Modeling of termokinetic oscillations at partial oxidation of methane

A V Arutyunov1,2*, A A Belyaev2, I N Inovenkov1, V V Nefedov1
1Lomonosov Moscow State University, Faculty of Computational Mathematics and Cybernetics (CMC), Russia, 119991, Moscow, GSP-1, 1-52, Leninskiye Gory
2Semenov Institute of Chemical Physics of Russian Academy of Sciences (ICP RAS), 119991, Kosygina 4, Moscow, Russia
*E-mail: aarutyunovv@gmail.com

Abstract. Partial oxidation of natural gas at moderate temperatures below 1500 K has significant interest for a number of industrial applications. But such processes can proceed at different unstable regimes including oscillating modes. Nonlinear phenomena at partial oxidation of methane were observed at different conditions. The investigation of the complex nonlinear system of equations that describes this process is a real method to insure its stability at industrial conditions and, at the same time, is an effective tool for its further enhancement. Numerical analysis of methane oxidation kinetics in the continuous stirred-tank reactor, with the use of detailed kinetic model has shown the possibility of the appearance of oscillating modes in the appropriate range of reaction parameters that characterize the composition, pressure, reagents flow, thermophysical features of the system, and geometry of the reactor. The appearance of oscillating modes is connected both with the reaction kinetics, heat release and sink and reagents introduction and removing. At that, oscillations appear only at a limited range of parameters, but can be accompanied by significant change in the yield of products. We have determined the range of initial temperature and pressure at which oscillations can be observed, if all other parameters remained fixed. The boundaries of existence of oscillations on the phase plane were calculated. It was shown that depending on the position inside the oscillation region the oscillations have different frequency and amplitude. It was reviled the role of heat exchange with the environment: at the absence of heat exchange the oscillating modes are impossible. In the vicinity of the boundary of phase range, where oscillations exist, significant change of concentration of some products were observed, for example, that of CO2, which in this case one of the principal products is. At that, insignificant increase in pressure not only change the character of CO2 behaving with time, but as well lead to significant increase of its mole fraction simultaneously twice decreasing the mole fraction of CO.

1. Introduction

The partial oxidation of methane — the basic component of natural gas — at moderate temperatures below 1500 K is described by a complex set of kinetic equations, which should include hundreds of elementary chemical steps for an adequate description of the process. The most important special feature of this chemical system, which is a branched-chain radical process, is its nonlinearity because the main chain propagation, branching, and termination steps occur with the participation of unstable highly reactive intermediate compounds. That is, the set of kinetic equations that describes the behavior of this system and, consequently, the corresponding set of differential equations are deliberately nonlinear with respect to the initial reagents [1]. This creates prerequisites for the complex behavior of the system, including the existence of different regimes under almost the same conditions.
with a sharp transition between them: for example, the appearance of the region of a negative temperature coefficient of reaction rate, cold flames, a temperature hysteresis of reaction rate, and also oscillating modes and other nonlinear processes. The majority of these phenomena were observed experimentally in studies of the partial oxidation of methane under various conditions [2]. However, with consideration for the enormous number of kinetic parameters that describe this system, it is impossible to study all its special features in a potentially interesting parameter region experimentally.

At the same time, at the industrial implementation of such processes, it is necessary to insure their stability: that is, a random jump of any parameter beyond the specified limits will not cause unstable process conditions with an uncontrollable course of events. On the other hand, it is not inconceivable that the highest yield of target products can be obtained at the values of parameters that cannot be reached under laboratory conditions; that is, the process efficiency can be considerably increased. Therefore, the study of this complex nonlinear system by mathematical simulation methods is of paramount importance for its stable industrial implementation; simultaneously, this is an effective tool for its further improvement. Here, we report on a study of the appearance of unsteady-state conditions in the partial oxidation of natural gas based on the analysis of a detailed kinetic model of the process.

