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Theoretical study of self-ignition and quenching limits in a catalytic micro-structured burner and their sensitivity analysis

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HIGHLIGHTS

- Analytical method for prediction of the self-ignition and quenching limits.
- It is based on the Zel'dovich–Semenov theory of the homogeneous reactor.
- Sensitivity analysis of the combustion limits of the catalytic micro-burner.
- Validation against data in the micro-burner with Pt-$LaMnO_3$ honeycomb.
- Method is not an alternative to the CFD simulations, but supplements them.

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ABSTRACT

This paper is devoted to the prediction of self-ignition and quenching limits in a catalytic micro-burner in the context of a zero-dimensional approach that was originally developed by Semenov and Zel'dovich for the analysis of self-accelerating chemical reactions and critical phenomena in an ideal homogeneous chemical reactor. We formulated the analytical criteria for self-ignition and quenching in the catalytic micro-burner, and the sensitivity equations that show the effect of the variations of geometrical, chemical and regime parameters on the boundary of the operating regimes.

We compare the theoretical self-ignition and quenching limits with those known in the literature for the CH_4–air and CH_4/H_2–air mixtures obtained on the micro-structured burner with a Pt-$LaMnO_3$ catalytic honeycomb. Agreement was found between the theoretical and experimental results. Our semi-empirical analysis explains qualitatively the different effects of hydrogen addition to a methane–air mixture on self-ignition and the quenching limits that were observed in the analyzed experiments, and predicts these limits for the operation regimes that were not tested in the experiments. We perform the sensitivity analysis of the self-ignition problem, which shows how small variations in the geometrical, chemical and thermodynamic parameters influence the minimal ignition temperature in the analyzed experiments with the CH_4–air and CH_4/H_2–air mixtures, and propose a way to perform sensitivity analysis for the quenching problem.

1. Introduction

One of the most promising applications of catalytic combustion is the micro-structured reactor, proposed to be the best route for the development of micro-generators of energy for portable applications (Fernandez-Pello, 2002) and micro-fuel processors (Park et al., 2005), where catalytic combustion produces the heat for driving endothermic reactions. One of the main drawbacks is related to the constrained operating window in terms of the total flow rate, operating temperature, pressure and so on.

An effective method for studying catalytic combustion is by performing numerical simulation of one-dimensional (Benedetto et al., 2003) and two-dimensional (Norton and Vlachos, 2003, 2004; Karagiannidis and Mantzaras, 2010, 2012; Landi et al., 2014) differential equations of the problem. Continuous dependence of a numerical solution of this equation on geometric and regime parameters can be broken at some boundaries of the parameters where their small variations completely change the character of the solution due to self-ignition or combustion quenching, i.e. the solutions at these boundaries show stick-slip behavior. As shown

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in Benedetto et al. (2003), the minimal self-ignition temperature T_{MIT} and quenching temperature T_{QT} in the numerical simulations agree with the corresponding experimental data, and the simulations describe the hysteresis window due to the inequality $T_{MIT} > T_{QT}$.

The problem is that the numerical simulations do not directly show dependence of the self-ignition and quenching boundaries on the geometric, thermodynamic and chemical characteristics of the system. Therefore, it is important to develop a simple method for the theoretical estimation of these critical temperatures to better understand the role of different factors affecting the self-ignition and quenching boundaries, as well as to widen the operating window and optimize the catalytic micro-burner. In order for such optimization to be achieved, a designer needs to know how small variations in the parameters of the system influence the minimum temperature of the combustible mixture when self-ignition and quenching take place in the burner. These are the kinds of questions addressed by sensitivity analysis for self-ignition and quenching of a micro-structured catalytic burner.

Modeling a complex system such as a catalytic burner in its entirety is impossible in a simple theory, as a significant simplification is inevitable. However, even a simple adequate theory must include a statement that allows the stick-slip behavior (self-ignition and quenching) of the steady state regimes of the catalytic combustion to be described. The paper statement is that this stick-slip behavior of the steady state regimes, which is observed in the burner, where the combustion rate depends continuously on temperature and other parameters, can be described theoretically by analyzing the global heat balance: self-ignition and quenching take place when the global heat release rate becomes higher or smaller than the global heat losses (heat loss through the walls and convective loss). To prevent misunderstanding, we stress that the stick-slip behavior does not mean that a stepwise change of the regime takes place in the process of self-ignition. Formation of the steady state combustion regimes in the catalytic micro-burners develops over a significant period of time both in experiments (Barbato et al., 2009, 2013) and in numerical simulations (Karagiannidis and Mantzaras, 2010, 2012; Landi et al., 2014; Sarli et al., 2015). The numerical simulations describe a continuous ignition process, which is described by smooth solutions of the corresponding differential equations depicting the local heat balances in the non-uniform flow.

