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PARALLEL AND CONSECUTIVE REACTIONS IN FUEL GAS COMBUSTION

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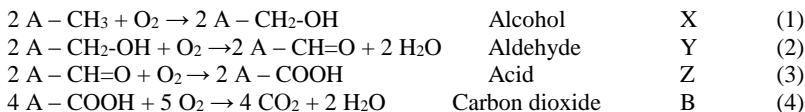
Abstract

The kinetics of the oxidation process of the organic substances known as fuel gas (the alkanes class in general) deals with reactions whose mechanisms are analyzed in many theories and models. Irrespective of the nature and excess of the carburant, all partial combustion intermediates are revealed: alcohols, aldehydes, organic acids (that together with other derivatives from catalytic reforming reactions are characterized by the global parameter VOCs), carbon monoxide and carbon dioxide and finely divided carbon under the form of soot. The volume of oxidation intermediates increases when the carburant excess decreases monotonously to values below the stoichiometric ratio, so that when the limit is reached the carbon dioxide and water vapor volumes can be minimal. This paper puts forward a kinetic combustion model based on the parallel and consecutive reactions producing part of the chemical compounds that form the concentration of VOC, carbon monoxide and finely divided particles of the gas produced by fuel gas combustion.

Keywords: *combustion, equations, nanoparticles, reactions, VOC.*

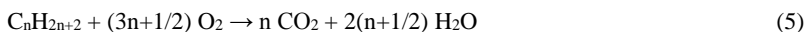
Introduction

The smoke produced by any quick oxidation reaction in the presence of the oxygen in the air is a composite mixture of finely divided solid particles, liquid particles difficult to volatilize at a given temperature and gas, mainly carbon dioxide and nitrogen oxides (Cornellier 2005). The reactions that take place during the combustion of fuel gas such as methane or calor gas (a combination of equal propane and normal butane concentrations) are consecutive combustion reactions rendered by the following equations:



taking into consideration only the oxidation reaction at the end of the chain.

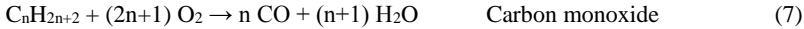
In reality, however, the equivalent reaction, quick and complete in case of oxygen excess, can be written as follows:



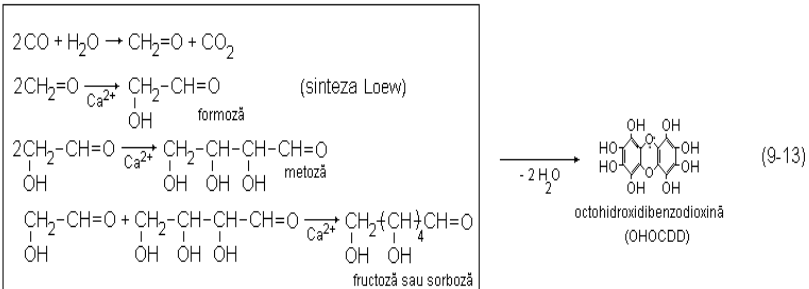
Nitrogen oxidation occurs simultaneously with carbon oxidation to CO₂. The higher the flame temperature, the more intense the oxidation (Strambeanu 2003):



Irrespective of the oxygen excess, at the same time with the oxidation process, the thermal decomposition of the fuel gas occurs as other parallel processes that produce carbon monoxide or finely divided carbon under the form of nanoparticles (smoke black or soot) (Strambeanu et al 2007, NATO 1988):



In addition, especially if carbon monoxide is present even in strictly limited concentrations, slow cooling involves other inevitable concurrent processes of reforming, through *de novo* or Loew synthesis, stable cyclic compounds of the carbohydrates and dioxin classes, in liquid and solid state respectively, that complete



the loading in particulate matter the flue gas flow.

Therefore, as far as the chemical composition is concerned, the gas released in the atmosphere during fuel gas combustion can be analyzed by interpreting three global parameters: VOC (TOC) (volatile or total organic carbon), particulate matter and carbon monoxide concentration. At the same time, the three parameters also characterize the quality of the combustion, since in oxygen-deficit combustion processes they increase significantly, proving that combustion is incomplete and as a result part of the fuel is lost in secondary and concurrent reactions (Lungu & Neculae 2014).