2. Calculation model
The possibility of the appearance of oscillating modes in the oxidation and combustion of methane was studied by a numerical calculation method. The onset of oscillations in chemical systems belongs to the critical phenomena of chemical kinetics. Their appearance is related to the accumulation of active products or heat in the reacting system [3]. In simple model systems, it is possible to find a range of parameters at which oscillations occur based on a parametric study of the problem (for example, see [4]). However, the real kinetic mechanism of the oxidation and combustion of methane contains hundreds of elementary steps with the participation of tens of components. Therefore, an analytical study is almost impossible in this case, and only a computer simulation makes it possible to characterize this system in sufficient detail and to predict at which values of the parameters oscillatory modes can appear.

This study was performed within the framework of the model of a chemical continuous stirred tank reactor because steady-state periodic oscillations in the oxidation of methane were found previously [5, 6] under these conditions. Note that the possibility of the onset of chemical oscillations is raised in flow systems, as compared with that in closed systems, because the parent substances consumed in reactors of this type are continuously supplied to the reactor. Figure 1 shows a schematic diagram of the continuous stirred tank reactor with the main parameters of input and output flows. The mathematical formulation of problem for this model is written in the form [7].

![Figure 1. Schematic diagram of a continuous stirred tank reactor and the main parameters of the inlet and outlet flows.](image-url)
\[
\begin{align*}
\rho \frac{\partial Y_j}{\partial t} &= \omega_j + \frac{\rho}{\tau_r} \left( Y_j^0 - Y_j \right), \quad j = 1,2,\ldots,M \\
\rho c_p \frac{\partial T}{\partial t} &= \Phi + \frac{\rho c_p}{\tau_r} (T_0 - T) + h \frac{S}{V} (T_0 - T)
\end{align*}
\]

(1)

Initial condition:
\[ T = 0, \quad T = T_0, \quad Y_j = Y_j^0 \]

(2)

Accepted notations are: \( t \) is time; \( M \) is the number of mixture components; \( Y_j \) is the weight fraction of the \( j_{th} \) component; \( T \) is the temperature of the mixture; \( \rho \) is the density of the mixture; \( c_p \) is the heat capacity at constant pressure; \( \omega_j \) is the rate of formation or consumption of the \( j_{th} \) component in the course of chemical reaction; \( \tau_r \) is the average turnover time of the reactor (the residence time of a reaction mixture in the reactor); \( \Phi \) is the heat release rate; \( h \) is the coefficient of heat transfer into the environment through the reactor walls (the reactor is spherically shaped); \( V \) and \( S \) are the reactor volume and surface area, respectively; and the subscript “0” refers to the conditions at the reactor inlet.

We assumed that the reactor wall temperature was kept constant and equal to the reactor inlet temperature \( T_0 \).

It is necessary to add a number of relationships to the Eqs. (1). These are expressions for the rates of reaction and heat emission, a perfect gas equation, and a relation between the weight and mole fractions of a component [8]:

\[
\omega_j = W_j \sum_{k=1}^{N} \left( \nu^{j}_{j,k} - \nu^{j}_{j,k} \right) A_k T^{b_k} \exp \left( -\frac{E_k}{R^0 T} \right) \prod_{i=1}^{M} \left( \frac{X_i P}{R^0 T} \right)^{\nu^{i}_{j,k}}
\]

(3)

\[
\Phi = \sum_{k=1}^{N} H_k A_k T^{b_k} \exp \left( -\frac{E_k}{R^0 T} \right) \prod_{i=1}^{M} \left( \frac{X_i P}{R^0 T} \right)^{\nu^{i}_{j,k}}
\]

(4)

\[
p = \rho R_0^0 T \sum_{j=1}^{M} \frac{Y_j}{W_j}
\]

(5)

\[
X_j = \left( \frac{Y_j}{W_j} \right) \left( \sum_{j=1}^{M} \frac{Y_j}{W_j} \right)^{-1}
\]

(6)

The following notations were used: \( N \) is the number of elementary steps of a chemical reaction; \( W_j \) is the molecular weight of the \( j_{th} \) component; \( X_j \) is the mole fraction of the \( j_{th} \) component; \( p \) is the pressure; \( R_0 \) is the gas constant; \( \nu^{j}_{j,k} \) and \( \nu^{j}_{j,k} \) are the stoichiometric coefficients of the \( j_{th} \) component as a reactant and a product in the \( k_{th} \) elementary reaction, respectively; \( A_k, b_k, \) and \( E_k \) are the preexponential factor, the exponent for temperature, and the activation energy of the \( k_{th} \) reaction, respectively; and \( H_k \) is the heat effect of the \( k_{th} \) reaction.

