Enhancement of time resolution in transient kinetics

Soheil Soltani, Ronnie Andersson, Bengt Andersson *

Competence Centre for Catalysis, Chemical and Biological Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

HIGHLIGHTS

- Enhancement of temporal resolution in the transient response of a reactive system.
- Description of an algorithm for deconvolution of a distorted concentration signal.
- Basics of regularization theory for inverse problems in heterogeneous catalysis.
- Deviations from the Beer–Lambert law and the consequent error in transient kinetics.

ARTICLE INFO

ABSTRACT

A methodology for enhancement of time resolution in transient experiments has been formulated where the mathematical background of the deconvolution problem is outlined. The analysis leads to an algorithm based on the discrepancy principle for calculation of the regularization parameter, which exhibits satisfactory convergence and can successfully handle the noise that is present in the original measurements. Application of the algorithm for different synthetic datasets has shown that the extent of enhancement in time resolution depends on the broadening function and the sampling frequency of the detector. Consequently, shorter residence times and higher sampling frequencies are in general desirable.

The impact of deviations from the Beer–Lambert law in Fourier-transform infra-red spectroscopy has also been evaluated using computational fluid dynamics simulations. The flow field and concentration distribution in a gas cell with ∼5 m optical pathlength have been simulated, and the absorbance–concentration correlations have been implemented in the analysis. Carbon monoxide and nitric oxide have been chosen as species with significant nonlinear infra-red absorption features, and their mixtures with different concentrations have been considered in separate simulations. Due to the nonlinear characteristics of the problem, various levels of error have been observed in the results, which are dependent on the concentration at the inlet of the gas cell and the gas phase species as well.

The variance of concentration distribution normalized with mean squared concentration has been defined as a measure of intensity of segregation, which displays strong similarity for the same flow field pattern and relatively close molecular diffusivities.

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1. Introduction

Transient kinetic methods are important tools in heterogeneous catalysis for studying the mechanistic features of a reactive system, which provide valuable information that is often impossible to be deduced from steady state measurements. This is due to the fact that all the elementary steps proceed at the same rate at steady state. In transient experiments, however, the system is driven out of its equilibrium state by using a known perturbation, and the dynamic response of the system is monitored as a function of time. As a result, plausible reaction pathways can be proposed, the corresponding kinetic parameters can be obtained, unlikely mechanisms can be rejected, and the existence of intermediates can be investigated. Kinetic models that are formulated based on transient studies can be used for simulating both the dynamic and steady state operation of the reactor, and the results can be more trustfully extrapolated beyond the studied ranges [1].

Hydrodynamic dispersion results in signal distortion, which has been considered to be a major limitation of transient techniques [2]. Particularly, in laboratory setups with predominant laminar flow the time scale of the dispersion effects is in fact comparable with that of the kinetic processes. In addition to heterogeneous catalysis, a fairly high time resolution is essential in dynamic

* Corresponding author. Tel.: +46 31 772 30 26.
  E-mail address: bengt.andersson@chalmers.se (B. Andersson).

Nomenclature

A	absorbance [–]		z	reconstructed signal [arb. u.]
a	absorption coefficient [1/m]		$\bar{z}$	exact solution [arb. u.]
C	concentration [ppm]			
G	operator matrix of the kernel [–]		*Greek letters*	
I	radiation intensity [W/sr]		α	regularization parameter [–]
K	kernel, transfer function [arb. u.]		ε	molar absorptivity [1/m]
$\vec{r}$	position vector [m]		δ	error in the measured signal [arb. u.]
$\vec{s}$	direction vector [m]		v	frequency [Hz]
s	pathlength [m]		ω	under-relaxation factor [–]
t	time [s]		ρ	discrepancy
$\bar{t}$	mean residence time [s]		σ	singular values (see e.g. singular value decomposition)
u	measured signal [arb. u.]		τ	error in the measured kernel [arb. u.]
$\bar{u}$	unperturbed measurements [arb. u.]			
y	mole fraction [–]			

analysis of ultrafast systems as in pulse radiolysis, laser and flash photolysis, where the time scale of the system is in the order of pico- or femtoseconds [3,4]. Therefore, a robust algorithm for enhancement of time-resolution to obtain the undisturbed transient response of a system serves as an indispensable tool for further data analysis. This study aims at providing the mathematical background that is required to solve the consequent deconvolution problem.

