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KINETIC ANALYSIS OF CO FORMATION UNDER OXY-COMBUSTION CONDITIONS

KINETYCZNA ANALIZA POWSTAWANIA CO W WARUNKACH OKSY-SPALANIA

Abstract: The paper reports the results of numerical computations concerning the formation of CO in the kinetic flame during natural gas oxy-combustion. The effect of temperature, reagent residence time and the composition of an atmosphere containing CO₂ with 21 and 29 vol % O₂ on the variation of CO concentration in the flame was examined. The oxy-combustion process was conducted with a 25 % excess oxygen. The analysis of reactions in flames at temperatures of 1500 K and 1800 K was performed within the Chemked II program using the combustion mechanism proposed by Mendiara & Glarborg, which includes 779 reactions. The computation results have confirmed that the rate of the key reactions responsible for the production of CO in the flame depends on the flame temperature and the oxy-combustion temperature. The peak CO concentrations are higher for the oxidizing mixture containing 29 vol % O₂. After attaining a maximum, the CO flame concentration drops faster for an atmosphere richer in oxygen. The longer the time of reagent residence in the flame region, the lower the CO concentration. In different atmospheres and at different combustion temperatures, an identical CO level can be achieved in wet combustion gas. Irrespective of the temperature and atmosphere of oxy-combustion, most CO is produced as a result of the reaction $\text{OH} + \text{CO} \rightleftharpoons \text{HCO}_2$. The reduction of oxygen in the oxidizing atmosphere at flame temperatures of 1500 and 1800 K lowers the CO production in the dominant reactions responsible for CO formation. The contribution of individual reactions in the CO production for the identical atmospheres is different with varying temperature. In the case of the reaction $\text{HCO} + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{CO}$, the temperature increase reduces the CO production. A reverse dependence of CO production on temperature characterizes the reaction $\text{H}_2 + \text{CO} + \text{M} \rightleftharpoons \text{CH}_2\text{O} + \text{M}$. In addition, change in temperature changes the order in which the dominant reactions occur. Within the residence time equal to 100 ms, two periods of intensified CO production and consumption can be identified. The peak concentrations of H, OH and O radicals in the flame attain a maximum within the same time; as time goes by, the highest concentration is achieved by OH radicals. The presence of considerable levels of CO₂ in the combustion substrates has an inhibiting effect on the natural gas oxidation process.

Keywords: oxy-combustion, flame CO concentration, combustion kinetics

Introduction

In the face of increasing concerns about climatic changes resulting from greenhouse gas emissions, CO₂ capture and storage technologies are the subject of intensive studies

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in Poland [1–3]. One of the techniques facilitating CO₂ capture is oxy-combustion. The source of oxygen may be a carrier, *eg* NiO during fluidized-bed combustion [4] or air. In view of the too high temperature of combustion in oxygen, its dilution with CO₂ is used. The combustion gas from oxy-combustion consists mainly of carbon dioxide and water vapour, and the capture of CO₂ is done by condensing the water vapour. The combustion gas carbon dioxide can be partially recycled and reintroduced to the combustion chamber as a cooling medium. Studies on the addition of CO₂ to methane are focused on the supply of gas turbines with the CH₄-CO₂ mixture. The CH₄-CO₂ mixture may originate from the anaerobic fermentation of biomass or organic industrial wastes [5].

The total elimination of nitrogen from the oxy-combustion process is impossible due to the insufficient oxygen purity, combustion chamber leakage or the nitrogen content of fuel. Nevertheless, oxy-combustion allows the NO_x concentration to be reduced as low as to 50 % compared to air combustion [6].

Substituting N₂ with CO₂ in the combustion mix (as compared to air) has an effect on, *eg*: adiabatic flame temperature, combustion rate, flame stability, the transfer and thermal properties of combustion gas, the rate of chemical reactions and heat radiation.

As the specific heat of CO₂ is higher than that of N₂, more energy is needed for raising the temperature of the mixture. Therefore, for the same oxygen fraction of the oxidizer and excess air, the adiabatic flame temperature in the CO₂/O₂ mixture is lower than in N₂/O₂ [7]. To achieve the identical temperature as for air, a higher percentage oxygen fraction of the oxidizer will be needed for oxygen combustion.

For each oxygen-fuel flame, an operation zone can be determined. Four critical problems are distinguished, which may limit the flame operation zone; these are: flameout, burner flashback, combustion instability and spontaneous ignition. Also pressure fluctuations caused by heat release in the combustion chamber may contribute to instability in oxy-combustion [8].

