

Modelling the Formation of NO, NO₂, CO₂ and CO During Natural Gas Combustion in High-temperature Heating Chamber

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Abstract: The article presents the results of computer simulations of the formation of selected natural gas combustion products in a high-temperature heating chamber, which is a model of a pusher heating furnace. Calculations were performed using the licensed ANSYS CHEMKIN-PRO software. The mechanism selected for the calculations was one of the most commonly employed chemical mechanisms for methane combustion, namely GRI-Mech 3.0. The calculations were based on the perfectly stirred reactor (PSR). The result of the calculations was an estimation of the influence of the temperature and residence time on the chemical composition of the exhaust gases, in particular undesirable combustion products such as NO, NO₂, CO₂ and CO. The obtained results of numerical calculations can constitute the basis for diagnostics of the combustion process in terms of emitted pollutants, and may also be useful in taking actions aimed at optimizing the entire combustion process. Knowledge of the mechanisms of pollutant formation may also play an important role in the energy use of process gases, including those from the thermal conversion of waste.

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1 Introduction

Fuel combustion is the most important way of generating energy and at the same time the main source of pollutant emissions [1]. As numerous studies indicate, one of the fundamental problems related to the energetic combustion of fuels in high-temperature heating chambers (e.g. metallurgical heating furnaces for heating and heat treatment of the charge) is the emission of NO_x nitrogen oxides. Nitrogen oxides are considered one of the basic air pollutants because of their negative impact on the environment, i.e. their participation in the formation of smog, acid rain and ozone depletion in the upper layers of the atmosphere [2]. They are emitted mainly in the form of NO, NO₂ and N₂O. The main sources of NO_x formation are shown in Fig. 1 [3].

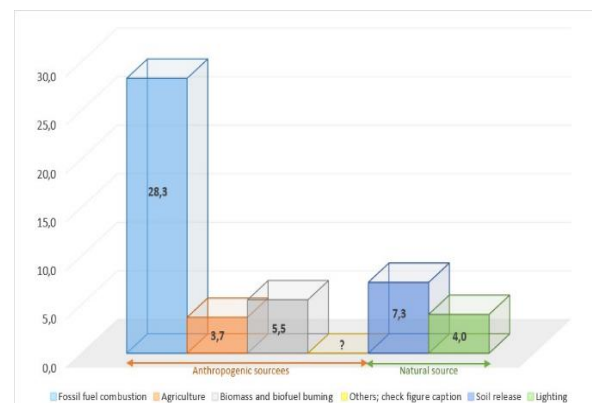


Figure 1 Sources of nitrogen oxide formation [3]

Among all anthropogenic sources, the largest share of NO_x emissions comes from the combustion of fossil fuels [3]. During combustion, most nitrogen oxides are produced in the form of nitrogen oxide NO (95 ÷ 99%), with a small share of nitrogen dioxide NO₂ (1 ÷ 5%). In

combustion technology, the concept of NO_x is used to refer to nitrogen oxides as a mixture of NO and NO_2 oxides [4][5]. The literature on the subject assumes the existence of several main mechanisms of NO_x formation, namely: [5][6][7][8]:

- Zeldovich (thermal)
- via N_2O
- via NNH
- prompt
- fuel

The thermal NO_x mechanism primarily refers to the combustion of gaseous fuels that do not contain chemically bound nitrogen. It is assumed that this mechanism occurs at temperatures above 1700 K, i.e. in most high-temperature heating processes [9]. The mechanism of NO formation via N_2O plays a particularly important role in the case of lean flames at temperatures below 1800 K. According to Gradonia [9], the extended thermal mechanism leads to NO formation up to three times faster than the Zeldovich mechanism. Nitric oxide can also be formed from nitrogen contained in the air using the so-called prompt mechanism, called flame [6]. It takes place at low temperatures (below 1400 K), for rich mixtures and for short residence times. It occurs in the initial stage of combustion, leading to the formation of stable nitrogen compounds such as NH, HCN, H_2CN and CN, which are in turn oxidized to NO. This mechanism was first identified by Fenimore. He then stated that NO is formed at an early stage in the flame (the highest concentration of hydrocarbon radicals occurs in the flame reaction zone) as a result of the attack of hydrocarbon free radicals in the N_2 atmosphere. Prompt nitrogen oxides are formed due to a relatively quick reaction between nitrogen radicals, oxygen and hydrocarbons. Hydrocarbon radicals are intermediate compounds produced during the combustion process. The mechanism of prompt NO_x formation usually plays an important role in the lower temperature of the combustion process.

The results of the authors' own research [10][11][12] clearly indicate that the mechanism of nitrogen oxide formation in high-temperature heating chambers is extremely complex, and its detailed understanding requires not only extensive experimental research, but above all, extensive theoretical studies employing modern computational tools. The most common programs used to model the course of gas-dynamic and chemical phenomena include: CHEMKIN, KIVA, STANJAN, CANTERA and others [13][14][15]. According to literature data, one of the most widely utilised programs for modelling chemical phenomena is the ANSYS CHEMKIN-PRO program proposed in article [16]. The capabilities of this software are demonstrated by the wide scope of its use in many industries (e.g. automotive) as well as global scientific and research centres, including the National Aeronautics and Space Administration (NASA) [17][18].

