_A is the diffusion coefficient for A in the liquid phase; and C_A is the molar concentration for A in the liquid film.

A mass balance of A and B in the quiescent liquid film next the interface gives the following partial differential equations (PDEs) with their respective initial and boundary conditions:

$$\frac{\partial C_A(x,t)}{\partial t} = D_A \frac{\partial^2 C_A(x,t)}{\partial x^2} - k_2 C_A(x,t) C_B(x,t) \qquad \forall\, x \in [0, \delta] \tag{7a}$$

$$\left.\begin{array}{ll} t = 0 & C_A(x,0) = 0 \\ t > 0 & C_A(0,t) = \dfrac{P}{H} y_A(t) \\ t > 0 & C_A(\delta,t) = C_A^b(t) \end{array}\right\} \tag{7b}$$

$$\frac{\partial C_B(x,t)}{\partial t} = D_B \frac{\partial^2 C_B(x,t)}{\partial x^2} - k_2 C_A(x,t) C_B(x,t) \qquad \forall\, x \in [0, \delta] \tag{8a}$$

$$\left.\begin{array}{ll} t = 0 & C_B(x,0) = C_{B0}^b \\ t > 0 & \left[\dfrac{\partial C_B(x,t)}{\partial x}\right]_{x=0} = 0 \\ t > 0 & C_B(\delta,t) = C_B^b(t) \end{array}\right\} \tag{8b}$$

where k_2 is the second-order kinetic rate constant, C_B is the molar concentration for B in the liquid film, H is the Henry constant, $C_A^b$is the molar concentration for A in the liquid bulk, D_B is the diffusion coefficient for B in the liquid phase, C_B^b is the molar concentration for B in the liquid bulk, and C_{B0}^b is its initial concentration.

Additionally, an unsteady state mass balance of A and B in the liquid bulk gives the following equations:

$$\frac{dC_A^b(t)}{dt} = -D_A a \left[\frac{\partial C_A(x,t)}{\partial x}\right]_{x=\delta} - k_2 C_A^b(t) C_B^b(t) \tag{9}$$

$$\frac{dC_B^b(t)}{dt} = -D_B a \left[\frac{\partial C_B(x,t)}{\partial x}\right]_{x=\delta} - k_2 C_A^b(t) C_B^b(t) \tag{10}$$

with their respective initial conditions $C_A^b(0) = 0$ and $C_B^b(0) = C_{B0}^b$.

The set of nonlinear PDEs (Eqs. 6–10) gives the representation of the physicochemical processes in a bubble-column reactor considering the gas and the liquid phases in complete mixed regime and with a second-order irreversible chemical reaction. Notice that these equations have mixed boundary conditions, such as Eq. 8b, and thus, its rigorous analytical solution cannot be realized by conventional techniques. Numerical integration techniques should be used instead. Let us consider an experiment oriented toward determining all the unknown constants and parameters defined in Eqs. 6–10 measuring the macroscopically observable concentrations of A and B. Assuming that in this hypothetical experiment $y_A(t)$, $C_A^b(t)$, and $C_B^b(t)$ are perfectly known, the fitting process is reduced to obtain the set of parameters in the Eqs. 6–10 model, which minimizes an objective function built from the state variables of the system. In our case we do not have analytical functions for $y_A(t)$, $C_A^b(t)$, and $C_B^b(t)$ to build the objective function, and so, it should be constructed from the numerical solution of a set of PDEs.

Because there are numerical optimization algorithms that can manage systems of ODEs,[24] our first guess is to transform the PDEs to a system of ODEs using a finite-difference discretization scheme.[25]

Let us consider that the quiescent liquid film of thickness δ defined next the interface is divided into N sections with $N + 1$ node concentrations (see details in Figure 1). To calculate the concentrations at the nodes, second-order central finite-difference approximations have been applied to the inner sections, forward difference approximations to the node point at the gas–liquid interface, and backward difference approximations to the node point at the liquid film–liquid bulk interface. Defining $C_{A0}^* = y_{A0} \cdot P/H$ as the equilibrium concentration of A at the liquid phase in relation to its concentration at the gas phase, and writing the dimensionless concentrations of A and B at the nodes, the set of differential Eqs. 6–10 could be expressed as

$$\dot{x}_1 = \frac{p_1}{p_2 - 1} U(t) - \frac{p_1}{p_2} x_1 - N p_3 p_4 (3x_1 - 4x_2 + x_3) - \frac{p_1}{p_2} \frac{x_1^2}{p_2 - x_1} \tag{11}$$

$$\dot{x}_i = N^2 p_5 (x_{i-1} - 2x_i + x_{i+1}) - p_6 x_i + p_6 x_i x_{N+i} \qquad i = 2 \cdots N \tag{12}$$

$$\dot{x}_{N+1} = -\frac{N}{2} p_4 (x_{N-1} - 4x_N + 3x_{N+1}) - p_6 x_{N+1} + p_6 x_{N+1} x_{2N+1} \tag{13}$$

$$\dot{x}_{N+2} = -\frac{2N^2}{3} p_7(x_{N+2} - x_{N+3}) + p_8 x_2 - p_8 x_2 x_{N+2} \quad (14)$$

$$\dot{x}_{N+i} = N^2 p_7(x_{N+i-1} - 2x_{N+i} + x_{N+i+1}) + p_8 x_i - p_8 x_i x_{N+i} \qquad i = 3 \cdots N \quad (15)$$

$$\dot{x}_{2N+1} = -\frac{N}{2} p_9(x_{2N-1} - 4x_{2N} + 3x_{2N+1}) + p_8 x_{N+1} - p_8 x_{N+1} x_{2N+1} \quad (16)$$

where $x_1 = y_A/y_{A0}$ is the dimensionless molar fraction of A in the gas phase, $x_{i=2\ldots N} = C_{Ai}/C^*_{A0}$ and $x_{i=N+2\cdots 2N} = 1 - C_{Bi}/C^b_{B0}$, where C_{Ai} and C_{Bi} are the molar concentrations of A and B in the ith layer in the quiescent liquid film, and x_{N+1} and x_{2N+1} are the dimensionless A and B bulk molar concentrations, respectively. All the state variables of this system have their initial condition set to zero, $x_{i=1,\ldots,2N+1}(0) = 0$.