Glarborg and Bentzen [9] interpreted experimental results using a detailed mechanism of hydrocarbon oxidation. They have concluded that the high CO₂ concentration around the burner prevents the complete oxidation of fuel at temperatures higher than 1200 K, in spite of the presence of oxygen. The increased CO concentration in oxy-combustion flue gas is explained by the reactions of CO₂ with free radical and the dissociation of CO₂ [9–15]. Carbon monoxide forms, *inter alia*, as a result of the reaction of CO₂ with:

a) hydrogen radicals:



which competes with the reaction:

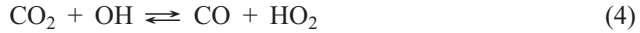


for H radicals. Reaction (1) proceeds relatively fast, even at lower temperatures. In that case, the concentration of H and O radicals in the flame is reduced, which is associated with a drop in the fuel combustion rate [12].

b) oxygen radicals:



c) hydroxide radicals:



The reactions of CO_2 with O and OH radicals are too slow to be able to play a significant role.

d) hydrocarbon radicals:



These reactions have no significant importance due to the low contents of these radicals of natural gas flame. Hydrocarbon radicals containing one carbon atom are less reactive than those containing two carbon atoms, such as HCCO.

The double bonds existing between the carbon and oxygen atoms in CO_2 make the thermal dissociation of CO_2 difficult. At high temperatures, the reaction of thermal dissociation of CO_2 (which is strongly endothermic) may occur in the presence of a high-energy body, M:



The above-mentioned reaction occurs in the flame and in the after-flame zone, depending on the burner and combustion chamber designs. The examination of the peak concentrations of reagents in the flame in the combustion process are of key importance. Experiments and numerical computations carried out using three different combustion mechanisms have shown that the peak CO concentrations in the flame during methane combustion in air increase with increasing CO_2 addition to the air-fuel mixture [10].

The effect of oxy-combustion stoichiometry and the reagent residence time are also reflected in the combustion gas CO level [14]. With the reduction of the reagent combustion chamber residence time, a rise in CO concentration and an increase in temperature occur.

Combustion kinetics

The description of reactions occurring in the flame is extremely difficult and depends on numerous factors, such as temperature, pressure, burner type, fuel and oxidizing mixture compositions, etc. Depending on the number of reagents and their stoichiometric coefficients, first-, second- and third-order reactions are distinguished.

For the general notation of the reaction:



whose order can be expressed as follows:

$$m = \sum_{i=1}^n v'_{ij} \quad (10)$$

the reaction rate constant for an any-order reaction running to the right, k_f , or to the left, k_r , is determined using the modified Arrhenius equation:

$$k = AT^\beta e^{-\frac{E_a}{RT}} \quad (11)$$

The resultant rate of production of the component Z_i is the sum for the reaction “j” running to the left-hand and the right-hand direction, respectively:

$$\left(\frac{d\{Z_i\}}{dt} \right)_j = (v''_{ij} - v'_{ij}) [k_f \Pi_i \{Z_i\}^{v'_{ij}} - k_r \Pi_i \{Z_i\}^{v''_{ij}}] \quad (12)$$

The total rate of production of the component Z_i is determined by summing all reactions:

$$\frac{d\{Z_i\}}{dt} = \sum_{j=1}^N \left(\frac{d\{Z_i\}}{dt} \right)_j \quad (13)$$

The concentration is denoted with the brace $\{ \}$. In the presented calculation results, the concentration is expressed in moles per unit of reaction product mass in the reactor under examination [16].

The mechanism of combustion of hydrocarbons consists of many consecutive, as well as overlapping, elementary reactions of different rates. The reactions describe combustion stages, such as the attack on the fuel molecule, the formation of a “bank” of radicals, the recombinations of radicals, oxidation, etc. Several dozen detailed models dedicated to the combustion of solid, liquid and gaseous fuels function in the literature on the subject. Detailed combustion mechanisms have been developed based on the following experimentally determined values: the coefficients of the gaseous phase reaction rate constant, laminar combustion rates, laminar flame concentration variation profiles, and ignition delay times. The most common natural gas combustion mechanisms include: GRI-Mech [17] and those developed by Konnov [18] and Mendiara, Glarborg [19]. The above-mentioned reaction mechanisms differ in the number of reactions, chemical compounds and elements and the values of activation energy E_a and the constants A , β .