The heat capacity of a gas mixture is found from the equation [8]
\[ C_p = \sum_{j=1}^{M} Y_j c_{pj} \] (7)

The heat capacity of each mixture component, \( c_{pj} \), is related to temperature by the polynomial equation

\[ c_{pj} = \frac{R_0}{W_j} \left( a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \right) \] (8),

where the polynomial’s coefficients \( \{a_1, a_2, a_3, a_4, a_5\} \) of each particular component are taken from a thermodynamic data base [9].

For describing a chemical reaction of methane with oxygen we have used the well-known detailed kinetic mechanism of the oxidation and combustion of methane [10], which includes 261 elementary steps with the participation of 30 components. We assumed that the mixture supplied to the reactor consisted of methane (CH\(_4\)) and oxygen (O\(_2\)) strongly diluted with nitrogen. The ratio between methane and oxygen was varied and characterized by the fuel–air equivalence ratio

\[ \varphi = \left( \frac{X_{CH_4}}{X_{O_2}} \right) \left( \frac{X_{CH_4}}{X_{O_2}} \right)^{-1}_{st} \] (9),

where the subscript \( st \) refers to a stoichiometric ratio.

The real test process usually occurs in a reactor under specific conditions (thermophysical properties, the composition and feed rate of a mixture, and the geometric parameters of the reactor). Therefore, the values of the parameters that characterize these properties should be specified. In our case these parameters are \( T_0, p, \varphi, X_{N_2}, h, \tau_r, \) and \( V \) (\( S \) is related to \( V \)), the values of which were varied in the course of a numerical study.

The calculations were performed with the aid of the Chemkin program package [11]. Note that de Joannon et al. [6] also studied such a system at \( X_{N_2} = 0.9 \) with the use of numerical calculations (together with experiments), but the aim of this work was essentially different from the problems solved-in [6]. First, in [6] experiments were performed at a fixed atmospheric pressure, a fixed reactor volume, a fixed residence time of a reaction mixture in the reactor, the constant conditions of heat emission into the environment, and \( X_{N_2} = 0.9 \). As noted above, we studied the dependence of the domain of existence of oscillating modes on these parameters, whose values were varied. Furthermore, unlike [6], we studied the possibility of minimizing the number of elementary steps in the kinetic mechanism at which the occurrence of the oscillating mode would be retained. Finally, the analysis of the behavior of the concentrations of gas mixture components at the boundary of existence of the oscillating mode is a fundamentally new issue in this work.

3. Results of the calculations

In the course of computations, it was established that the periodic sustained oscillations of process temperature were observed in a specific range of varied parameters. The amplitude and frequency of these oscillations depend on the parameters that characterize the properties of a gas mixture and a reactor. In certain cases, the amplitude of temperature oscillations can reach hundreds of degrees (Figure 2). Note that analogous oscillations were also observed for the concentrations of many components of this chemical mixture. The range of variation of the parameters \( T_0, p, \varphi, \tau_r, h \) and \( V \)
in which oscillations were observed is relatively small. In all of the other cases, a steady state process was established with time; that is, the temperature and concentrations became time-constant.

