Identifying the scaling parameters of neutral kinetics in DBD plasma atomizers using screening and variance-based sensitivity analysis

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Abstract: This contribution focuses on argon/oxygen/hydrogen plasma kinetics in a DBD-based atomizer intended for hydride production. It aims to identify what are the scaling parameters of neutral species' kinetics in filamentary and homogeneous DBD reactors. We utilize the methods of sensitivity analysis to understand why it seems equivalent to model the neutral species' kinetics in filamentary DBD using homogeneous "effective" electron densities and temperatures.

Keywords: Sensitivity analysis, scaling parameters, atomizer, DBD

1. Introduction

In the recent years, DBD (dielectric-barrier-discharge) plasma reactors have been extensively used in a number of applications, such as plasma catalysis, plasma medicine (especially in jet-like configurations) or plasma polymerization. Using a DBD reactor for hydride production in analytical chemistry is yet another of the many plasma chemical applications of this class of discharges.

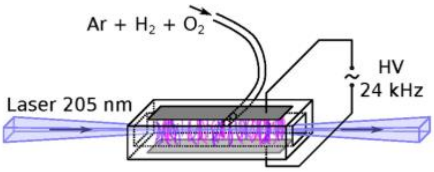

Fig. 1: A schematic view of the DBD plasma atomizer, here shown with the 205 nm laser used for the diagnostics in [1], [2].

It is well known that DBD reactors can operate in two distinct regimes – either as highly-transient filamentary plasma or as a quasi-homogeneous or homogeneous plasma which uniformly fills the entire interelectrode volume [3]. It is obvious that these two discharges are very different from the perspective of plasma dynamics. By analogy, it is often assumed that the either filamentary or homogeneous regime of the discharge has key influence on the neutral kinetics in the plasma, although there have been few systematic studies investigating this assumption.

This research is motivated by our earlier work on DBD plasma atomizers, where we modeled 0D kinetics of the neutral species in the atomizer to support and understand the measurements of atomic oxygen and atomic hydrogen concentration performed by LIF and TALIF techniques.

2. Previous work and motivation

As mentioned in the introduction, we have previously studied the neutral kinetics in the DBD plasma atomizer using LIF and TALIF diagnostics combined with a 0D model of the neutral species kinetics [1], [2]. Despite the fact that the plasma in the DBD atomizer is completely filamentary (filaments are visible not only by short-exposure imaging but also by naked eye), we were able to achieve good agreement between the kinetics model and the experiment when the plasma was modeled as homogeneous with spatially uniform "effective" electron density and temperature. For these "effective plasma properties", we solved the Boltzmann equation for electrons using BOLSIG+ and obtained the reaction rates for all the electron-impact dissociation channels. The reactions for electron-impact dissociation were then added to a kinetic scheme for hydrogen/oxygen combustion retarded by Argon.

Even though the approach that we used for the kinetic simulation is very crude, it yielded surprisingly good agreement with experiment, as illustrated in the figures below.

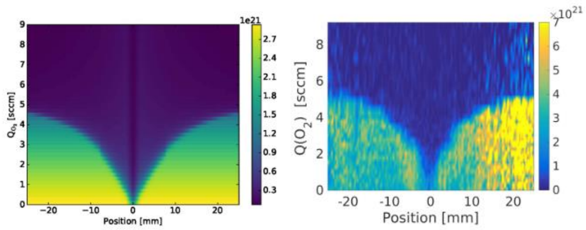

Fig. 2: Comparison of simulated (left) and measured (right) density of atomic hydrogen in the atomizer for argon flow rate of 147 sccm and hydrogen flow rate of 10.3 sccm

This contribution aims to understand why the simulation of uniform DBD plasma with "effective" properties is equivalent to the experiment performed on filamentary DBD plasma. To do so, we are using two methods of sensitivity analysis.

3. Choice of inputs and observables

To understand why it is possible to simulate the highly transient filamentary plasma by uniform plasma with "effective" properties, it is necessary to choose the observables and model inputs properly.

Since we want to consider the plasma a chemical reactor, the investigated output are the fluences of active species leaving the plasma.