2 Research methodology

The GRI-Mech mechanism, version 3.0, the most widely used in the literature, was employed in the numerical calculations. The perfectly stirred reactor was chosen for the calculations, among others, owing to the fact that in real conditions the issue of exhaust gas flow is an intermediate state, between perfectly stirred and plug flow. This is because of the fact that in plug flow reactors there is always the phenomenon of mixing the streams in the direction of the flowing exhaust gases (longitudinal mixing) [19]. The calculations were performed for a cylindrical heating chamber with an internal diameter of 0.12 m and a length of 3.0 m, which is a model of a pusher furnace. The flow parameters were determined in laboratory conditions and implemented for the calculations, namely:

- gas flow: $0.00045 \text{ m}^3 \cdot \text{s}^{-1}$
- air flow: $0.004906 \text{ m}^3 \cdot \text{s}^{-1}$

The following were assumed for the calculations:

- temperature range from 1000 to 2200 K
- residence time $0.0001 \div 0.02 \text{ s}$
- natural gas composition: $\text{CH}_4=97.8\%$;
 $\text{C}_2\text{H}_6=1\%$; $\text{N}_2=1\%$; $\text{CO}_2=0.2\%$.

3 Calculation results

The calculation results were presented as a function of the residence time and temperature. The figures were made in the graphic post-processor of the ANSYS CHEMKIN-PRO program. For all the calculations, the same number of "nodes" was assumed, equal to 50.

The calculations indicate that as the residence time increases, the mole share of nitrogen oxides rises, while the share of CO decreases. From the ecological point of view, in order to burn carbon monoxide to a safe level (i.e. 0.004%), it is necessary to extend the residence time to 1 s. Fig. 2 shows that the initiation of nitric oxide formation takes place in a very short residence time, shorter than that assumed in the calculations. In order to precisely estimate the time in which NO is formed, additional calculations were performed, as a result of which it was determined that NO is formed in the range from 0.00001 s to 0.0002 s. As for the share of nitrogen dioxide (NO_2) in the exhaust gases, as can be seen in Fig. 2 d), the share of this compound grows with the increase in residence time. A similar situation occurs for N_2O . In addition to the residence time, the combustion temperature also plays an important role in the chemical analysis of the phenomena occurring during the combustion process.

The combustion temperature is closely related to the air-to-fuel mass ratio (excess air coefficient λ). The temperature of the heated air also determines the combustion temperature.

As can be seen from Fig. 3, the share of nitrogen oxide, in a certain temperature range, increases with the

rise in combustion temperature for all the analysed residence times. The shorter the residence time and the lower the combustion temperature, the smaller its share. In shorter residence times, i.e. 0.001 s and 0.01 s, nitric oxide begins to form at a temperature of approximately 1430 K. This is a very valuable observation, taking into account the fact that the literature on the subject

estimates the formation temperature of so-called thermal nitrogen oxides at levels above 1523 K and even 1623 K [20], which is confirmed for longer residence times, i.e. 0.1 and 1 s.

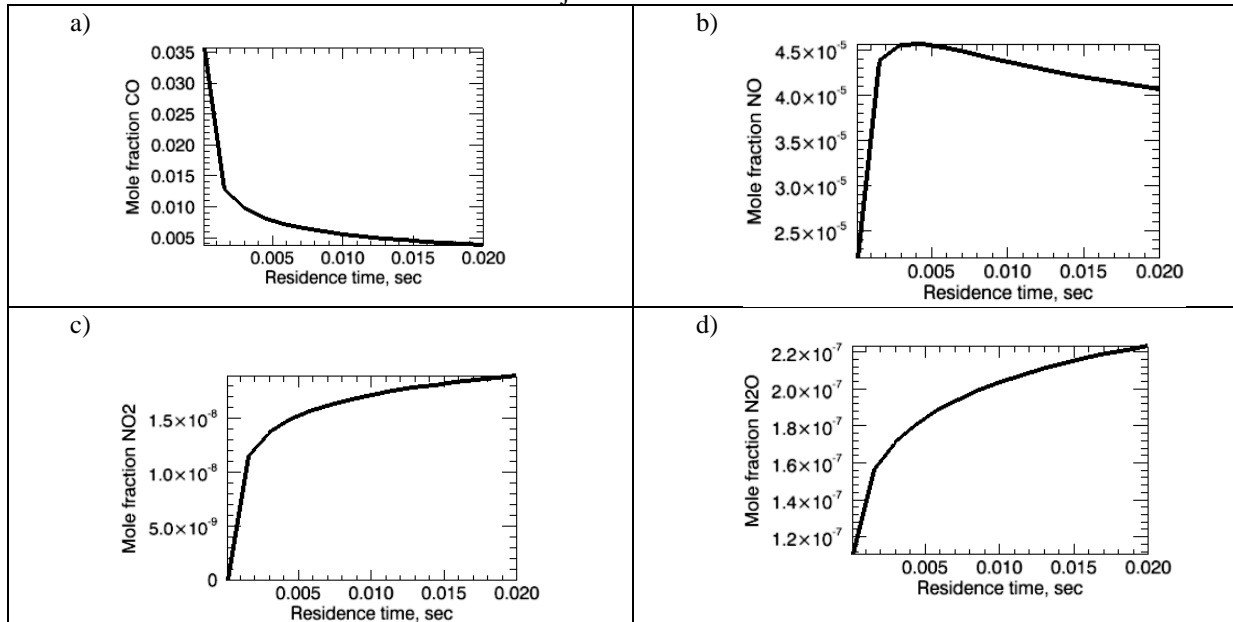


Figure 2 Influence of residence time on mole fraction of a) CO; b) NO; c) NO₂; d) N₂O in exhaust gases (combustion temperature 1763 K).