Hydrodynamic dispersion in both the reactor setup and the gas cell of a Fourier-transform IR spectrometer (FTIR) has been detailed in an earlier study [5]. Consequently, not only is the transient period of a dynamic experiment distorted by dispersion effects, the systematic error that arises from a nonhomogeneous concentration profile of species with nonlinear IR absorbance during the same time interval has also been pointed out. In the current work, this problem is addressed using computational fluid dynamics (CFD) simulations. Further insights that have been obtained from the numerical analysis of the deconvolution algorithm regarding the impact of mean residence time in the gas cell and sampling frequency of the detector on time resolution are elaborated.

2. Material and methods

2.1. Experimental instrument

The focus of this study is on the gas cell of an FTIR spectroscope (MKS MultiGas 2030, USA) with an optical pathlength of ~5 m. The measured diameter of the inlet and outlet connections is 1.03 cm. The walls of the gas cell are electrically heated and external insulations help maintain a constant temperature of 191 °C throughout the cell. The FTIR's detector provides a sampling frequency of 1 Hz. Fig. 1 shows the exact shape of the cell and its measured dimensions. The setup normally runs at a gas flow rate of 3.5 L/min in order to reduce the time lag of the analyzer.

2.2. Computational model

ANSYS Academic package has been used to formulate and solve the computational model of the gas cell. A three-dimensional model has been created and discretized to about 386,000 computational cells. The cells fulfil a minimum orthogonal quality of 0.18 and an average aspect ratio of 1.8. The transport equations of mass, momentum, species' concentration and energy have been solved using a third order (MUSCL) discretization scheme [6]. Grid-independent solutions were obtained by subsequent, global refinements of an original, coarser mesh with 203,000 elements until no significant changes in the field variables were observed.
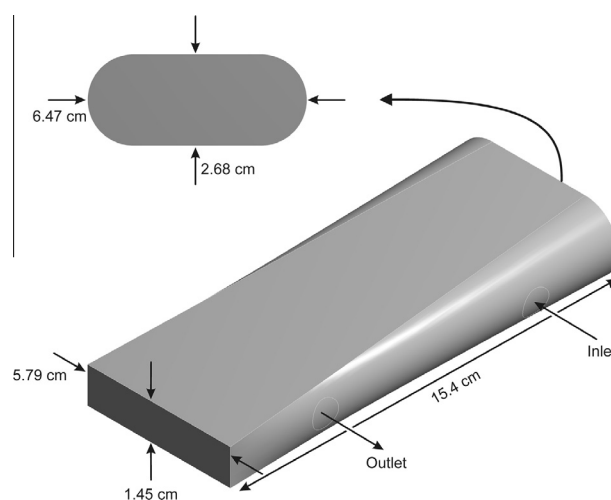

Fig. 1. Geometry and dimensions of the gas cell.

Time-dependent concentration distribution inside the cell has been simulated, and the solutions have been tested to be independent from temporal discretization by refining the time step size down to 0.05 s. At each time step, the mixed-cup concentration of the tracer at the outlet is used to simulate the residence time distribution of the gas cell.

2.2.1. Implementation of the Beer–Lambert law

Quantitative FTIR analysis assumes a linear correlation between the absorbance and concentration of the gas phase species; however, specific molecules like carbon monoxide and nitric oxide are known to exhibit non-linear absorption pattern, and the aforementioned assumption needs to be corrected for these molecules by non-linear regression of calibration data [7]. Nevertheless, a prerequisite for using this correction is a uniform concentration profile throughout the cell as an integrated absorbance is used to predict the concentration. However, this criterion is very likely to be violated during a transient period particularly in laboratory applications, since the rather low flow rate that is used in reactor setups delays mixing in the gas cell [5]. In order to investigate the consequences of deviations from the Beer–Lambert law when a nonhomogeneous concentration distribution pertains in the gas cell, the absorbance–concentration correlations of CO and NO have been implemented in the transient simulations that were described earlier assuming a step-change from zero to a defined concentration dosed at the cell's inlet.