KINETIC RATE CONSTANTS DETERMINATION IN BIOGAS COMBUSTION: AN ILL-POSED INVERSE PROBLEM ANALISYS

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Abstract. *The use of biogas produced in anaerobic reactors for wastewater treatment or intensive pig farming activities increases in Brazil. There are different applications for this fuel to power generation as gas turbines, boilers, steam generators and internal combustion engines. In the last case, the use of biogas as fuel is the most practice, simple and probably economic way to transform this kind of alternative energy in net power. In this work, the combustion of biogas in spark ignition engines is investigated with the focus on the kinetic reactions of methane, which represents 60% of biogas. Kinetic rate constants are calculated from product concentration in a generally kinetic model of irreversible consecutive methane combustion reaction. Since experimental data are used, an ill-conditioned inverse problem has to be solved and robust mathematical algorithms are necessary. In the present work, recurrent neural network was chosen, being compared with Simplex and Levenberg-Marquardt methods, frequently used in nonlinear regression techniques. The approach is numerically stable and robust with respect to deviations in the initial conditions or experimental noises.*

Keywords*: methane combustion, kinetic rate constants, inverse problem*

1. INTRODUCTION

The utilization of alternative fuels derived from non-fossil carbon sources, like Biogas produced in anaerobic reactors for wastewater treatment or intensive pig farming activities, increases in Brazil. There are different applications for this fuel to power generation as gas turbines, boilers, steam generators and internal combustion engines (Yao-hua *et al*. 2009). In the last case, the use of Biogas as fuel is probably the most advantage way to transform this alternative energy into net power. In this work, the combustion of Biogas is investigated with the focus on the kinetic reactions of CH_4, which represents about 60% of this fuel.

Generally, models representing methane combustion use more than 300 reactions (Westbrook and Dryer, 1984) to define combustion products, which demands a great computationally task. To simplify this problem, the well known and tested Westbrook and Dryer model (WD-modified) can be used for chemical kinetic calculations (Andersen *et al.* 2009). The use of simplified reaction mechanisms is also very useful in Computational Fluid Dynamics analysis (CFD) since, for the same reason, the modeling of industrial combustion requires great computational efforts. The CFD analysis becomes an important industrial tool for trouble-shooting and optimization, in which chemical reactions are often represented by a mixed-burned assumption or by a chemical equilibrium (Oslon and Gardiner, 1977).

Simulated and real conditions as biogas concentration, excess air ratio (λ) and temperature in Spark Ignition engine can be considered in the simulation (Porpatham *et al.* 2008). Hopfield Neural Network (HNN) was chosen, being compared with Simplex and Levenberg-Marquardt methods, frequently used in nonlinear regression techniques. Kinetic rate constants of irreversible consecutive methane combustion are calculated from the product concentration using the WD-modified kinetic model. For this problem, the differential equations property and the usage of noisily concentration data implies an ill-conditioned inverse problem, which justify the employment of robust mathematical algorithms. The HNN approach shows to be numerically stable, robust with respect to deviations in the initial conditions or experimental noises and non restrictive in respect to the system (Lemes *et al.* 2007).

2. METHODOLOGY

2.1 Methane Combustion Kinetic Modeling

All calculations performed in this work considered the well-known C. K. Westbrook and F.L. Dryer (WD) model. The methane oxidation is governed by a chain process which consists of three reactions. The CO to CO_2 reaction is treated as an irreversible reaction. The Westbrook *et al.* (1977) mechanisms are represented by

$$\begin{aligned} CH_4 + 1.5O_2 &\xrightarrow{K1} CO + 2H_2O \\ CO + 0.5O_2 &\xrightarrow{K2} CO_2 \\ CO_2 &\xrightarrow{K3} CO + 0.5O_2 \end{aligned} \tag{1}$$

The oxidation kinetic mechanism of hydrocarbons has been widely used for studies involving CFD modeling for conventional combustion in air. The reaction mechanism used in this study derives from the comprehensive mechanism (WD) used to CH_4 oxidation in flow reactors (Westbrook and Dryer, 1981). The modified WD mechanisms are proposed by Andersen *et al.* (2009) to improve CO concentration simulation, which is not accurately predicted by the original model.