**Figure 2.** Process temperature oscillations at \( T_0 = 1050 \text{ K}, p = 1 \text{ atm}, \varphi = 0.8, X_{N2} = 0.9, \) \( h = 0.0042 \text{ cal/(cm}^2\text{s·K}), \) \( \tau_r = 0.5 \text{ s}, \text{ and } V = 0.1 \text{ m}^3. \)

**Figure 3.** Domain of existence of the oscillating mode on the initial temperature–pressure phase plane at \( \varphi = 0.8, X_{N2} = 0.9, h = 0.0042 \text{ cal/(cm}^2\text{s·K}), \) \( \tau_r = 0.5 \text{ s}, \) and \( V = 0.1 \text{ m}^3. \) Solid and broken lines refer to the complete kinetic mechanism [10] and a reduced kinetic mechanism (57 reactions and 20 components), respectively.
We have determined the ranges of the initial temperature and pressure in which oscillations were observed at the fixed values of other parameters (\( \varphi = 0.8 \), \( X_{N2} = 0.9 \), \( h = 0.0042 \text{ cal cm}^2 \text{ cm}^{-2} \text{ K} \), \( r_\tau = 0.5 \text{ s} \), and \( V = 0.1 \text{ m}^3 \)). The boundary of a region in which oscillations were observed is shown by a solid line on the \((T_0, p)\) phase plane (Figure 3). The oscillating mode has different frequency and amplitude depending on the position of a point inside the region. As the upper boundary of the region is approached (with increasing pressure), the oscillation frequency increases, but a decrease in the amplitude is simultaneously observed and oscillations disappear at the boundary. On the contrary, oscillation frequency decreases and its amplitude increase as the lower boundary approaches (with decreasing pressure). At the boundary, the oscillation period approaches to infinity. At the left boundary, changes in the amplitude and frequency are not so pronounced. At the right boundary, there is a special feature related to the fact that oscillations appear after a time rather than immediately.

We studied the possibility of reducing the number of elementary steps in a kinetic mechanism. The number of elementary steps was decreased so that, in this case, not only the main properties of the process of methane oxidation but also the occurrence of the oscillating mode were retained. As a result of a regular decrease, we managed to reduce the number of elementary steps from 261 to 57 and the number of chemical components from 30 to 20. The domain of existence of the oscillating mode for this reduced mechanism is shown by a broken line in the \((T_0, p)\) phase plane (Figure 3). It is evident that the domain of existence of the oscillating mode for the reduced kinetic mechanism is shifted toward higher temperatures.

For other varied parameters, it is also possible to find a range of their changes within which oscillations are observed. However, to construct the region of oscillations on the reference plane based on all of the parameters is a very labor-consuming process; therefore, we have restricted ourselves to the demonstration of the behaviors of the system under variations of other parameters. These calculations were performed using a published complete kinetic mechanism [10].

Figure 4 shows different reactor conditions depending on the fuel–air equivalence ratio \( \varphi \) the other parameters being fixed. It is evident that periodic oscillations were observed at \( \varphi = 0.8 \) and 0.9; however, there were no fluctuations in both lean and stoichiometric mixtures. In the two last-named cases, a swift temperature rise was observed with the subsequent decrease to a steady-state value.
Figure 4. Time dependence of temperature at different fuel–air equivalence ratios $\varphi$: (1) $\varphi = 1$ (stoichiometry), (2) $\varphi = 0.9$, (3) $\varphi = 0.8$, and (4) $\varphi = 0.7$; $T_0 = 1050$ K, $p = 1$ atm, $\varphi = 0.8$, $\varphi = 0.9$, $h = 0.0042$ cal/(cm$^2$·s·K), $\tau_r = 0.5$ s, and $V = 0.1$ m$^3$.

We also studied the dependence of the behavior of steady-state reactor conditions on parameters such as the heat-transfer coefficient $h$, the reactor volume $V$, and the parameter (which is inversely proportional to the mass feed rate to the reactor). For each of these parameters, there is also a specific range of changes in which oscillations are observed. As an example, Figure 5 shows the dependence of temperature on the heat transfer coefficient $h$. In the absence of heat emission ($h = 0$) or at its low value, there were no oscillations. But they appeared with increasing $h$ and their amplitude initially increased; however, the oscillations disappeared with a further increase in the heat emission. It is obvious that the steady-state temperature (or its equilibrium value about which oscillations occur) decreases with $h$. Thus, oscillations do not appear at either strong or weak heat emission.
Figure 5. Time dependence of temperature at different heat transfer coefficients $h$, cal/(cm$^2$·s·K): (1) $h = 0$, (2) $h = 0.001$, (3) $h = 0.003$, (4) $h = 0.004$, and (5) $h = 0.005$; $T_0 = 1050$ K, $p = 1$ atm, $\varphi = 0.8 = 0.9$, $\tau_r = 0.5$ s, and $V = 0.1$ m$^3$.