Computation data and procedure

Modelling of the natural gas combustion kinetics was performed in the present study within the Chemked II software program, version 3.5.2 [20], using the combustion mechanism proposed by Mendiara, Glarborg [19] and an extended thermodynamic

database [17]. The combustion mechanism includes 779 elementary reactions between 97 chemical compounds. The ideal mixing of the combustion substrates in the burner was assumed for the computation. The solver of the program Chemked II uses the thermodynamic database [17].

The computation was conducted for flame temperatures of 1500 K and 1800 K with a constant pressure of $p = 0.1$ MPa. The reagent flame residence was 100 ms. The examined temperature values were achieved by averaging the results of temperature measurements done in the flame of a low-swirl kinetic burner installed in the combustion chamber. The results of the above-mentioned tests have not been published yet. The natural gas composition was as follows: $\text{CH}_4 = 98$ %; $\text{C}_2\text{H}_6 = 0.6$ %; $\text{C}_3\text{H}_8 = 0.3$ %; $\text{N}_2 = 1$ %; $\text{CO}_2 = 0.1$ %. Oxy-combustion with a 25 % excess oxygen was conducted. The following oxy-combustion atmospheres were examined: 21 % O_2 /79 % CO_2 and 29 % O_2 /71 % CO_2 . Constant values of natural gas and oxygen were examined. The computation was started from the mixture 29 % O_2 /71 % CO_2 and then CO_2 was added, thus causing, at the same time, a decrease in the oxygen fraction and an increase in mixture mass.

Computation results

The presented concentrations of free radicals and carbon monoxide relate to wet combustion gas and are expressed in moles of the substance per 1 gram of the reaction product. Figure 1 represents the profiles of CO flame concentration variations as a function of temperature and oxidizing mixture composition. As follows from the

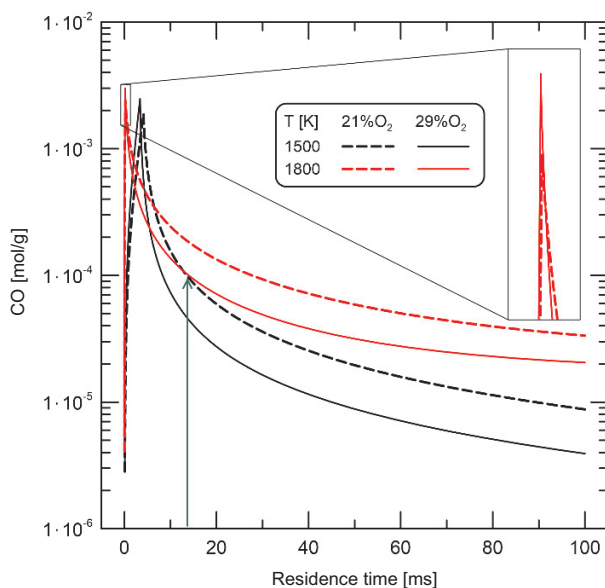


Fig. 1. CO flame concentration as a function of residence time

figure, the peak CO concentrations are higher for the oxidizing mixture containing 29 vol. % O_2 . After attaining the maximum, the CO flame concentration drops faster for the atmosphere richer in oxygen. The longer the time of reagent residence in the flame region, the lower the CO concentration. In different atmospheres and at different combustion temperatures, an identical CO content of wet combustion gas can be obtained, as displayed in the diagram for a residence time of approx. 13 ms.

For each of the considered oxy-combustion variants, the key reactions responsible for CO production in the kinetic flame are detailed in Figs. 2a–d. The term CO production