The WD-modified model consists in a system of chemical rates that can be represented, to methane combustion, as,

$$\begin{aligned} \frac{dCH_4}{dt} &= -k_1[CH_4]^{0,7}[O_2]^{0,8} \\ \frac{dO_2}{dt} &= -k_1[CH_4]^{0,7}[O_2]^{0,8} - k_2[CO][O_2]^{0,25}[H_2O]^{0,5} + k_3[CO_2][H_2O]^{0,5}[O_2]^{-0,25} \\ \frac{dCO}{dt} &= k_1[CH_4]^{0,7}[O_2]^{0,8} - k_2[CO][O_2]^{0,25}[H_2O]^{0,5} + k_3[CO_2][H_2O]^{0,5}[O_2]^{-0,25} \\ \frac{dH_2O}{dt} &= k_1[CH_4]^{0,7}[O_2]^{0,8} \\ \frac{dCO_2}{dt} &= k_2[CO][O_2]^{0,25}[H_2O]^{0,5} - k_3[CO_2][H_2O]^{0,5}[O_2]^{-0,25} \end{aligned} \tag{2}$$

These coupled differential equations are solved from the chemical species concentrations to retrieve the kinetic rate constants of the process.

2.2 Neural Network Theoretical Background

Artificial neural networks are computer codes designed to simulate the human brain mechanism. Recurrent neural networks, as Hopfield Neural Network (HNN) is constructed with all neurons connected working to minimizing the energy function, which is established by the difference between measured and calculated properties (Sebastião and Braga, 2003). Considering C_{cal} and $C_{\exp}$ as the calculated and experimental properties, respectively, this error function is defined as (Vemuri and Jang, 2002),

$$E = \frac{1}{2}\sum_{j=1}^{m}(C_{cal,j} - C_{\exp,j})^2 \tag{3}$$

The neurons state are established by an activation function, $f(u_i(\tau))$, which have direct dependence with C_{cal}. For example, in this problem the neurons stand for the rate constants, whereas the calculated property is the chemical concentration. The neurons state are changed during the learning time, τ, and the derivative of the energy function is, (Hopfield, 1984)

$$\frac{dE}{d\tau} = \sum_{i=1}^{n}\sum_{j=1}^{m}(C_{cal,j} - C_{\exp,j})\frac{\partial(C_{cal})_j}{\partial f_i}\frac{\partial f_i}{\partial u_i}\frac{du_i}{d\tau} \tag{4}$$

In this equation, *n* represents the number of neurons used in the network and consequently, the number of variables to be retrieved, with *m* experimental data.

To guarantee the convergence of the energy function, some conditions in the algorithm needs to be imposed. From the eq. (4), the first condition is related with the neurons state in the learning process, being represented as (Sebastião and Braga, 2005):

$$\frac{du_i}{d\tau} = -\sum_{j=1}^{m}\frac{\partial(C_{cal})_j}{\partial f_i}e_j \tag{5}$$

This transforms eq. (4) in

$$\frac{dE}{d\tau} = -\sum_{i=1}^{n}\frac{\partial f_i}{\partial u_i}\left(\frac{du_i}{d\tau}\right)^2 \tag{6}$$

At this point, a second condition can be established, $\partial f_i / \partial u_i > 0$, i.e. the activation function should be an increasing function of the neurons state, what will imply $\frac{dE}{d\tau} < 0$ in eq. (4) (Hopfield, 1984).

During the network performance, infinite solutions are obtained from Eq. (5) integration. Nevertheless, after the network convergence, a solution that best reproduces the experimental property is obtained (Hopfield and Tank, 1985). To propagate the neural state differential equation, an initial guess are necessary and the error function reaches the minimum when $du_i / d\tau = 0$, stopping the learning process (Sebastião and Braga, 2006). For numerical integration, the fourth order Runge-Kutta method was used.