The set of ODEs (Eqs. 11–16) is also characterized by a set of parameters that should be calculated fitting the data to the model. These parameters are defined as

$$p_1 = \frac{RT}{PV}\frac{1-\varepsilon}{\varepsilon}\frac{F_i}{y_{A0}} \quad (17a)$$

$$p_2 = \frac{1}{y_{A0}} \quad (17b)$$

$$p_3 = \frac{RT}{2H}\frac{1-\varepsilon}{\varepsilon} \quad (17c)$$

$$p_4 = \frac{D_A}{\delta} a \quad (17d)$$

$$p_5 = \frac{D_A}{\delta^2} \quad (17e)$$

$$p_6 = k_2 C^b_{B0} \quad (17f)$$

$$p_7 = \frac{D_B}{\delta^2} \quad (17g)$$

$$p_8 = k_2 C^*_{A0} \quad (17h)$$

$$p_9 = \frac{D_B}{\delta} a \quad (17i)$$

Let us consider the smallest possible approximation of Eqs. 6–10. Using Eqs. 11–16 with $N = 3$, we have

$$\begin{cases} \dot{x}_1 = \dfrac{p_1}{p_2 - 1} U(t) - \dfrac{p_1}{p_2} x_1 - 3p_3 p_4(3x_1 - 4x_2 + x_3) - \dfrac{p_1}{p_2}\dfrac{x_1^2}{p_2 - x_1} \\ \dot{x}_2 = 9p_5(x_1 - 2x_2 + x_3) - p_6 x_2 + p_6 x_2 x_5 \\ \dot{x}_3 = 9p_5(x_2 - 2x_3 + x_4) - p_6 x_3 + p_6 x_3 x_6 \\ \dot{x}_4 = -\dfrac{3}{2} p_4(x_2 - 4x_3 + 3x_4) - p_6 x_4 + p_6 x_4 x_7 \\ \dot{x}_5 = -6p_7(x_5 - x_6) + p_8 x_2 - p_8 x_2 x_5 \\ \dot{x}_6 = 9p_7(x_5 - 2x_6 + x_7) + p_8 x_3 - p_8 x_3 x_6 \\ \dot{x}_7 = -\dfrac{3}{2} p_9(x_5 - 4x_6 + 3x_7) + p_8 x_4 - p_8 x_4 x_7 \end{cases} \quad (18)$$

with the initial conditions:

$$x_i(0) = 0 \qquad i = 1 \cdots 7 \quad (19)$$

Notice that this system of ODEs satisfies the conditions imposed by Eqs. 1 and 2. So, the methodology proposed earlier for structural identifiability analysis can be applied to the equation system 18.

As was previously stated, the identifiability analysis will be performed using only the linear part of Eq. 18. Thus, by comparing this system with Eqs. 1a–1c we have the perturbation matrix $\mathbf{B}(\mathbf{p})$, given by

$$\mathbf{B}(\mathbf{p}) = \begin{bmatrix} \dfrac{p_1}{p_2 - 1} & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}^T \quad (20)$$

and the $\mathbf{A}(\mathbf{p})$ matrix by

$$\mathbf{A}(\mathbf{p}) = \begin{bmatrix} -\dfrac{p_1}{p_2} - 9p_3p_4 & 12p_3p_4 & -3p_3p_4 & 0 & 0 & 0 & 0 \\ 9p_5 & -18p_5 - p_6 & 9p_5 & 0 & 0 & 0 & 0 \\ 0 & 9p_5 & -18p_5 - p_6 & 9p_5 & 0 & 0 & 0 \\ 0 & -\dfrac{3}{2}p_4 & 6p_4 & -\dfrac{9}{2}p_4 - p_6 & 0 & 0 & 0 \\ 0 & p_8 & 0 & 0 & -6p_7 & 6p_7 & 0 \\ 0 & 0 & p_8 & 0 & 9p_7 & -18p_7 & 9p_7 \\ 0 & 0 & 0 & p_8 & -\dfrac{3}{2}p_9 & 6p_9 & -\dfrac{9}{2}p_9 \end{bmatrix} \quad (21)$$

This matrix describes the linear part of equation system 18, which is in turn an approximation of Eqs. 6–10 for a discretization scheme with $N = 3$. $\mathbf{A}(\mathbf{p})$ compiles all the relevant information of the system including the gas–liquid mass transfer process, the irreversible second-order chemical reaction, and the specific hydrodynamic regime in bulk phases (CSTR for both phases), becoming the key element for the structural identifiability analysis.

Finally, different observation matrices $\mathbf{C}(\mathbf{p})$ can be adopted, depending on which state variables defined in the system are accessible by experiments. Of course, the number of available state variables in our system is restricted to those that are macroscopic. The concentration of A or B at the interface or in liquid film will never be available at all because there does not exist such a tiny instrument that is capable of locally measuring these concentrations. Then, by considering Eq. 18, only x_1, x_4, and x_7 are at hand to construct the observation matrices. Identifying x_1 with the concentration of A in the gas phase, and x_4 and x_7 with the concentration of A and B, respectively, in the liquid bulk, all the possible observation matrices describing all the experimental situations, are given by

$$\mathbf{C_I}(\mathbf{p}) = [1 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0] \tag{22a}$$

$$\mathbf{C_{II}}(\mathbf{p}) = [0 \quad 0 \quad 0 \quad 1 \quad 0 \quad 0 \quad 0] \tag{22b}$$

$$\mathbf{C_{III}}(\mathbf{p}) = [0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 1] \tag{22c}$$

$$\mathbf{C_{IV}}(\mathbf{p}) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} \tag{22d}$$

$$\mathbf{C_V}(\mathbf{p}) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{22e}$$

$$\mathbf{C_{VI}}(\mathbf{p}) = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{22f}$$

$$\mathbf{C_{VII}}(\mathbf{p}) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{22g}$$

where $\mathbf{C_I}(\mathbf{p})$, $\mathbf{C_{II}}(\mathbf{p})$, and $\mathbf{C_{III}}(\mathbf{p})$ correspond to experiments where single measurements of $y_A(t)$, $C_A^b(t)$, and $C_B^b(t)$ are carried out separately. $\mathbf{C_{IV}}(\mathbf{p})$, $\mathbf{C_V}(\mathbf{p})$, and $\mathbf{C_{VI}}(\mathbf{p})$ correspond to experiments where two state variables are simultaneously measured, corresponding to the pairs $[y_A(t), C_A^b(t)]$, $[y_A(t), C_B^b(t)]$, and $[C_A^b(t), C_B^b(t)]$, and the last observation matrix (Eq. 22g) corresponds to the case where $y_A(t)$, $C_A^b(t)$, and $C_B^b(t)$ are measured simultaneously.