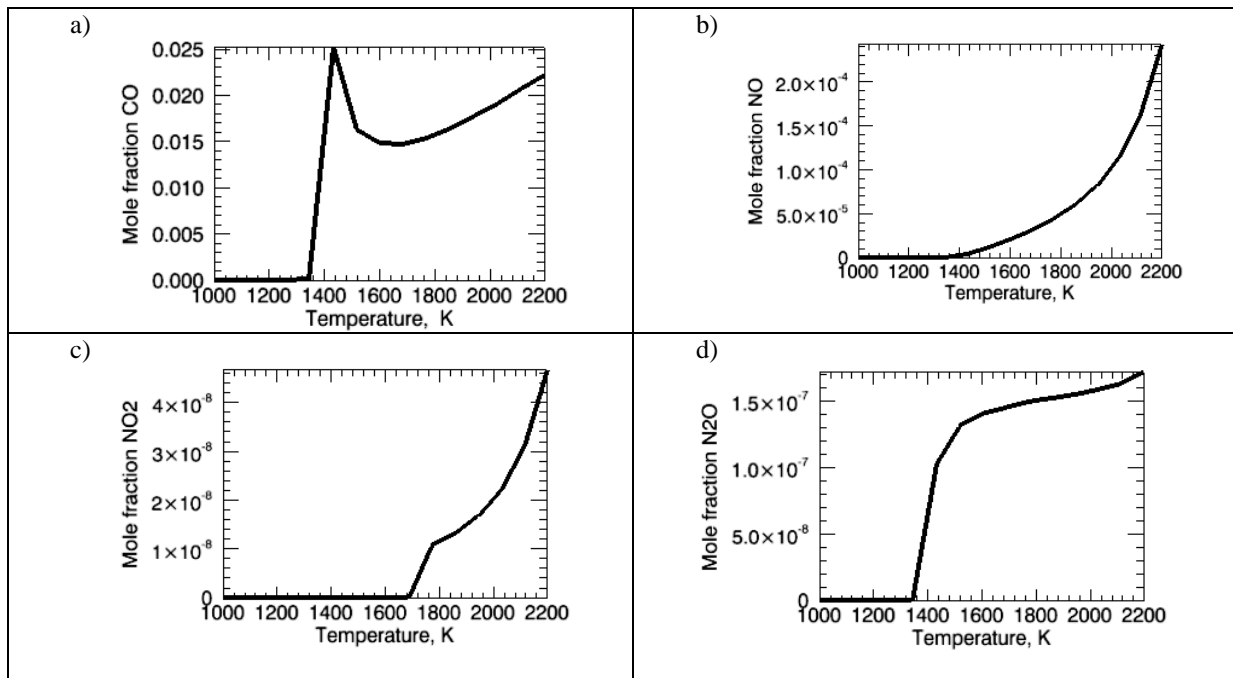


Figure 3 Effect of temperature on mole fraction of a) CO; b) NO; c) NO₂; d) N₂O in exhaust gases (residence time 0.001 s)

4 Summary and conclusions

The computer simulation results presented in this article demonstrated the wide possibilities of using ANSYS CHEMKIN-PRO software in predicting the chemical composition of exhaust gases. For selected combustion products of one of the most common gas fuels, namely natural gas, the mechanisms of the formation of important combustion products, such as CO, NO, NO₂ and N₂O, were explained. Without knowledge of the above-mentioned mechanisms, it is not possible to undertake optimization activities aimed at minimizing the amount of harmful combustion products while maintaining the technological regimes of the process. The results of the computer simulations indicate that the longer the reactants stay in the high temperature zone, the lower the mole share of carbon monoxide. The opposite situation is observed for nitrogen oxides, the share of which grows with increasing residence time. It was noticed that carbon monoxide needs a relatively long time to oxidize. It was estimated that the time needed for a partial, but ecologically satisfactory level of oxidation of CO to CO₂ is equal to 1 s for a combustion temperature of 1763 K. In analysing the influence of temperature on the formation of selected pollutants, it was noticed that high temperature favours the formation of thermal nitrogen oxides in the analysed residence time range. Moreover, the formation of NO involves the mechanism of its formation via N₂O, examined in detail in [19] and [20]. This mechanism becomes important behind the flame front, in the zone of the highest temperatures. The amount of NO emissions is then determined by the combustion temperature and the concentration of oxygen and nitrogen in the reaction zone.

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