The reaction rates for the consecutive chemical processes of a complete combustion process (1–5) are given by the following system of first-order differential equations written under a matrix form (Abdi & Hojjati 2011):

$$\frac{d}{dt} \begin{bmatrix} C_A \\ C_X \\ C_Y \\ C_Z \\ C_B \end{bmatrix} = \begin{bmatrix} -k_1 & 0 & 0 & 0 & 0 \\ k_1 & -k_2 & 0 & 0 & 0 \\ 0 & k_2 & -k_3 & 0 & 0 \\ 0 & 0 & k_3 & -k_4 & 0 \\ 0 & 0 & 0 & k_4 & 0 \end{bmatrix} \begin{bmatrix} C_A \\ C_X \\ C_Y \\ C_Z \\ C_B \end{bmatrix} \quad (14)$$

or a scalar form:

$$\begin{cases} \frac{dC_A}{dt} = -k_1 C_A \\ \frac{dC_X}{dt} = k_1 C_A - k_2 C_X \\ \frac{dC_Y}{dt} = k_2 C_X - k_3 C_Y \\ \frac{dC_Z}{dt} = k_3 C_Y - k_4 C_Z \\ \frac{dC_B}{dt} = k_4 C_Z \end{cases} \quad (15)$$

A and B are the initial concentrations of alkanes and carbon dioxide produced in the gas flow. The last equation of the system is not a differential equation *per se*, and the initial conditions are the following:

$$C_A(0) = C_A^0, C_X(0) = C_Y(0) = C_Z(0) \text{ and } C_B(0) = 0 \quad (16)$$

Consequently, the solutions to these equations, namely the concentrations of the intermediates of the consecutive reactions can be written as follows:

$$C_A(t) = C_A^0 e^{-k_1 t} \quad (17)$$

$$C_X(t) = k_1 C_A^0 \left[\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right]$$

$$C_Y(t) = k_2 k_1 C_A^0 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_1 - k_3)(k_2 - k_3)} \right], \quad (18)$$

$$\begin{aligned} C_Z(t) = & k_3 k_2 k_1 C_A^0 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)(k_4 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)(k_3 - k_2)(k_4 - k_2)} + \right. \\ & \left. + \frac{e^{-k_3 t}}{(k_1 - k_3)(k_2 - k_3)(k_4 - k_3)} + \frac{e^{-k_4 t}}{(k_1 - k_4)(k_2 - k_4)(k_3 - k_4)} \right] \quad (19) \end{aligned}$$

$$C_B(t) = k_4 \int_0^t C_Z(\xi) d\xi = C_A^0 \left[1 - \frac{k_4 k_3 k_2 e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)(k_4 - k_1)} - \frac{k_4 k_3 k_1 e^{-k_2 t}}{(k_1 - k_2)(k_3 - k_2)(k_4 - k_2)} - \frac{k_4 k_2 k_1 e^{-k_3 t}}{(k_1 - k_3)(k_2 - k_3)(k_4 - k_3)} - \frac{k_3 k_2 k_1 e^{-k_4 t}}{(k_1 - k_4)(k_2 - k_4)(k_3 - k_4)} \right] \quad (20)$$

The kinetic model put forward in this paper is a linear, ideal one, solved with the Laplace transform method. It can be optimized, but it will no longer be linear. For this reason, an exact solution is impossible. However, the equations of the model can be solved with adequate numerical methods.

Experimental

The variation of the VOC concentration in flue gas includes all the volatile compounds of organic nature existing in the flue gas flow: alcohols, aldehydes (ketones), organic acids and the compounds resulted through the *de novo* syntheses in which carbon monoxide or the other volatile organic compounds take part.

In incomplete combustion systems (with oxygen deficit), the carbon monoxide concentration can become significant. Therefore, especially at temperatures between 200 and 600°C carbon monoxide can produce compounds with cyclical organic structures, some of which can harm the environment and the population's health. In a similar manner, in fuel gas combustion, the particulate matter concentration contains exclusively finely divided carbon produced by the carbon-producing reaction (8).

Figure 1 shows VOC variation with temperature at the start-up of a special waste industrial incineration plant fueled only with methane. As seen in this figure, the higher the temperature, the lower the VOC concentration in flue gas, due to the gradual reach of the operating temperature (600°C), at which VOC declines towards zero.

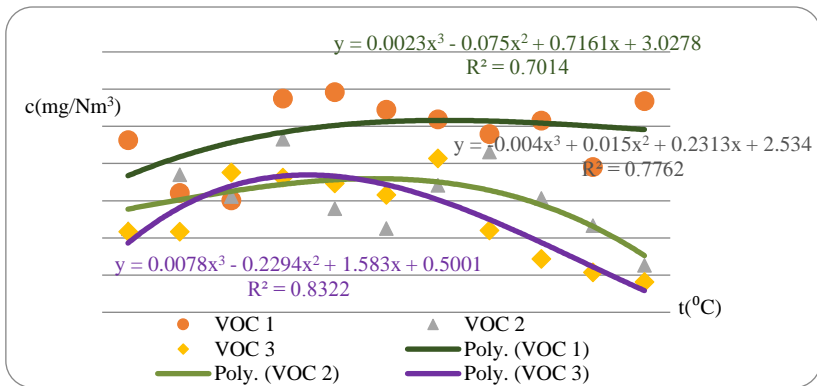


Figure 1. VOC variation with temperature at the start-up of a special waste industrial incineration plant fueled exclusively with methane