Once the mathematical model is built (Eq. 18) and the observation matrices defined, it is possible to perform the identifiability analysis restricted to the linear part of the model (Eqs. 3a–3c) for each of the matrix Eqs. 22a–22g. First, we will proceed to analyze the gas–liquid transfer process without chemical reaction and, afterward, with chemical reaction in the slow and in the fast kinetic regimes.

Results

Gas–liquid mass transfer without chemical reaction

The simplest case to be analyzed is the physical process of the mass transfer from the gas to the liquid phase. Considering the general model given by Eqs. 11–16, this is done by simply considering $p_6 = p_8 = 0$. Moreover, there is no reacting species B on the liquid and, then, the number of state-space variables is considerably reduced to $N + 1$. Consider the smallest number of layers satisfying the discretization scheme, that is, $N = 3$. In this situation, the model is reduced to

$$\begin{cases} \dot{x}_1 = \dfrac{p_1}{p_2 - 1} U(t) - \dfrac{p_1}{p_2} x_1 - 3p_3p_4 \\ \qquad \times \left(3x_1 - 4x_2 + x_3\right) - \dfrac{p_1}{p_2} \dfrac{x_1^2}{p_2 - x_1} \\ \dot{x}_2 = 9p_5(x_1 - 2x_2 + x_3) \\ \dot{x}_3 = 9p_5(x_2 - 2x_3 + x_4) \\ \dot{x}_4 = -\dfrac{3}{2} p_4(x_2 - 4x_3 + 3x_4) \end{cases} \tag{23}$$

Comparing this model with the Eq. 1 system and considering that the observable magnitudes of the system are $y_A(t)$ or $C_A^b(t)$, the perturbation vector $\mathbf{B}(\mathbf{p})$, and all the possible observable matrices $\mathbf{C}(\mathbf{p})$ are given by

$$\mathbf{B}(\mathbf{p}) = \begin{bmatrix} \dfrac{p_1}{p_2 - 1} & 0 & 0 & 0 \end{bmatrix}^T \tag{24}$$

$$\mathbf{C_I}(\mathbf{p}) = [1 \quad 0 \quad 0 \quad 0] \tag{25}$$

$$\mathbf{C_{II}}(\mathbf{p}) = [0 \quad 0 \quad 0 \quad 1] \tag{26}$$

$$\mathbf{C_{III}}(\mathbf{p}) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \tag{27}$$

Additionally, the $\mathbf{A}(p)$ matrix is

$$\mathbf{A}(\mathbf{p}) = \begin{bmatrix} -\dfrac{p_1}{p_2} - 9p_3p_4 & 12p_3p_4 & -3p_3p_4 & 0 \\ 9p_5 & -18p_5 & 9p_5 & 0 \\ 0 & 9p_5 & -18p_5 & 9p_5 \\ 0 & -\dfrac{3}{2}p_4 & 6p_4 & -\dfrac{9}{2}p_4 \end{bmatrix} \tag{28}$$

The resulting matrix equations (Eqs. 3a–3c) for the equation system 23 were solved after Chapman et al.,[21] giving the following result:

$$\mathbf{T} = \begin{bmatrix} \mathbf{1} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{1} \end{bmatrix} = \mathbf{1} \tag{29a}$$

$$p_1 = q_1 \qquad p_2 = q_2 \qquad p_3 = q_3 \qquad p_4 = q_4 \qquad p_5 = q_5 \tag{29b}$$

This result is independent of the used observation matrices of Eqs. 25, 26, or 27. Thus, the dynamic gas–liquid film model for mass transfer process without chemical reaction in a CSTR, such as that described by equation system 23, is *structurally globally identifiable*.

As we have previously noted, the number of slabs used in the discretization of the film could have some effect on this analysis. Then, repeating the analysis for $N = 4$ and $N = 5$ gives, in both cases, the unity matrix for $\mathbf{T}$ simultaneously with the result (Eq. 29b). Then, by inference, it is expected that the system remains structurally globally identifiable for any $N \in \mathbb{Z}$.

Recalling the definition of p_1–p_5 (see Eqs. 17a–17e), the precedent analysis could be interpreted such that a particular input–output response of the model is given only by a unique vector parameter $\mathbf{p} = [p_1, p_2, p_3, p_4, p_5]$. Thus, if a parameter vector is obtained after fitting the experimental data to the model Eq. 23, we are certain that no other possible combination of parameters will give the same response. Additionally, Eqs. 29a and 29b imply that only some groups of constants in the model could be determined by fitting. Because the operation magnitudes such as P, T, V, and F_i are previously known to the experiment, after fitting the data to the model to obtain p_1 to p_5, it is possible to calculate the gas holdup ε, from p_1 and p_2, and the Henry constant H, from p_3.

These parameters refer to stationary properties of the reactor but the dynamical ones are determined from p_4 and p_5. Recall that p_4 should be identified with the global mass transfer coefficient k_La. A less common parameter that arises from this analysis is the parameter p_5. To our knowledge, this parameter does not appear in classical texts concerning the gas–liquid mass transfer processes. The mathematical model studied here includes the macroscopic modeling of the reactor, where k_La quantifies the mass transfer rate once the steady state has been reached. However, because our model is essentially nonstationary it includes a second time constant, p_5^{-1}, which accounts for the mass transport rate of A across the diffusion layer of thickness δ. Let us call this constant *diffusion time constant*, $\tau_{\delta i} = \delta^2/D_i$, which refers to the substance i through its diffusion coefficient. This kind of time constants appears commonly in solving nonstationary problems related to heat conduction or diffusive transport across semi-infinite plates and membranes.[26,27] These constants involve diffusion constants and the thickness of the diffusion space and, as previously shown, cannot be uncoupled from each other when this class of experiments is carried out. Thus, determination of diffusion coefficients of soluble gases in liquids—when the film model is used to explain the experimental data—is not allowable because this magnitude is always linked to the film thickness.