The Hopfield neural network presents some important advantages against other optimization techniques. For example, the inversion of matrix is not actually necessary, because the neurons are adapted themselves to meet the objective function. Another one is that in extreme cases this recursive theory is capable to find the solution of even rank deficient cases.

3. RESULTS AND DISCUSSION

Simulated data with random noises was used in this work to analyze the efficiency of the Hopfield neural network method against Simplex and Levenverg-Marquardt algorithms. For this, investigation about the inversion procedure is performed in the methane combustion process, when the objective is to obtain kinetic rate constants from chemical concentration. Figure 1 presents the simulated data obtained from numerical solution of Eq. (1), without any error. The rate constants used to calculate the concentrations in this direct problem was k_1=881s^{-1}, k_2=2464s^{-1} and k_3=0.600s^{-1}. These values were chosen due to the correspondence of real conditions as biogas concentration, excess air ratio (λ) and temperature in Spark Ignition (SI) engine (Andersen *et al.* 2009).

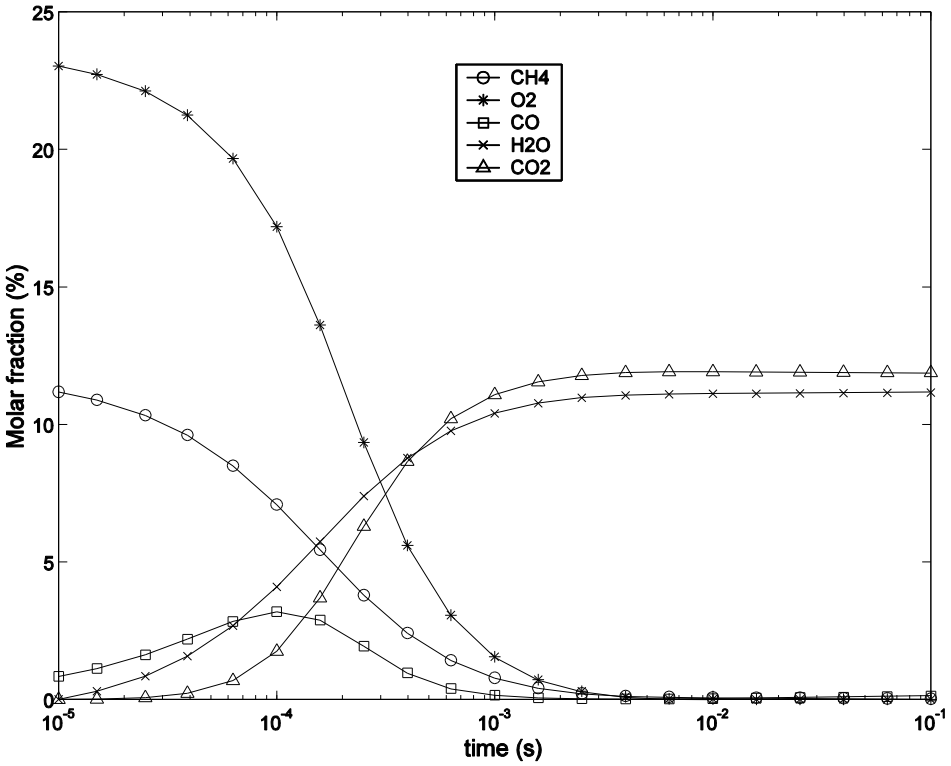

Figure 1. Molar fraction % simulated concentration data.

Using analytical functions or numerical results as the concentration data implicitly assumes these are the correct values, which is only true if experimental errors are not considered in the problem. For this case, an approximated solution is retrieved and rate constants obtained in this way have a meaning only within this restriction. Levenberg-Marquardt method requires matrix inversion and applying this inverted matrix to data presenting errors, large fluctuation on the results is verified due to the matrix condition. For Simplex algorithm, matrix inversion is not performed, but this method is very sensitive with respect to experimental error. This is not the case of the Hopfield Neural Network, which solves the problem using the dynamical character of the neurons. In this work, our objective is to analyze the influence of the error in the inversion procedure by these three methodologies. It is important to emphasize that WD consecutive kinetic model is just a prototype, which allows a comparison between these most used techniques to deal with this kind of problem.

