

THE INFLUENCE OF OH FREE RADICAL ON CO CONCENTRATION IN BURNING GASES FROM MIXTURES CH₄-AIR

M. MARINESCU¹ D. STANCIU¹ C. IONITA¹

Abstract: The burning process of hydrocarbon fuels includes some active radicals through OH, which has an important role in reduction of carbon monoxide. Beyond the temperature 1300K, if temperature gradient is about 1,32 K/ms, the small concentrations of CO decrease to zero

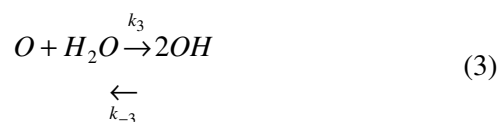
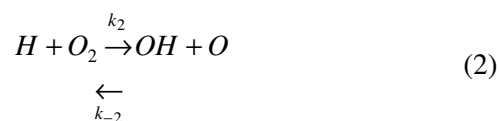
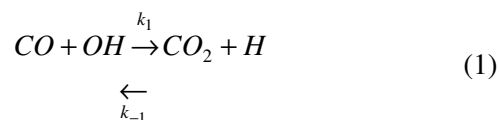
Keywords: Radical, Carbon monoxide, temperature gradient.

1. Introduction

The great share of combustion processes in which CH₄ is the major component, led to the fact that the scientific research regarding the real mechanism of chemical reactions to be considered of a significant importance. In the chain of intermediate reactions and formation of temporary products, CO represents a very dangerous component for alive organisms. The percentage share of the carbon monoxide in the evacuated gases from the burning equipment is ranged between 0 and 2%, and for the internal burning engines – in transition regimes, between 1 and 8 per cent. Although the combustion gases exhausted in atmosphere have a semnificant decline of CO – obtained by diffusion, danger of intoxication with CO may also appears in very low concentration of 0,025 per cent, corresponding to a 30% saturation of hemoglobine with CO. The very strong toxic of CO leads to a maximum limit of concentration in atmosphere of only 50 ppm (0,005%), compared – for example, with CO₂ which has a limit of 5000 ppm (0,5%).

2. Kinetic Model

Acording to model and conclusions of Sootmaekers and Van Tiggelen [2], the oxidation of relative small CO concentrations in burning gases (1...2%), at temperatures of (1100-1700)°C follow to reactions model:



The kinetic model shows the role of OH radicals on the reduction of CO and there fore the possibility of reappearance of OH radical.

¹ Dept. of Thermodynamics, University *Politehnica* of Bucharest

3. Theoretical Results

Taking into consideration the fact that initial CO percentage in the burning gases can exceed the equilibrium concentration, it results that the reduction speed of CO concentration is given by:

$$-\frac{d[CO]}{dt} = k_1[OH][CO] - [CO]_{ech} \quad (4)$$

where $[CO]$, $[OH]$ and $[CO]_{ech}$ represents component concentrations, t -time and k_1 – equilibrium constant of reaction (1).

The equilibrium concentration $[CO]_{ech}$ results from the mas action law for reactions (1)...(3), and is:

$$[CO]_{ech} = \frac{k_{-1}k_{-2}k_{-3}[CO_2][OH]^2}{k_1k_2k_3[O_2][H_2O]} \quad (5)$$

where k_1, \dots, k_3 are the equilibrium constants of direct and revers reactions (1), (2) and (3).

By introducing the expression of equilibrium concentration $[CO]_{ech}$ in relation (4), and using the notation:

$$\alpha = -\frac{d[OH]}{dt} \cdot \frac{1}{k_1[OH]^2} \quad \alpha \in (0, \infty) \quad (6)$$

it is obtained:

$$\alpha \frac{d\left\{\frac{[CO]}{[CO]_{ech}}\right\}}{\frac{[CO]}{[CO]_{ech}}} = -\frac{d[OH]}{[OH]} \quad (7)$$

For the value $\alpha = 0$, it is results the radical concentration $[OH] = 0$, and for

$$\alpha = \infty \text{ it is obtained } \frac{[CO]}{[CO]_{ech}} = 1.$$

Coming back to relation (4), by separating variables, it is obtained:

$$\frac{d\left\{\frac{[CO]}{[CO]_{ech}}\right\}}{\frac{[CO]}{[CO]_{ech}}} = -k_1[OH] \cdot dt \quad (8)$$

By integration, considering that values for k_1 and $[OH]$ remain constant:

$$\ln\left\{\frac{[CO]}{[CO]_{ech}} - 1\right\} = -k_1[OH] \cdot t + ct. \quad (9)$$

From this, according to Fig.1 it is results a linear decreasing of expression

$\ln\left\{\frac{[CO]}{[CO]_{ech}} - 1\right\}$ in time, and $[OH]$ radical determining a decline of initial CO concentration.