Another result that can be derived from Eq. 29b is that the global mass transfer coefficient, k_La, cannot be split into its component parts, k_L and a. Such components cannot be obtained by direct combination of the identified parameters $\mathbf{p}$, which means that k_L and a cannot be uncoupled.

Because this last assertion results after the parameter definition given by Eqs. 17a–17i, let us consider an alternative and more robust demonstration of the impossibility of uncoupling the mass transport coefficient k_L and the specific interfacial area a. First, let us define the parameters in an alternative way:

$$p_1 = \frac{1-\varepsilon}{\varepsilon} \qquad p_2 = H \qquad p_3 = D_A \qquad p_4 = \delta \qquad p_5 = a \tag{30}$$

with a set of known constants:

$$K_1 = \frac{RT}{PV}\frac{F_i}{y_{A0}} \qquad K_2 = y_{A0}^{-1} \qquad K_3 = \frac{1}{2}RT \tag{31}$$

Rewriting matrix Eqs. 24 and 28 and solving the matrix Eqs. 3a–3c, the following result is obtained for each of the observation matrices defined by Eqs. 25–27:

$$\mathbf{T} = \begin{bmatrix} \mathbf{1} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{1} \end{bmatrix} = \mathbf{1} \tag{32a}$$

$$p_1 = q_1 \qquad p_2 = q_2 \qquad \frac{p_3}{p_4^2} = \frac{q_3}{q_4^2} \qquad p_4p_5 = q_4q_5 \tag{32b}$$

The meaning of Eq. 32b is that p_1 and p_2 could be independently determined from experimental data, whereas p_3, p_4, and p_5 could not be evaluated separately. Only the parameter groups p_3/p_4^2 and $p_4 \cdot p_5$ could be determined from experimental data. Note that these groups give the diffusion time constant of A and the ratio between the quiescent liquid film volume and the reactor volume:

$$\frac{p_3}{p_4^2} = \frac{D_A}{\delta^2} \equiv \tau_{\delta A}^{-1} \qquad p_4p_5 = \delta a \tag{33}$$

The importance of the last group will be discussed in detail later when chemical reactions are considered. In conclusion, analysis of the model with the parameters defined according to Eq. 30 leads to the same conclusive result about k_L and a: these parameters cannot be uncoupled. Again, the knowledge of the film thickness or the specific interfacial area could decouple the parameters, allowing their determination from experimental data. However, these magnitudes are not accessible or derivable after the measurement of the state variables of the system, that is, the macroscopic concentrations of chemical species; they should then be evaluated using alternate experimental techniques.

A partial conclusion of this work, then, is that the measure of the dynamics of the mass transfer process in the absence of chemical reactions allows us to determine all the parameters defined by Eqs. 17a–17i. When pure gas–liquid mass transfer applies, the measurable magnitudes will be $y_A(t)$, $C_A^b(t)$, or a combination of both. By fitting the observed magnitudes to a model such as Eq. 23 by increasing the number of layers in the liquid film ($N > 3$), the asymptotic values of ε, H, k_La, and $\tau_{\delta A}$ could be calculated. These

parameters will depend only on the hydrodynamic conditions in the reactor and then, if they remain unchanged, we will expect that the presence of a chemical reaction does not have any effect on these parameters.

Gas–liquid mass transfer with chemical reaction

In this work the identifiability analysis of model Eqs. 11–16 concerns the analysis of the linear part of the system given by Eqs. 3a–3c. Calculation of the matrix **T** implies the solution of a set of nonlinear algebraic equations given by Eq. 3c and, thus, its solution depends on the complexity of the matrix $\mathbf{A}(\mathbf{p})$; that is, the presence of algebraic terms instead of constant ones in the diagonal of the matrix, the range of the matrix, or the number of unknown parameters to be determined. The inclusion of the chemical reaction at the liquid film and in the bulk as previously described, makes this analysis difficult. Consider, then, some limiting cases that simplify the matrix $\mathbf{A}(\mathbf{p})$.

By inspecting Eq. 21 we can deduce the existence of the matrix element $-2N^2p_5 - p_6$ at the upper half of $\mathbf{A}(\mathbf{p})$, which in turn describes the behavior of the reactive gas in the system. Here, for convenience, we have considered the general term instead the particular one with $N = 3$. Neglecting $2N^2p_5$ against p_6, it is possible to switch from a fast chemical reaction to a slow one. In fact, the ratio between p_6 and p_5 gives the square of the well-known Hatta (Ha) modulus for a global second-order chemical reaction:

$$\frac{p_6}{p_5} = \frac{\delta^2 k_2}{D_A} C_{B0}^b = \mathrm{Ha}_2^2 \tag{34}$$

This quantity gives us the maximum conversion of the chemical reaction compared with the mass transport through the film.[28,29] This adimensional number appears here logically: just considering the dynamic gas–liquid film discretized model such as a compartmental model where the sink terms are associated with mass transport or chemical reactions and, then, the mass depletion in each compartment is the result of the competition between both processes. Thus, considering the classical values of Ha for fast or slow chemical reactions in gas–liquid systems, simplification of the diagonal terms in matrix Eq. 21 is viable.