We propose to test the sensitivity of these concentrations with respect to the following inputs:

- peak electron density,
- peak electron temperature,
- total energy carried by electrons integrated over discharge volume,
- gas temperature
- pulse duration
- energy per pulse

4. Sensitivity analysis methods

Full factorial approach

The full factorial sensitivity analysis techniques are reviewed for example in [4] and have been used in the field of plasma simulation e.g. [5]. The full factorial method relies on calculation of partial derivatives of each model output with regard to each model input. For instance, let us consider the sensitivity of a model output output y_i to an input x_r. In the full factorial approach, this would be calculated as

$$S_i(x_r) = \frac{x_r}{y_i}\frac{\partial y_i}{\partial x_r}$$

This method has little practical use in models with many inputs, perhaps apart from the fact that it is relatively easy to assess its convergence. The disadvantage is the incapability to predict second-order coupling between the model inputs. This is because the derivatives in equation (1) are calculated at constant values of the other input parameters.

Many better alternatives to the full factorial approach have been developed. There are the so-called *variance-based methods* which enable full exploration of the configuration space at the expense of a large number of required model evaluations. The second alternative is the class of so-called *screening methods* which do not quantify sensitivity exactly and only identify "influential" outputs.

Elementary Effects Screening Method

The method of elementary-effects was introduced by Morris et al. [6]. Unlike the conventional method described above, it does not attempt to calculate the exact values of the derivatives. Instead, it relies on sampling of the *k*-dimensional space of the model, thereby also reducing the number of model runs necessary (in the EE method, it is approximately proportional to *k* while in the conventional methods, it is proportional to k^2).

Instead of the finite partial differences, the EE methods operates with so-called *elementary effects*. The algorithm begins at a random position in the *k*-dimensional space of the inputs, changes one of them by Δ and calculates the elementary effect of *r*-th input on an *i*-th output as

$$d_i(x_r) = \frac{f(x_1,\ldots,x_r+\Delta,\ldots x_k) - f(x_1,\ldots,x_r,\ldots x_k)}{\Delta} \qquad (3)$$

The algorithm then proceeds onto another input (one that has not yet been modified in the current trajectory). In this manner, m trajectories in the k-dim space of the input parameters are generated, which should cover as much of it as possible.

In the EE method, it is necessary to uniformly populate the phase space of the input coefficients, as thoroughly discussed in [7]. Once it is done and several elementary effects have been obtained for each input (several trajectories were generated), the mean value μ_i and their standard deviation σ_i are calculated and then act as a measure of sensitivity.

$$\mu_i = \frac{1}{m}\sum_{r=1}^{m} d_i(x_r)$$

$$\sigma_i = \sqrt{\frac{1}{r-1}\sum_{r=1}^{m}(d_i(x_r) - \mu_i)^2}$$

Simply speaking, the value of μ_i is high when the input influences the model linearly and σ_i is high if the input influences the result depending on another input.

Figure 1 provides an illustration how the population of the phase space with trajectories could look like in a simple case of a few input parameters. An elementary effect is calculated in each point of the trajectory which is not its starting point.

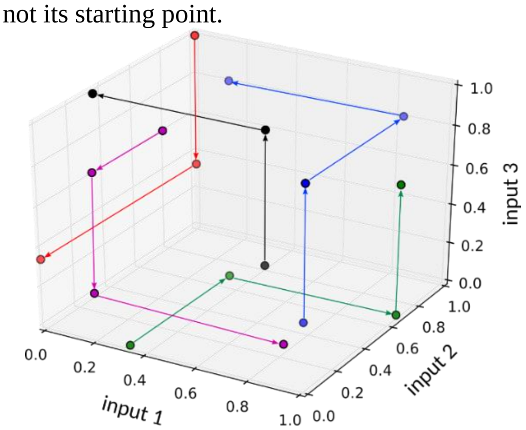

Fig. 1: Population of 3-dim phase space of the model inputs by trajectories.

Sobol variance-based method

The elementary effects method described above has been successfully used for identifying the influential reactions in kinetic systems and it has proven very instrumental in that regard [8], [9]. In this study, however, we are not dealing with an extensive number of inputs, which allows to complement the elementary effects screening method with a more information-rich variance-based method.