The nitrogen content of the mixture should be specially noted. We studied the influence of the fraction of nitrogen in the mixture on the range of pressures in which the oscillating mode occurred. Figure 6 shows this dependence. Two lines indicate the upper and lower boundaries, respectively, of a pressure range in which the oscillating mode occurs at the fixed other parameters. It is evident that the pressure range initially somewhat enlarged but then gradually decreased with decreasing the mole fraction of nitrogen. The above dependence was obtained at $T_0 = 1050$ K, but an analogous behavior was also observed at other initial temperatures. This behavior may be explained by two tendencies: on the one hand, a decrease in the fraction of nitrogen facilitates the complete occurrence of the reaction; however, at the same time, the rate of consumption of the initial products (methane and oxygen) is not compensated by their supply into the reactor as the value of $\varphi$ is decreased. Note that both the amplitude and the frequency of oscillations increased with decreasing; this fact is indicative of the more rapid occurrence of the reaction and an increase in the effect of the supply of a fresh mixture on the process.
As noted above, the detailed kinetic mechanism can be strongly reduced with the retention of basic regularities in the behavior of the system at the specific values of parameters. Therefore, at the given values of the parameters, many elementary steps weakly influence (or, under the given conditions, some of them do not actually influence) the occurrence of the chemical reaction as a whole. However, there are elementary steps that have a very strong effect on the process. De Joannon et al. [6] found that the following recombination reaction of methyl radicals ($\text{CH}_3^*$) exerts a very strong effect on the occurrence and characteristics of the oscillations:

$$\text{CH}_3^* + \text{CH}_3^* \leftrightarrow \text{C}_2\text{H}_6$$

Our studies confirmed a dramatic effect of this reaction on the process as a whole. In addition to this, we found that the chain branching reaction also has a very strong effect:
Figure 7. Time dependence of temperature at different values of the pre-exponential factor $A_{br}$:
(1) $A_2 = 0.95 A_2^0$, (2) $A_2 = A_2^0$, and (3) $A_2 = 1.1 A_2^0$; $T_0 = 1050$ K, $p = 1$ atm, $\varphi = 0.8$, $\varphi = 0.9$, $h = 0.0042$ cal/(cm$^2$·s·K), $\tau_r = 0.5$ s, and $V = 0.1$ m$^3$.

Let us consider this reaction in more detail. We designate the pre-exponential factor of forward reaction as $A_{br}$ (the parameters of reverse reaction are calculated through the parameters of forward reaction based on an equilibrium constant [10]) and the base value of the pre-exponential factor as $A_{br}^0$ ($A_{br}^0 = 2 \cdot 10^{14}$ cm$^3$ mol$^{-1}$ s$^{-1}$). Figure 7 demonstrates that even a small change in the pre-exponential factor of this reaction has a strong effect on the course of the process. Thus, as the pre-exponential factor decreases by only 5%, the oscillating mode disappears, and a steady-state solution is reached. It is evident that, as the pre-exponential factor of this elementary step increases by a factor of 1.1, the oscillation frequency dramatically increases but the amplitude considerably decreases.

Figures 2, 4, 5, and 7 show the behavior of temperature with time because temperature oscillations the most illustrative. However, as mentioned above, the oscillations of concentrations of chemical mixture components were also observed. In certain cases, a strong change in the concentration of reaction products was observed near the boundary of the phase domain of existence of temperature oscillations (Figure 3). The behavior of the concentration of carbon dioxide (CO$_2$), which is one of the main products of the reaction of methane with oxygen under the given conditions, serves as a very clear example. Figure 8a shows this behavior at the pressure $p = 1.4$ atm. A small, by only 5 K, increase in the initial temperature not only changed the behavior of carbon dioxide concentration with time (oscillations appeared) but also led to a several-fold increase in the mole fraction of CO$_2$. This was related to a significant decrease in the mole fraction of unburned methane, that is, with an increase in the degree of its conversion (Figure 8b). In this case, the mole fraction of carbon monoxide (CO)
decreased by a factor of more than 2. The analysis of sensitivity showed that, under the given conditions, the interaction of CO with the hydroxyl radical is the main step of the formation of CO$_2$:

$$\text{CO} + \text{OH}^• \leftrightarrow \text{CO}_2 + \text{H}^•$$

It is likely that an increase in the temperature by 5 K shifts the equilibrium of this reaction to the side of CO$_2$ formation accompanied by a notable increase in the conversion of methane (Figure 8b). Thus, a transition to the region of the oscillating mode due to a redistribution of rates between the processes of the partial and deep oxidation of methane dramatically changes both the course of the process and the composition of the resulting products. We note once again that this abrupt change in the behavior of concentrations with an insignificant change in the initial temperature was observed only near the boundary of the phase domain of existence of oscillations.

\[\text{Figure 8. Time dependence of the mole fractions of (a) 1) CO}_2, 2) \text{CO}_2, \text{ and (b) CH}_4 \text{ at two initial temperatures: dashed and solid lines refer to } T_0 = 1010 \text{ and } 1015 \text{ K, respectively; } p = 1.4 \text{ atm, } \varphi = 0.8, \varphi = 0.9, h = 0.0042 \text{ cal/(cm}^2\text{s-K), } \tau_r = 0.5 \text{ s, and } V = 0.1 \text{ m}^3.\]

4. Conclusions
The study of the system of kinetic equations that describes the oxidation of methane under the conditions of a continuous stirred tank reactor showed the possibility of the appearance of oscillating modes. These modes appear at the specific values of the parameters that characterize the thermophysical properties of a mixture, its composition, the feed rates of reagents, and the reactor geometry. The oscillating process conditions are related to the chemical mechanism (reaction kinetics) and the release and removal of heat and reactants. The role of heat exchange between the reactor and the environment is great: under the conditions of this work, it was impossible to obtain oscillating modes in the absence of heat exchange. Oscillations are observed only in a comparatively small range of changes in the parameters that characterize the properties of the system; however, they can be accompanied by considerable changes in the course of the process and in the yields of products.
5. References

[1] V. S. Arutyunov, *Oxidative Conversion of Methane* (KRASAND, Moscow, 2011) [in Russian].

[2] V. Arutyunov, *Direct Methane to Methanol: Foundations and Prospects of the Process* (Elsevier, Amsterdam, 2014).

[3] D. A. Frank-Kamenetskii, *Diffusion and Heat Exchange in Chemical Kinetics* (Nauka, Moscow, 1987; Springer, Heidelberg, 1995).

[4] V. I. Bykov and S. B. Tsybenova, *Nonlinear Models in Chemical Kinetics* (KomKniga, Moscow, 2011) [in Russian].

[5] B. F. Gray, J. F. Griffiths, G. A. Foulds, B. G. Charlton, and G. S. Walker, Ind. Eng. Chem. Res. **33**, 1126 (1994).

[6] M. de Joannon, P. Sabia, A. Tregrossi, and A. Cavaliere, Combust. Sci. Technol. **176**, 769 (2004).

[7] Theory Manual. Chemkin Software, RD01400-C01-004-001A (June 2004). https://ay14-15.moodle.wisc.edu/prod/pluginfile.php/119333/mod_resource/content/1/CHEMKIN_Theory.pdf.

[8] F. A. Williams, *Combustion Theory* (Benjamin, Menlo Park, CA, 1985).

[9] Thermodynamic Data at the Web Site of the Laboratory for Chemical Kinetics. Alexander Burcat’s. Ideal Gas Thermodynamic Data in Polynomial Form for Combustion and Air Pollution Use. http://garfield.chem.elte.hu/Burcat/burcat.html.

[10] J. Warnatz, U. Maas, and R. W. Dibble, *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation* (Springer, Berlin, 2006).

[11] CHEMKIN-PRO Release 15083 (2009).