The representations of $VOC = f(t)$ values within the 100-600°C range, during three successive start-ups after maintenance works that required cooling the combustion

and post-combustion chambers of the incinerator in 2017, indicate that the variation of this parameter corresponds to a correlation coefficient acceptable to the modelling of a global characteristic parameter of an industrial process with a third-degree polynomial function having the following form:

$$y = ax^3 + bx^2 + cx + d \quad R^2 = 0.7014 - 0.8322 \quad (21)$$

As confirmed by the brief theoretical considerations above, VOC has maximum concentrations between 250 and 350°C. This shows that the mixture of partially oxidized methane fractions and fractions reformed through *de novo* and Loew synthesis or other parallel complex reactions reaches maximum values. At the same time, carbon monoxide has minimum values corresponding to the maximum VOC values, which characterizes its conversion to organic compounds (figure 2).

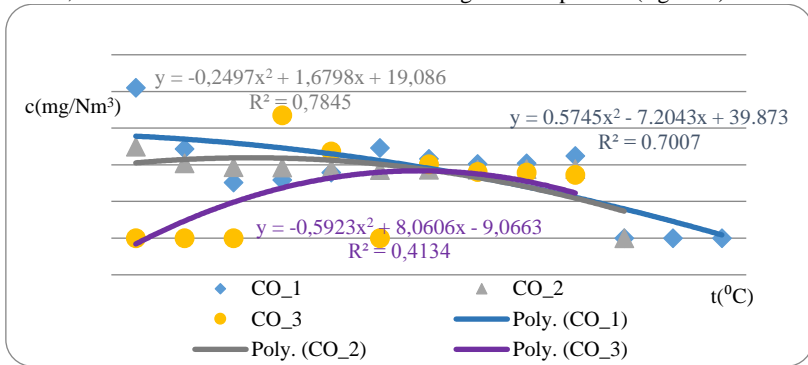
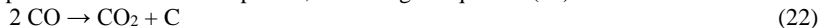


Figure 2. Variation of carbon monoxide concentrations in a special waste industrial incineration plant fueled exclusively with methane, during three successive cold start-ups after maintenance – data registered in 2017

The particulate matter concentrations reach maximum values within the same temperature range of 250–400°C. They can be formed both directly from methane through the carbon-producing reaction (8) and *de novo* forming, following a reaction parallel to the oxidation phases, according to equation (22):



It should be noted that both for carbon monoxide and particulate matter the concentration the variations represent second-degree polynomial curves with correlation coefficients varying between 0.0522 and 0.9364, acceptable to industrial applications.

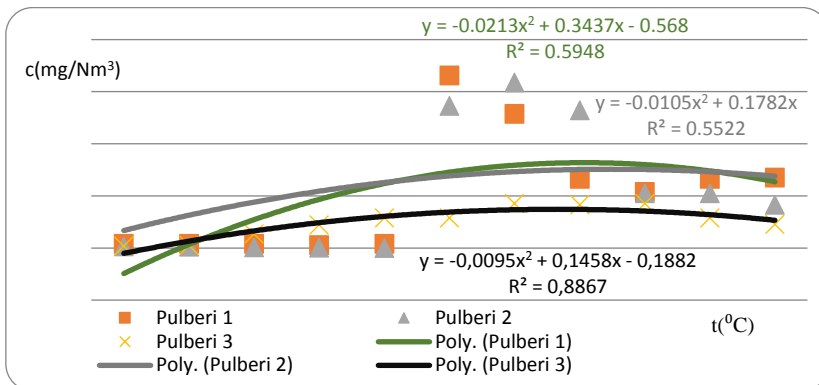


Figure 3. Variation of particulate matter concentration in a special waste industrial incineration plant fueled exclusively with methane, during three successive cold start-ups after maintenance – data registered in 2017

Conclusions

Fuel gas combustion involves consecutive and parallel reactions producing carbon oxidation intermediates whose oxygen concentration in the molecule increases successively and monotonously from 0 (the alkane phase) to values higher than 73% (the CO₂ phase). The successive oxidation reactions have first-order kinetics, but the succession of the registered reactions makes it impossible to solve the system of equations other than with numerical methods.

The parallel reactions occurring in gas hydrocarbons combustion produce reaction intermediates whose number increases with the decrease of the oxygen excess in the oxidation (combustion) phase. Nevertheless, it should be noted that however high the oxygen excess may be, fuel combustion is never total, as shown by the registered values of VOC, carbon monoxide and finely divided carbon (soot).

The experimental studies will continue with specific measurements of the VOC constitutive elements to reveal the parallel and consecutive mechanisms of the oxidation process of gas hydrocarbons combustion.

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