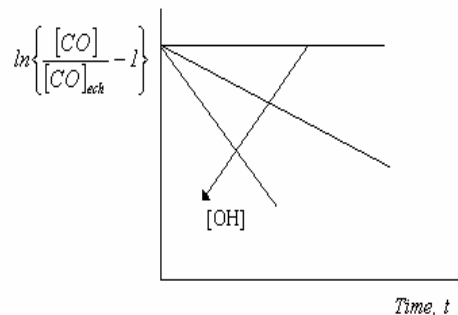


Fig. 1. Time dependence of

$\ln\left\{\frac{[CO]}{[CO]_{ech}} - 1\right\}$ expression

If considering that the equilibrium constant k_1 is given by the relation $k_1 = 5,6 \cdot 10^{11} \exp(-4,25/RT)$ [3], it results that $\ln\left\{\frac{[CO]}{[CO]_{ech}} - 1\right\}$ depends on time, temperature and $[OH]$ concentration.

Accepting a minimum value of temperature of cca 1100°C at which

formation of OH radical take place an equilibrium concentration of $[OH]=0,16$ ppm and considered that initial concentration of $[CO]$ of about 10 times greater than the equilibrium concentration $\frac{[CO]}{[CO]_{ech}} = 10$ at the temperature $T=1373K$, from Fig.2 results:

$$tg\beta = -5,6 \cdot 10^{11} \exp(-4,25/RT) \cdot [OH] \quad (10)$$

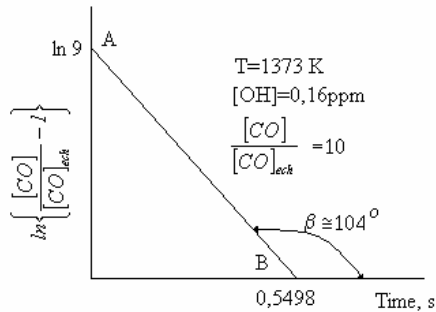


Fig. 2. Plot of $\ln \left\{ \frac{[CO]}{[CO]_{ech}} - 1 \right\}$ versus time

For this values, the angle $\beta \cong 104^\circ$ and the time for a total reduction of CO is 0,5498s; this corresponds to a temperature gradient of:

$$\frac{dT}{dt} = \frac{T_{max} - T_{min}}{t_B} \quad (11)$$

For a hydrocarbon – air mixture flame the maximum and minimum temperatures corresponding to formation of OH radical, are $T_{max} \cong 2100K$ and $T_{min} \cong 1373K$, and the temperature gradient becomes:

$$\begin{aligned} \frac{dT}{dt} &= \frac{2100 - 1373}{0,5498} = 1322 \text{ K/s} = \\ &= 1,322 \text{ K/ms} \end{aligned} \quad (12)$$

The confirmation of these theoretical results is given by Hardy and Lyon [1], which determined by experiment the

dependence of $\lg \left\{ \frac{[CO]}{[CO]_{ech}} - 1 \right\}$ on $t\sqrt{[H_2O]}$. This is represented in Fig.3

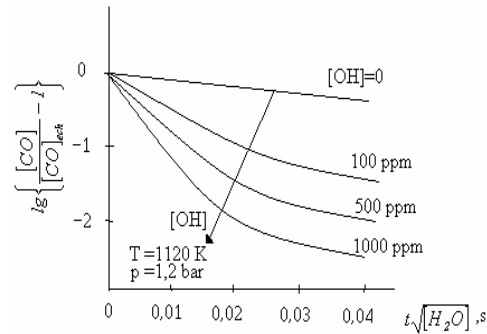


Fig. 3. Plot of $\lg \left\{ \frac{[CO]}{[CO]_{ech}} - 1 \right\}$ - $t\sqrt{[H_2O]}$, for different values of $[OH]$ concentrations

The first curve is referring to $a[OH]=0$, with a very small decrease of $[CO]$ in time; this represents an argument of the fact that at reduced temperature ($T < 1120K$), the global reaction $CO + \frac{1}{2}O_2 \rightarrow CO_2$ presents a negligible velocity.

The maximum concentration of radical $[OH]$ can not exceed approximately 2000ppm because of the endothermic effect of the formation reaction.

4. Conclusions

- The reduction of small concentration of CO in gases, can take place according to the kinetic model.
- The OH radical can be obtained by thermic decomposition of water or by hydrogen injection; the OH radical equilibrium concentration being of 0,16 ppm at a 1100°C temperature.
- The decrease of CO concentration can be obtained through the optimisation of temperature gradient of gases, of cca. 1,32 K/ms; this assumes a correct

mix with secundar air and a corresponding heat transfer

References

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