To understand how the variance of the output can be linked to the interaction of input variables, let us again consider a model with one output *y* such as

$$y = y(\boldsymbol{x}) = y(x_1, x_2, \dots, x_n)$$

and assume that every model parameter *x* is randomly distributed over the interval [0,1]. Under this interpretation, the output $y(\boldsymbol{x})$ is a randomly distributed variable with the mean value of

$$< y > = \int y(\boldsymbol{x}) d\boldsymbol{x}$$

and the variance of

$$D = \int y(\boldsymbol{x})^2 d\boldsymbol{x} - < y >^2$$

The Sobol method is based on the decomposition of variance into contributions from single parameters, pairs of parameters, etc. Practically, this is realized by decomposing $y(\boldsymbol{x})$

$$y(\boldsymbol{x}) = y_0 + \sum_{i=1}^{n} y_i(x_i) + \sum_{i=1}^{n} \sum_{i \neq j}^{n} y_{ij}(x_i, x_j) + \cdots$$

where it must be satisfied that for any s < n

$$\int y_{i1,\dots,is}(x_i, \dots, x_s) dx_k = 0$$

It can be shown that if the condition above is satisfied, the decomposition can be squared, yielding (note the different maximum indices in the sums)

$$D = \sum_{i=1}^{n} D_i + \sum_{i=1}^{j} D_{ij} + \cdots$$

And finally, the Sobol sensitivity indices for an input or a subset of inputs are defined as

$$S_{i1,\dots is} = \frac{D_{i1,\dots is}}{D}$$

These sensitivity indices are then the measure of how does an input or a set of inputs influence the output of the model.

5. Summary

This work presents a highly exploratory study, especially in the way that the sensitivity analysis methods are going to be used to better understand to identify the scaling parameters of the neutral species' plasma kinetics. However, if it is confirmed that the methods of sensitivity analysis can be used for identifying the scaling parameters of plasma kinetics, it would enable better kinetic control of plasma chemical reactors.

6. References

[1] P. Dvořák, M. Mrkvičková, A. Obrusník, J. Kratzer, J. Dědina, and V. Procházka, "Fluorescence measurement of atomic oxygen concentration in a dielectric barrier discharge," *Plasma Sources Sci. Technol.*, vol. 26, no. 6, 2017.

[2] P. Dvorák, M. Talába, A. Obrusnik, J. Kratzer, and J. Dědina, "Concentration of atomic hydrogen in a dielectric barrier discharge measured by two-photon absorption fluorescence," *Plasma Sources Sci. Technol.*, vol. 26, no. 8, 2017.

[3] F. Massines, C. Sarra-Bournet, F. Fanelli, N. Naudé, and N. Gherardi, "Atmospheric pressure low temperature direct plasma technology: Status and challenges for thin film deposition," *Plasma Process. Polym.*, vol. 9, no. ii, pp. 1041–1073, 2012.

[4] T. Turányi, "SENSITIVITY ANALYSIS OF COMPLEX KINETIC SYSTEMS. TOOLS AND APPLICATIONS," *J. Math. Chem.*, vol. 5, pp. 203–248, 1990.

[5] V. Mazánková, D. Trunec, Z. Navrátil, J. Raud, and F. Krčma, "Study of argon–oxygen flowing afterglow," *Plasma Sources Sci. Technol.*, vol. 25, p. 035008, 2016.

[6] M. D. Morris, "Factorial Sampling Plans for Preliminary Computational Experiments," *Technometrics*, vol. 33, no. 1, pp. 161–174, 1991.

[7] F. Campolongo, J. Cariboni, and A. Saltelli, "An effective screening design for sensitivity analysis of large models," *Environ. Model. Softw.*, vol. 22, no. 10, pp. 1509–1518, 2007.

[8] M. M. Turner, "Uncertainty and error in complex plasma chemistry models," *Plasma Sources Sci. Technol.*, vol. 24, no. 3, p. 035027, 2015.

[9] A. Obrusník, P. Bílek, T. Hoder, M. Šimek, and Z. Bonaventura, "Electric field determination in air plasmas from intensity ratio of nitrogen spectral bands: I. Sensitivity analysis and uncertainty quantification of dominant processes," *Plasma Sources Sci. Technol.*, vol. 27, no. 8, p. 085013, Aug. 2018.

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