The neural network inputs are established by initial guesses for the rate constants and the converged neuron states correspond to inverted rate constants. The usage of an exact initial guess and simulated concentration data, without error, is a good strategy to test the consistency of the computational method, since in this case, activated neuron states cannot change in the learning time. This test was applied to this problem using the CO concentration presented in Fig. 1 and the non divergence of the neuron states confirmed the computational algorithm. Other test consist in provide different initial conditions to propagate the coupled differential equations. In this problem, initial guesses up to 30% away for k_1 and k_2 and up to 300% away for k_3 from the correct values were used and in all neural network inversions, the inverted rate constants produce an error of about 10^{-6} in relation to simulated CO concentrations.

A comparison between the methods is shown in Tab. 1, in which the robustness of the three methods was checked by adding random noises to the simulated concentrations. Random noises of 3, 5, 7 and 10% were added to the simulated CO concentrations. Even at a noise level of 10%, the algorithm was stable and in comparison with the Simplex and Levenberg-Marquardt algorithms, the neural network presented smaller error in the rate constants calculation and in the residual error of the concentration reproduction, as shown in Table 1. The maximum residual error from HNN is verified when 10% of random noises is added in the simulated data. The Simplex and Levenberg-Marquardt methods cannot handle errors greater than 7%, giving unphysical results for the concentration.

Table 1. Kinetic Rate Constants errors from CO molar fraction percent concentration data.

		Random noise added in CO concentration			
		3%	5%	7%	10%
Neural Network	Error in K_1 / s^{-1}	1.2%	1.0%	4.9%	5%
	Error in K_2 / s^{-1}	1.0%	0.96%	4.6%	5%
	Error in K_3 / s^{-1}	14%	30%	43%	50%
	Error(1)	0.0311	0.0790	0.1348	0.3905
Simplex	Error in K_1 / s^{-1}	2.0%	1.2%	5%	Unphysical results
	Error in K_2 / s^{-1}	2.0%	1.14%	4.6%	Unphysical results
	Error in K_3 / s^{-1}	16%	40%	44%	Unphysical results
	Error(1)	0.0330	0.0792	0.1349	Unphysical results
Levenberg-Marquardt	Error in K_1 / s^{-1}	1.2%	1.2%	4.9%	Unphysical results
	Error in K_2 / s^{-1}	1.0%	1.2%	4.6%	Unphysical results
	Error in K_3 / s^{-1}	16%	40%	44%	Unphysical results
	Error(1)	0.032	0.0792	0.1349	Unphysical results

(1): Defined as Equation (4).

If simulated concentrations without random noises are employed, the three techniques have similar efficiency. The advantage of neural networks while dealing with experimental data can be attributed to its dynamical character, since matrix inversion is not necessary in the algorithm. The neurons are adjusted to reach an objective function.

4. CONCLUSION

Hopfield Neural Network was used in the present work to solve an inverse kinetic problem related to methane combustion. Simulated data were first calculated considering real conditions as biogas concentration, excess air ratio (λ) and temperature in SI engine. From these data and a well-known WD kinetic model, the Levenberg-Marquardt and Simplex algorithms were confronted to the Hopfield network methodology. These algorithms efficiency were investigated using random noises in the simulated data. Neural network is a superior method to retrieve rate constants from simulated data with random noise, as evident from the above considerations.

The HNN is non restrictive to the system and can be used for any set of differential equations which describe a consecutive reaction mechanism. The algorithm was numerically stable in relation to different initial conditions and also it was more robust for all noise level tested here, in comparison with Levenberg-Maquardt and Simplex algorithms, common optimization methods used to solve this kind of problem. The numerical stability of the method allows treatment of data with large experimental noises and guarantees an efficient convergence of the neurons even for initial conditions away to the real estimated parameters.

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