Nevertheless, the preceding reasoning is partial and, in our opinion, an additional condition is required to distinguish between fast or slow chemical reactions. As stated earlier, a microscopic modeling of the gas–liquid mass transfer at the interface level together with a macroscopic modeling of the mass balance of the whole reactor should be considered for a complete description of our system. Equation 34 is a condition that affects the model just at the microscopic level and, thus, another condition should be imposed from a macroscopic perspective. Notice the component a_{44} in matrix $\mathbf{A}(\mathbf{p})$ (see Eq. 21). In our case with $N = 3$, the fourth row corresponds to the differential equation describing the concentration evolution of the reactive gas in the liquid bulk, a "macroscopic " state-space variable. Because its value is the result of competition between the gas–liquid mass transfer process and the rate of the chemical reaction, the macroscopic criterion to distinguish between the fast or the slow chemical reaction could be given by

$$\frac{p_6}{p_4} = \frac{k_2 C_{B0}^b}{k_L a} = \frac{\mathrm{Ha}_2^2}{a\delta} \tag{35}$$

Note that the numerator of Eq. 35 gives the chemical reaction rate in the liquid bulk, whereas the denominator gives the gas–liquid mass transfer rate observed macroscopically at the reactor. This number give us the ratio between the rate at which A disappears in the liquid bulk by chemical reaction and the rate at which disappears from the gas phase by physical transfer to the liquid. Finally, by combining Eqs. 34 and 35, the ratio between the total volume of liquid in the liquid film and the total liquid volume in the reactor is obtained:

$$\frac{p_4}{p_5} = a\delta = \frac{\text{volume of the liquid film}}{\text{volume of the liquid in the reactor}} \tag{36}$$

This number is always a very small quantity because the liquid film volume is smaller than that of the reactor. Then, the relation $p_4 \lll p_5$ is always accomplished.

Considering these criteria, the objective in the next sections is to show which state variables should be measured to obtain the maximum information of our system when an irreversible chemical reaction holds. In the context of this paper, after inspecting Eqs. 35 and 36, a slow chemical reaction is a chemical reaction that accomplishes the following condition:

$$2N^2p_5 \gg \frac{3N}{2} p_4 \gg p_6 \tag{37}$$

The two first terms of the inequality are always in this order by Eq. 36, and the last inequality expresses that the reaction rate is less than the mass transfer process (see Eq. 35). Conversely, we define a fast chemical reaction as that which achieves the following condition:

$$\frac{3N}{2} p_4 \ll 2N^2p_5 \ll p_6 \tag{38}$$

The last two equations will be useful to simplify the matrix $\mathbf{A}(\mathbf{p})$ (Eq. 21) and the calculations in solving the system given by Eqs. 3a–3c.

Slow Chemical Reaction: $2N^2p_5 \gg (3N/2)p_4 \gg p_6$. According to Eqs. 34 and 35, a chemical reaction could be considered slow when it is coupled with a gas–liquid mass transfer and the condition in Eq. 37 holds. In this case, the matrix $\mathbf{A}(\mathbf{p})$ can be written as

$$\mathbf{A}(\mathbf{p}) = \begin{bmatrix} -\frac{p_1}{p_2} - 9p_3p_4 & 12p_3p_4 & -3p_3p_4 & 0 & 0 & 0 & 0 \\ 9p_5 & -18p_5 & 9p_5 & 0 & 0 & 0 & 0 \\ 0 & 9p_5 & -18p_5 & 9p_5 & 0 & 0 & 0 \\ 0 & -\frac{3}{2}p_4 & 6p_4 & -\frac{9}{2}p_4 & 0 & 0 & 0 \\ 0 & p_8 & 0 & 0 & -6p_7 & 6p_7 & 0 \\ 0 & 0 & p_8 & 0 & 9p_7 & -18p_7 & 9p_7 \\ 0 & 0 & 0 & p_8 & -\frac{3}{2}p_9 & 6p_9 & -\frac{9}{2}p_9 \end{bmatrix} \tag{39}$$

The first four rows of this matrix account for the reactive gas A, and the last three, for the solute B (see Eq. 18). The only chemical kinetic parameter appearing in this matrix is p_8, whereas the others are related to mass transfer and mass transport processes through the interface. The structure of this matrix agrees with the fact that for a slow chemical reaction, this process takes place only in the liquid bulk and not in any place of the film.[28,29]

Additionally, let us consider that p_2 is known. This is not unreasonable provided that this parameter is simply related with the concentration of the reactive gas at the input of the CSTR (see Eq. 17b) and that this kind of magnitude is usually well known by the experimenter. By solving the matrix Eqs. 3a–3c using Eqs. 20, 22, and 39, it can be concluded that the system is *structurally globally identifiable* when matrices $\mathbf{C_V}(\mathbf{p})$, $\mathbf{C_{VI}}(\mathbf{p})$, or $\mathbf{C_{VII}}(\mathbf{p})$ are given to describe the experimental observations. These matrices are those that include one state variable of each substance, that is, A and B, taking place in the chemical reaction. One consequence of this result is that the parameters p_1–p_9 can be uniquely determined in a CSTR when a slow chemical reaction proceeds simultaneously with the transfer process. Then, magnitudes such as the gas holdup ε, the Henry constant H, the mass transfer coefficient k_La, the diffusion time constant $\tau_{\delta A}$, and the chemical kinetic constant k_2 could be calculated uniquely and simultaneously.

Furthermore, this result implies that parameters such as p_7, p_8, and p_9, which include transport properties of the solute B through the double layer, are accessible from the experimental observations. The parameter p_4 gives the global mass transfer coefficient of the reactive gas A that, by definition, is related to the diffusion constant D_A. The parameter p_9 is, by definition, similar to p_4 but here the diffusion coefficient refers to the substance B. Then, the physical meaning of this parameter is not related to the gas–liquid mass transfer, but with the mass transfer of B from the liquid bulk. By labeling ξ as the ratio of both diffusion coefficients, $\xi = D_B/D_A$, we have

$$p_7 = \xi p_5 \tag{40a}$$

$$p_9 = \xi p_4 \tag{40b}$$

Because the ratio p_7/p_5 can be obtained from experiments, the diffusion coefficient of A or B can then be calculated irrespective of whether either of the diffusion coefficients is known. Nevertheless, the diffusion coefficients of the substances reacting in a bubble-column reactor cannot be uncoupled from each other or uncoupled from the liquid film thickness.