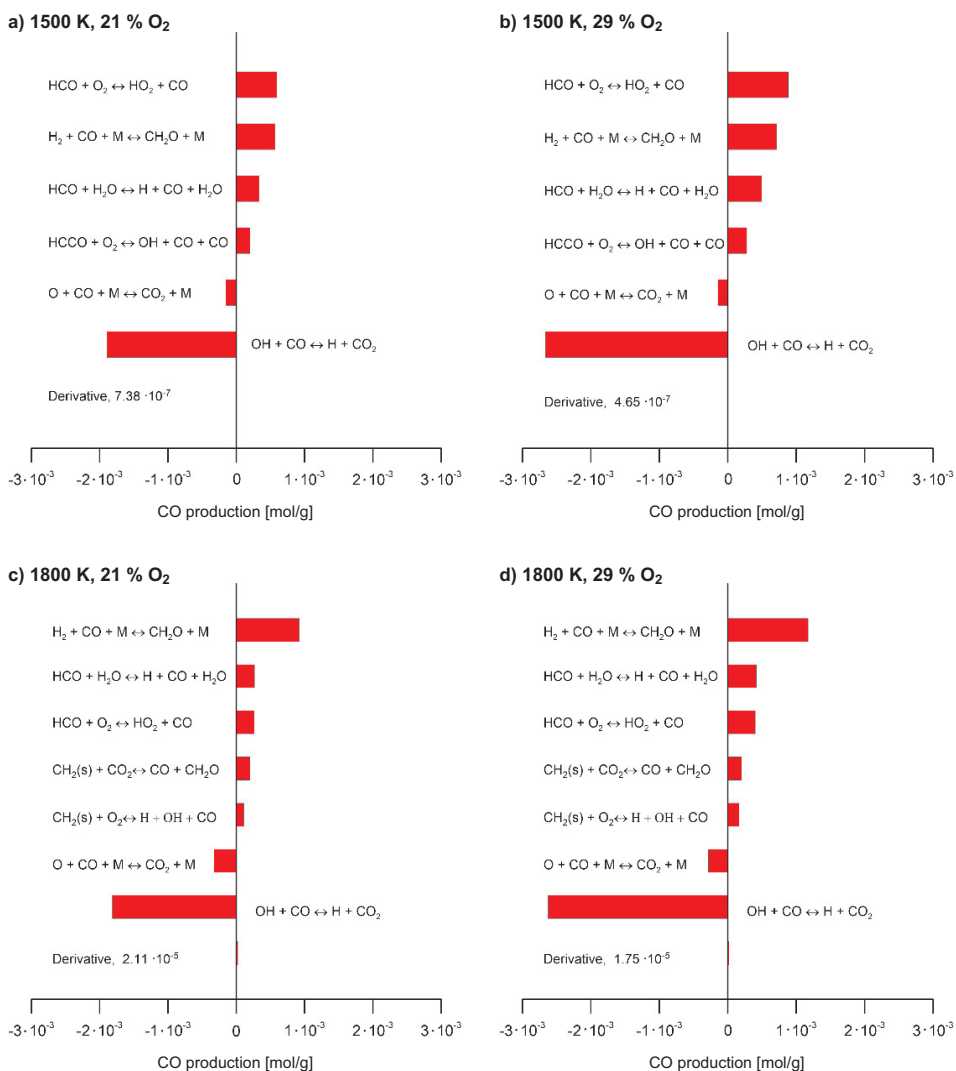


Fig. 2. The key reactions of CO formation for $\lambda = 1.25$ as a function of temperature and atmosphere composition: a) 1500 21 % O_2 ; b) 1500 29 % O_2 ; c) 1800 21 % O_2 ; d) 1800 29 % O_2

should be understood as the number of CO moles contained in 1 gram of products within a residence time of 100 ms.

Irrespective of temperature and combustion atmosphere, most CO is produced as a result of the reaction $\text{OH} + \text{CO} \rightleftharpoons \text{H} + \text{CO}_2$. The reduction of oxygen in the oxidizing atmosphere at flame temperatures of 1500 and 1800 K lowers the CO production in the predominant reactions responsible for CO formation. The contribution of individual reactions in the CO production for the identical atmospheres is different with varying temperature. For the reaction $\text{HCO} + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{CO}$, the increase in temperature reduces the CO production and lowers the position held (from 2 to 4). A reverse dependence of CO production on temperature characterizes the reaction $\text{H}_2 + \text{CO} + \text{M} \rightleftharpoons \text{CH}_2\text{O} + \text{M}$. In addition, changing the temperature from 1500 K to 1800 K results in a new reaction, $\text{CH}_{2(s)} + \text{O}_2 \rightleftharpoons \text{H} + \text{OH} + \text{CO}$, to arise in the fifth position in place of the reaction $\text{HCCO} + \text{O}_2 \rightleftharpoons \text{OH} + \text{CO} + \text{CO}$.

The overall CO production/consumption rate, in accordance with Eq. (13) for the considered oxy-combustion variants, is illustrated in Fig. 3. Within the examined residence time, two periods of intensified CO production and consumption can be identified. Figure 3 highlights the differences in the overall reaction rate associated with the change in the temperature and O_2/CO_2 atmosphere.