Our theoretical study of the self-ignition and quenching boundaries and their sensitivity analyses are based on zero-dimensional (0-D) equations, which describe the global heat balance in the catalytic micro-burner. It is obvious that the 0-D approach is incomplete and insufficient for comprehensive modeling of the catalytic combustion in the micro-burner. At the same time, it is appropriate for an analysis of thermal self-ignition and quenching, which are controlled by the global heat balance described by the 0-D equations. Hence, our purpose was to formulate analytical criteria of self-ignition and quenching employing the 0-D balance equations, and propose an analytical method to estimate the effect of variations in the design and process parameters on the boundaries of self-ignition and quenching. The developed method allows sensitivity analysis of the self-ignition and quenching boundaries of catalytic micro-burners obtained from experiments or numerical simulations to be performed analytically, which shows the effect of small variations in the geometric, chemical and regime parameters on the self-ignition and quenching limits, and it can be used to analyze possible ways to optimize the operating window.

The main difficulty with the quantitative description of the self-ignition and quenching limits is that we cannot exactly estimate the effective gas–solid heat transfer coefficient appearing in the 0-D balance equations, which controls the heat flux thorough the catalytic surfaces. For this reason, we interpreted the 0-D approach as a semi-empirical method: using the values of the effective heat transfer coefficient that exactly described these limits. We quantitatively predicted the sensitivity of the limits to small parameter variations, and provided only the semi-quantitative prediction of the effects of large variations, as the effective heat transfer coefficient can vary significantly.

The zero-dimensional approach to the problem of catalytic combustion has been reported in the literature. In the paper by Nelson et al. (2000), the numerical simulations of the zero-dimensional balance equations (a model of a continuously stirred tank reactor) were performed to obtain boundaries of the self-ignition and quenching limits. In a recent work (Sarli, 2014), which was focused on the role of hydrogen presence in the catalytic pilot stream in enlarging the operating window, the numerical analysis was performed using the homogeneous reactor network model. As our aim was to study the problem analytically, we used a method developed by Semenov (in old transcription, Semenoff) (Semenoff, 1928) and Zel'dovich et al. (1985) for a homogeneous ideally-mixing chemical reactor. This approach allows us to deduce (quite similar to the case of the homogeneous reactor) the expressions for the minimal self-ignition and quenching temperatures of the inlet mixture as a function of the geometrical and regime parameters of the catalytic micro-structured burner, and then to estimate the relative sensitivity coefficients in the sensitivity equations. We believe that the Zel'dovich-type zero-dimensional analysis of these boundaries and their sensitivity analyses have their own value as it allows the analytical investigation of the influence of different operational factors on the boundaries of the operating regimes of the catalytic micro-burner, and the sensitivity equations describe the relative influence of different factors on these boundaries. We hope that these results will be useful (along with numerical simulations) for practical improvement and optimization of catalytic micro-structured burners.

We compare the theoretical results with the experimental data reported by Barbato et al. (2009) for CH_4–air and CH_4/H_2–air mixtures obtained using a micro-structured burner with a Pt-$LaMnO_3$ catalytic honeycomb. This comparison demonstrates the merits and limitations of using this approach. On the one hand, it allows us to describe self-ignition and quenching limits, and to explain some experimental effects that, at first glance, appear to be paradoxical. However, on the other hand, this approach cannot describe the transient processes of self-ignition and quenching observed in the catalytic micro-burner.

2. Zero-dimensional approach to the problem

We analyzed the critical regimes in the micro-burner with the Pt-$LaMnO_3$ catalytic investigated in Barbato et al. (2009); see Fig. 1. The geometric characteristics of the honeycomb are as follows: diameter $D = 17$ mm, length $L = 11$ mm, and the number of passageways with a diameter $d = 0.74$ mm was 319. Three thermocouples were inserted into the central channel of the catalyst monolith, providing the measurement of temperature to indicate self-ignition and the quenching of catalytic combustion. In the steady state regime of combustion, there is a balance between heat release rate q_+ and heat loss rate q_- connected with the mass flux $\dot{m}$ though the burner and heat transfer in the wall. In the context of the zero-dimensional approach, all parameters inside the reactor are assumed to be uniform and the temperature of the gas inside the reactor T_g is equal to the temperature of gas at the exit of the reactor $T_{out} = T_g$.

Fig. 2 shows the mutual position of the curve q_+, which describes the rate of heat release in the burner due to combustion and is controlled by chemical kinetics, and the line q_-, which