Fast Chemical Reaction: $(3N/2)p_4 \ll 2N^2p_5 \ll p_6$. Fast chemical reactions imply that the kinetic constant is sufficiently large to neglect the transport terms in the stagnant film. Here, fast kinetic stands for reactions in which the condition Eq. 38 holds. Then, the $\mathbf{A}(\mathbf{p})$ matrix is written as

$$\mathbf{A}(\mathbf{p}) = \begin{bmatrix} -\frac{p_1}{p_2} - 9p_3p_4 & 12p_3p_4 & -3p_3p_4 & 0 & 0 & 0 & 0 \\ 9p_5 & -p_6 & 9p_5 & 0 & 0 & 0 & 0 \\ 0 & 9p_5 & -p_6 & 9p_5 & 0 & 0 & 0 \\ 0 & -\frac{3}{2}p_4 & 6p_4 & -p_6 & 0 & 0 & 0 \\ 0 & p_8 & 0 & 0 & -6p_7 & 6p_7 & 0 \\ 0 & 0 & p_8 & 0 & 9p_7 & -18p_7 & 9p_7 \\ 0 & 0 & 0 & p_8 & -\frac{3}{2}p_9 & 6p_9 & -\frac{9}{2}p_9 \end{bmatrix} \tag{41}$$

In this matrix, p_6 and p_8 are related with the kinetic constant and, thus, its presence along the matrix has a direct influence on all the state variables except for the one concerning the gas phase, x_1. However, the gas–liquid mass transfer process is

driven to some extent by the chemical reaction that enhances the observable mass transfer coefficient.

Once more, solving the matrix Eqs. 3a–3c using Eqs. 20, 22, and 41, the system is *structurally globally identifiable* when the matrix $\mathbf{C_V}(\mathbf{p})$ or $\mathbf{C_{VII}}(\mathbf{p})$ is given to describe the experimental observations. These matrices are those that consider the measurement of one state variable in each phase and for each substance defined in the system. $\mathbf{C_V}(\mathbf{p})$ implies the measurement of A in the gas phase simultaneously with the measurement of B in the liquid bulk. A fast chemical reaction implies that insignificant or no amounts of A reach the liquid bulk because B is reacting in the solution. Thus, its measurement for instance considering matrices $\mathbf{C_{II}}(\mathbf{p})$, $\mathbf{C_{IV}}(\mathbf{p})$, and $\mathbf{C_{VI}}(\mathbf{p})$—besides the experimental problems associated with extremely low concentrations—will not provide information relevant enough to characterize uniquely the system and to calculate the kinetic constant. On the other hand, with matrices $\mathbf{C_V}(\mathbf{p})$ and $\mathbf{C_{VII}}(\mathbf{p})$ the same parameters obtained with slow kinetics, that is, ε, H, k_La, τ_δ, can be calculated when the chemical reaction progress is almost completely into the liquid film.

Combining absorption data with chemical reaction experiments

In the preceding identifiability analysis we have always tried to keep the highest possible number of unknown parameters in the model. One question that arises from the study of gas–liquid systems is whether the chemical reaction itself can have an effect on physical parameters such as ε, H, or k_La. To answer this question, it is compulsory to determine the parameters under study both with and without chemical reaction. First, however, the identifiability analysis should elucidate whether such parameters are uniquely related to the output of the system.

Moreover, the analysis has been done considering a concrete experimental design, that is, the simultaneous measurement of a system's state variables in a single nonstationary experiment. In this section, another experimental design will be considered in an attempt to reduce the complexity of the experiments that should be carried out to determine the parameters. The new strategy consists in combining results of previous reactions.

First, consider an absorption experiment without chemical reaction where the simplified model described earlier is appropriate. By measuring gas A at the outlet of the reactor or in the liquid bulk, it will be possible to determine the parameters p_1 to p_5. Now assume the hypothesis that these parameters remain invariable when a chemical reaction happens in the reactor. Then, a new series of experiments will be required to obtain parameters p_6 to p_9. Again we have the matrices $\mathbf{C_I}$–$\mathbf{C_{VII}}$ to characterize these new experiments. Because the number of unknown parameters has been drastically reduced, let us consider the general case without any a priori assumption about the rate of the chemical reaction.

Using the matrix $\mathbf{A}(\mathbf{p})$ written as Eq. 21 and considering that p_1–p_5 are known, the system is *structurally globally identifiable* when observation matrices $\mathbf{C_V}(\mathbf{p})$, $\mathbf{C_{VI}}(\mathbf{p})$, and $\mathbf{C_{VII}}(\mathbf{p})$ are given to describe the experimental observations. Once more, the system is globally identifiable if measurements of state variables concerning each substance involved in the chemical reaction are done. In these circumstances the parameters p_6 to p_9 are uniquely identified, which include the kinetic rate constant and the diffusion constant of B in the film. Again, we should recall the definitions of the parameters to notice how they are linked with each other. For example, the diffusion coefficient of B cannot be uncoupled from the film thickness and the kinetic rate constant from the initial concentration of A or B in the bulk solution (see Eqs. 17f–17i).

Finally, let us consider a more specific situation. Suppose that in our experiment we still know p_1–p_5 and we just measure the concentration evolution of B in the bubble-column reactor. The identifiability analysis allows us to determine in which conditions it is possible to obtain relevant information of the system. Let ρ be the ratio of the equilibrium concentration of A and the initial concentration of B in the reactor:

$$\rho = \frac{C^*_{A0}}{C^b_{B0}} = \frac{p_8}{p_6} \tag{42}$$

If ρ and ξ are known, then the system is *structurally globally identifiable* when matrices $\mathbf{C_{II}}(\mathbf{p})$, $\mathbf{C_{III}}(\mathbf{p})$, $\mathbf{C_{IV}}(\mathbf{p})$, $\mathbf{C_V}(\mathbf{p})$, $\mathbf{C_{VI}}(\mathbf{p})$, and $\mathbf{C_{VII}}(\mathbf{p})$ are considered to describe the experimental observations. Notice that $\mathbf{C_{III}}(\mathbf{p})$ is the situation described above: the only observed state variable is the concentration of B in the liquid bulk. In this situation the sole parameter of the system to be calculated is the parameter p_6, which is related to the kinetic rate constant. So, we can conclude that the kinetic rate constant of the chemical reaction occurring in a gas–liquid reactor is accessible when the concentration of only one species involved in the reaction is measured, and if and only if the ratio of diffusion constants and initial concentrations, ξ and ρ, are respectively known. Knowledge of these parameters is not always possible or even accurate, leading to an erroneous determination of the kinetic constants. Furthermore, considering a few observation matrices, that is, $\mathbf{C_{VII}}(\mathbf{p})$ or $\mathbf{C_V}(\mathbf{p})$, they involve complex experimental procedures where two or more state variables should be simultaneously measured in both the gas and liquid phases. All this leads us to conclude that the single measurement of the concentration depletion of substance B in the liquid phase is insufficient to characterize a gas–liquid process coupled with a chemical reaction. Note that in these circumstances eight of nine parameters should be known before the experiment and, then, only one will be computable afterward.

Discussion

The analysis carried out in the previous section shows the main features of the identifiability analysis: it provides better knowledge about the significance of the parameters and their relationship in a particular model structure and gives us useful information about parameter determination for an appropriate experimental design. Thus, the analysis developed earlier reveals that the unsteady two-film model without chemical reaction needs almost two time constants for the dynamic description of the gas–liquid mass transfer process, whereas classical theories make use of one: the global mass transfer coefficient. Keep in mind that in the classical two-film model, the concentration profiles are obtained considering a steady state for stagnant films close to the interface.[29] Thus, the constant times associated with mass transport inside the liquid film are hidden from the model when the steady-state simplification step is

Table 1. Observation Matrices (22) Satisfying the Structurally Globally Identifiable Condition (SGI) for the Gas–Liquid Dynamic Film*

Case	Parameters** Known	Parameters** Unknown	SGI Condition	Physical Parameters†
No chemical reaction	—	p_1–p_5	$\mathbf{C_I}$, $\mathbf{C_{II}}$, $\mathbf{C_{III}}$††	ε, H, y_{A0}, k_La, $\tau_{\delta A}$
Slow chemical reaction	p_2	p_1–p_9	$\mathbf{C_V}$, $\mathbf{C_{VI}}$, $\mathbf{C_{VII}}$	ε, H, k_La, $\tau_{\delta A}$ k_2, $(D_B/\delta)a$, $\tau_{\delta B}$
Fast chemical reaction	p_2	p_1–p_9	$\mathbf{C_V}$, $\mathbf{C_{VII}}$	ε, H, k_La, $\tau_{\delta A}$ k_2, $(D_B/\delta)a$, $\tau_{\delta B}$
General chemical reaction	p_1–p_5	p_6–p_9	$\mathbf{C_V}$, $\mathbf{C_{VI}}$, $\mathbf{C_{VII}}$	k_2, $(D_B/\delta)a$, $\tau_{\delta B}$
	p_1–p_5, ρ, ξ	p_6	$\mathbf{C_{II}}$, $\mathbf{C_{III}}$, $\mathbf{C_{IV}}$ $\mathbf{C_V}$, $\mathbf{C_{VI}}$, $\mathbf{C_{VII}}$	k_2

*The last column collects the physical parameters that can be derived after fitting the data to the model.
**See Eqs. 17a–17i.
†See the text for definitions.
††These matrices are defined after Eqs. 25–27.

applied. Moreover, it was shown earlier that the presence of a chemical reaction leads to consideration of new time constants associated with diffusive transport of the reacting species in the liquid film (see Eqs. 17g and 17i). These groups of parameters show the coupling between the diffusion coefficient of B and the liquid film thickness and the need for a dynamic description of the bubble-column reactor.

Another characteristic that differentiates our analysis from classical ones is that the time base used to integrate the ODEs describing the bubble-column reactor is the same both for the liquid film and the global reactor. In classical models, the equations governing the dynamics of the interface are solved first and, then, this solution is used to establish the mass balance equations of the chemical reactor. These two steps normally imply two bases of time, one for the liquid film and the interface, another for the chemical reactor. This dissociation could not be physically justified because all the processes are concurrent at both the microscopic level (liquid film) and the macroscopic level (reactor). Thus, by using the dynamic film model, this problem is avoided.

Furthermore, two aspects should be considered before carrying out the structural identifiability analysis of a model: which types of data are available to fit the model and which parameters could be considered unknown in the model. In this work, it has been considered that the data were provided by a semibatch bubble-column reactor. Because of its nonstationary character, only the concentration evolution of the species defined in the model is a valid observable of the system. Once we have a set of candidate observable variables, the model is built by grouping constants and parameters, with consideration of which ones we want to calculate from experimental data. In particular, although in our case the diffusion coefficients D_A and D_B appear in the model, they were maintained grouped with the film thickness δ, and the specific interfacial area a, to give the global mass transfer coefficient k_La, or the film diffusion-time constants t_δ: first, because they appear logically when the model is built; second, because the film thickness of the model is also unknown; and, finally, because it simplifies the computational calculus. Nevertheless, whenever the parameters of the model are maintained ungrouped, the structural identifiability analysis can inform us as to how they are related internally and how they can be determined, although at the expense of increasing computing time.

In this work, the impossibility of uncoupling k_La into its constituents has also been demonstrated, even when experiments with or without chemical reactions are combined. This result disagrees with the classical procedures—that is, the Danckwerts-plot method—based on fast chemical reactions to determine simultaneously the mass-transfer coefficient and the interfacial area of gas–liquid equipment.[30] Danckwerts' method is based on measurement of the rate of absorption of a gas in the presence of a fast chemical reaction. Plotting the gas-absorption rate against the kinetic rate constant, the values of k_L and a can be determined simultaneously.[31-34]

Danckwerts' approach is based on the stationary solution of Eqs. 6–10 with stationary boundary conditions, whereas in this work the system is nonstationary by definition. So, neither the solution of the equations nor the data obtained in experiments can be compared to each other. However, that does not justify the discrepancy between these two mathematical models. They are based on the same physical principles and the parameters k_L and a have the same physical meaning. If in one of the models both parameters could be decoupled, the same results should be retrieved in the other. Although the criteria to apply Danckwerts' method have recently been revised by Cents et al.,[31,32] the same authors show experimental evidences on the discrepancy between a measured by chemical methods (CO_2 absorption in CO_3^{2-}/HCO_3^- solutions) or measured by physical methods (ultrasounds). In our opinion, these discrepancies could have their origin in the impossibility of uncoupling k_L and a, thus inducing a systematic error in Danckwerts' methodology.