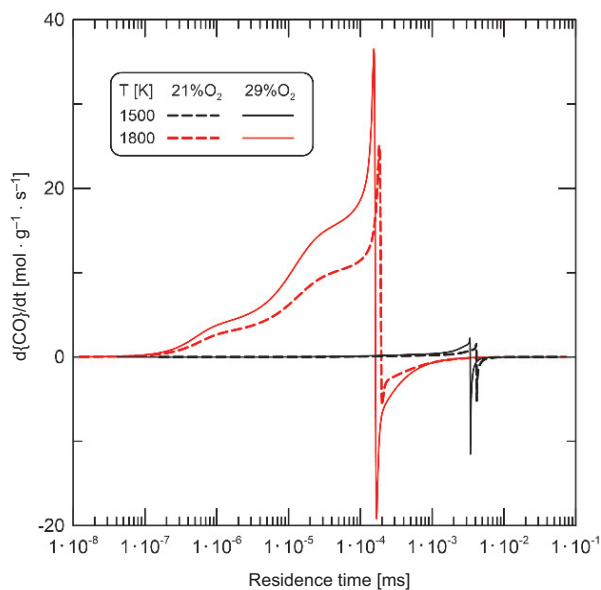


Fig. 3. Variations in CO production rate in time

The selected reactions may occur due to the formation of a free radical “bank”. According to the reaction (1) proceeding in the left-hand direction, the H radicals are used, while OH radicals form. The peak concentrations of H, OH and O radicals attain a maximum within a time identical to that shown in Fig. 4. After a duration of 12 ms, there are most OH radicals in the flame.

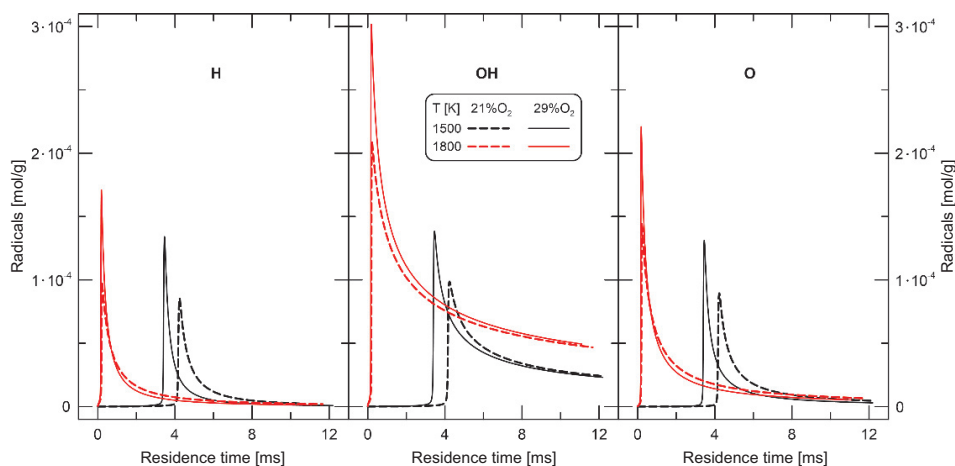


Fig. 4. The peak concentrations of H, OH and O in the flame

Conclusions

The interpretation of the computation results for natural gas oxy-combustion in atmospheres containing CO₂ and 21 % O₂ and 29 % O₂ has enabled the following conclusions to be drawn:

1. The peak CO concentrations are higher for the oxidizing mixture containing 29 vol % O₂. After attaining the maximum, the CO flame concentration drops faster for the atmosphere richer in oxygen.
2. The longer the time of reagent residence in the flame region, the lower the CO concentration.
3. Many reactions are responsible for the formation of CO in the flame, with the primary being $\text{OH} + \text{CO} \rightleftharpoons \text{H} + \text{CO}_2$. A reaction classified as second in terms of CO formation rate is $\text{HCCO} + \text{O}_2 \rightleftharpoons \text{OH} + \text{CO} + \text{CO}$.
4. Irrespective of temperature and combustion atmosphere, most CO is produced as a result of the reaction $\text{OH} + \text{CO} \rightleftharpoons \text{H} + \text{CO}_2$.
5. The reduction of oxygen in the oxidizing atmosphere at flame temperatures of 1500 and 1800 K lowers the CO production in the predominant reactions responsible for CO formation.
6. The contribution of individual reactions in the CO production for the identical atmospheres is different with varying temperature. For the reaction $\text{HCO} + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{CO}$, the increase in temperature reduces the CO production and lowers the position held.
7. Carbon monoxide forms very fast in the flame in the oxy-combustion process, as indicated by its maximum concentrations in the vicinity of the burner. However, the oxidation of carbon monoxide to CO₂ is much slower, which is due to the decrease in the CO molar fractions with increasing residence time.
8. The peak concentrations of H, OH and O radicals attain a maximum within the same.