Additionally, it has been demonstrated that for a unique determination of all the model parameters, it is necessary to simultaneously measure concentrations in both the liquid phase and the gas phase. In Table 1 these results are summarized, showing which observation matrix makes the system structurally globally identifiable, and which parameters can be uniquely identified in the model. Let us consider a particular example such as the matrix $\mathbf{C_V}(\mathbf{p})$ for slow or fast chemical reactions. This matrix implies the determination of A in the gas phase and B in the liquid phase. In a previous work, Abad et al.[35] showed the problems and how to correct systematic errors associated with dynamic measurements when continuous-flow analysis techniques are used in bubble-column reactors. Although only the liquid bulk is considered in that work, similar corrections should be applied to the gas phase mainly to correct the dilution effect arising from the gas chamber at the reactor's overhead and the dispersion phenomena to the detector, if any.

Thus, analysis of the model imposes a specific experimental setup that implies not only the simultaneous measurement of two magnitudes [three if $\mathbf{C_{VII}(p)}$ is considered] but also a few postprocessing procedures to modify the raw experimental data to obtain the true observable state variables defined in the model.

Finally, a comment is required about the observation matrices that do not appear in Table 1. The weakest point in our analysis is the use of built-in routines existing in symbolic algebra software (such as Maple® or Mathematica®) to solve the matrix Eqs. 3a–3c. This equation implies the resolution of a set of nonlinear polynomial equations that are usually solved using the Gröbner-bases method.[15] From an engineering perspective, these computer algorithms are commonly used (such a "black box ") where the details of their machinery do not matter but results do. Then, when these algorithms do not converge in a solution, for instance, because the computer is overloaded on its calculation capacity, different analytical or semianalytical mathematical procedures should be considered to solve the linear part of the identifiability analysis. Therefore, after the results collected in Table 1 we can guarantee that the model is structurally globally identifiable for the observable matrices of the table, but nothing about the absent ones can be ensured.

Conclusions

The structural identifiability analysis applied to the dynamic gas–liquid film model allows identification of the relevant parameters in the model and how they are related. The information about the model structure provided by the analysis can be used in the design of experiments oriented toward determining the parameters of the model. Considering a nonstationary semibatch bubble column, where a gas stream containing A bubbles in a liquid phase containing the reactive solute B, it has been demonstrated that the parameters that define the dynamic behavior of the macroscopic observable concentrations are: (1) the gas holdup, ε; (2) the Henry's constant, H; (3) the global mass transfer with respect to A, $k_L a$; (4) the diffusion-time constant of A, $\tau_{\delta A}$; (5) the kinetic rate constant, k_2; (6) the global mass transfer with respect to B, $D_B/\delta a$; and (7) the diffusion-time constant of B, $\tau_{\delta B}$. It has also been demonstrated that these parameters cannot be uncoupled in its constituents and so, neither the diffusion coefficients D_A or D_B nor the specific interfacial area a could be determined with this kind of experiments.

After the identifiability analysis it can also be concluded that the equations concerning the gas–liquid contactor must be included together in the physicochemical model for the mass transfer process. Because the observable magnitudes are macroscopic, averaged on the entire space defined by the contactor, the model should include this characteristic. The precedent analysis has shown that the coupling between the macroscopic and the microscopic modeling of the CSTR bubble column and the transfer mass process allows us to define the diffusion-time constants $\tau_{\delta A}$ and $\tau_{\delta B}$, which do not appear in classical steady-state models in the modeling of gas–liquid mass transfer processes.

The impossibility of calculating the specific interfacial area of a gas–liquid contactor from dynamical experiments has been discussed comparing the classical results predicted from the Danckwerts' plot. The different nature of both experiments, nonstationary and stationary, respectively, causes this apparent contradiction. To apply Danckwerts' method, the kinetic constant of the chemical process should be known and, as has been demonstrated in this work, it could be determined only by a proper experimental design in a nonstationary gas-bubble column reactor.

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Notation

a = interfacial specific area, S/V, m^{-1}
C_i = molar concentration of i in the liquid phase, mol m^{-3}
C^*_{A0} = saturation concentration of A in the liquid, $y_{A0}(P/H)$, mol m^{-3}
D_i = diffusion coefficient of i, m^2 s^{-1}
F_i = flow rate of inert gases at the inlet, mol s^{-1}
H = Henry constant, Pa m^3 mol^{-1}
Ha_2 = Hatta modulus for a second-order chemical reaction, $\sqrt{(\delta^2 k_2/D_A)C^b_{B0}}$
k_2 = second-order reaction rate constant, m^3 mol^{-1} s^{-1}
$k_L a$ = global mass transfer of A
N = number of equally spaced grid points dividing the interval $[0, \delta]$
P = pressure, Pa
R = universal gas constant, 8.13 J K^{-1} mol^{-1}
S = exchange interfacial surface, m^2
T = temperature, K
$U(t)$ = unit step function (0 for $t \leq 0$; 1 for $t > 0$)
V = volume of the liquid phase in the reactor, m^3
x_i = dimensionless concentration at the ith interval (see text for details)
y_i = molar fraction of i in the gas phase

Greek letters

δ = bubble quiescent liquid film thickness, m
ε = reactor gas holdup
ρ = ratio of initial molar concentrations, C^*_{A0}/C^b_{B0}
$\tau_{\delta i}$ = diffusion-time constant, δ^2/D_i, s
ξ = ratio of diffusion coefficients, D_B/D_A

Subscripts and superscripts

A = gas substance soluble in the liquid phase
B = nonvolatile solute in the liquid phase
b = bulk of the liquid phase
0 = reactor inlet (gas phase) and/or initial concentration (liquid phase)

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