Nomenclature

- A – pre-exponential factor [$(\text{cm}^3 \cdot \text{mol}^{-1})^{m-1} \cdot \text{s}^{-1}$]
 E_a – activation energy of a chemical reaction [$\text{J} \cdot \text{mol}^{-1}$]
 j – number of reactions,
 k – reaction rate coefficient [$(\text{cm}^3 \cdot \text{mol}^{-1})^{m-1} \cdot \text{s}^{-1}$]
 m_i – order of a reaction [-]
 M – third body [-]
 R – ideal gas constant [$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$]
 T – temperature [K]
 Z_i – chemical symbol “i”
 β – temperature exponent of the pre-exponential factor [-]
 λ – excess of oxygen [-]
 v'_i – the stoichiometric ratio of the substrate “i” in the reaction “j” [-]
 v''_i – the stoichiometric ratio of the product “i” in the reaction “j” [-]

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KINETYCZNA ANALIZA POWSTAWANIA CO W WARUNKACH OKSY-SPALANIA

Akademia Górniczo-Hutnicza w Krakowie

Abstrakt: W pracy zaprezentowano wyniki obliczeń numerycznych dotyczących tworzenia CO w kinetycznym płomieniu podczas oksy-spalania gazu ziemnego. Badano wpływ temperatury, czasu przebywania reagentów oraz składu atmosfery zawierającej CO₂ i 21 oraz 29 % obj. O₂ na zmianę stężenia CO w płomieniu. Proces oksy-spalania prowadzony był z 25 % nadmiarem tlenu. Analizę reakcji w płomieniach o temperaturach 1500 i 1800 K przeprowadzono w programie Chemked II, z zastosowaniem mechanizmu spalania zaproponowanego przez Mendiara, Glarborg zawierającego 779 reakcji. Wyniki obliczeń potwierdziły, że szybkość najistotniejszych reakcji odpowiedzialnych za tworzenie CO w płomieniu zależy od temperatury płomienia oraz atmosfery oksy-spalania. Szczytowe stężenia CO są większe dla mieszanki utleniającej zawierającej 29 % obj. O₂. Po osiągnięciu maksimum, stężenie CO w płomieniu spada szybciej dla atmosfery bogatszej w tlen. Im dłuższy czas przebywania reagentów w obszarze płomienia, tym niższe stężenie CO. W różnych atmosferach oraz temperaturach spalania można uzyskać identyczny poziom CO w spalaniach mokrych. Bez względu na temperaturę oraz atmosferę oksy-spalania każdorazowo najwięcej CO utworzone zostaje w wyniku reakcji $\text{OH} + \text{CO} \rightleftharpoons \text{H} + \text{CO}_2$. Redukcja tlenu w atmosferze utleniającej przy temperaturach płomienia wynoszących 1500 i 1800K obniża produkcję CO w dominujących reakcjach odpowiedzialnych za tworzenie CO. Wkład poszczególnych reakcji w produkcję CO dla tych samych atmosfer ze zmianą temperatury płomienia jest zróżnicowany. W przypadku reakcji $\text{HCO} + \text{O}_2 \rightleftharpoons \text{HO}_2$ CO wzrost temperatury zmniejsza produkcję CO. Odwrotna zależność produkcji CO od temperatury charakteryzuje reakcję $\text{H}_2 + \text{CO} + \text{M} \rightleftharpoons \text{CH}_2\text{O} + \text{M}$. Dodatkowo zmiana temperatury zmienia kolejność dominujących reakcji. W zakresie czasu rezydencji równego 100 ms wyróżnić można okresy wzmoczonego tworzenia oraz zużywania CO. Szczytowe stężenia rodników H, OH i O w płomieniu osiągają maksimum w tym samym czasie, a w miarę jego upływu najwyższe stężenie posiadają rodniki OH. Obecność znacznych ilości CO₂ w substratach spalania ma działanie hamujące proces utleniania gazu ziemnego.

Słowa kluczowe: oksy-spalanie, stężenie CO w płomieniu, kinetyka reakcji