

Eight-step global mechanism for methane oxidation and NO formation

Reaction 1	$\text{CH}_4 + 1.5 \times \text{O}_2 \rightarrow \text{CO} + 2 \times \text{H}_2\text{O}$
Reaction 2	$\text{CO} + 0.5 \times \text{O}_2 \rightarrow \text{CO}_2$
Reaction 3	$\text{CO}_2 \rightarrow \text{CO} + 0.5 \times \text{O}_2$
Reaction 4	$\text{N}_2 + \text{O}_2 \rightarrow 2 \times \text{NO}$ (via non-thermal N_2O and Zeldovich mechanisms)
Reaction 5	$\text{N}_2 + \text{O}_2 \rightarrow 2 \times \text{NO}$ (via NNH and prompt mechanisms)
Reaction 6	$\text{N}_2 + \text{O}_2 \rightarrow 2 \times \text{NO}$ (via thermal $\text{N}_2\text{O} + \text{H}$)
Reaction 7	$\text{N}_2 + \text{O}_2 \rightarrow 2 \times \text{NO}$ (via thermal $\text{N}_2\text{O} + \text{O}$)
Reaction 8	$\text{N}_2 + \text{O}_2 \rightarrow 2 \times \text{NO}$ (via thermal Zeldovich)

Tuned to the GRI 3.0.

T_{inlet} is based on the compressor discharge temperature with 85% efficiency. Fuel-air equivalence ratio range is 0.45 to 0.7. The rates are:

$$R_1 = 10^{13.354 - 0.004628 \times P} [\text{CH}_4]^{1.3 - 0.01148 \times P} [\text{O}_2]^{0.01426} [\text{CO}]^{0.1987} \exp(-(21932 + 269.4 \times P)/T)$$

$$R_2 = 10^{14.338 + 0.1091 \times P} [\text{CO}]^{1.359 - 0.0109 \times P} [\text{H}_2\text{O}]^{0.0912 + 0.0909 \times P} [\text{O}_2]^{0.891 + 0.0127 \times P} \exp(-(22398 + 75.1 \times P)/T)$$

$$R_3 = 10^{15.8144 - 0.07163 \times P} [\text{CO}_2] \times \exp(-(64925.8 - 334.31 \times P)/T)$$

$$R_4 = 10^{14.122 + 0.0376 \times P} [\text{CO}]^{0.8888 - 0.0006 \times P} [\text{O}_2]^{1.1805 + 0.0344 \times P} \exp(-(46748 + 126.6 \times P)/T)$$

$$R_5 = 10^{29.8327 - 4.7822 \times \log(P)} [\text{CO}]^{2.7911 - 0.04880 \times P} [\text{O}_2]^{2.4613} \exp(-(61265 + 704.7 \times P)/T)$$

$$R_5 = 10^{14.5476 + 0.10779 \times P} [\text{CH}_4]^{1.6674 + 0.04122 \times P} [\text{O}_2]^{-2.0886 + 0.3193 \times P} \exp(-(48772.3 + 789.05 \times P)/T)$$

$$R_6 = 10^{14.592} [\text{N}_2][\text{H}_2\text{O}]^{0.5} [\text{O}_2]^{0.25} \times T^{-0.7} \exp(-69158/T)$$

$$R_7 = 10^{10.317} [\text{N}_2][\text{O}_2] \times \exp(-52861/T)$$

$$R_8 = 10^{14.967} [\text{N}_2][\text{O}_2]^{0.5} T^{-0.5} \times \exp(-68899/T)$$

The units used in the rate expressions are: activation energy = K, concentrations = kmol/m^3 , reaction rates = $\text{kmol}/(\text{m}^3 \times \text{s})$.

- Reaction 1 should be used in the kinetic mode only when modeling flames with very short mixing time, $\text{Da} = 0.1$, this would be applicable for JSR type of reactors. In the GT application the best results was obtained when choosing the rate between the kinetic rate and EBU expression for product controlled rate. To assure this, the constants in the EBU expression were assigned values of: $A = 10000$, $B = 0.0002$ so the product $A \times B = 2$ is the same as in the Magnussen et al. paper. Based on the modeling affords at UW these coefficient appear to be too small to predict correct flame speed, we recommend to increase “A” value to adjust the flame length.
- Reactions 2 and 3 were tuned to get the correct equilibrium temperature and CO concentration if the are in the kinetic mode. Thus we recommend increasing the EBU rate so it will not limit the reaction rate. Also, since in the lean premixed application, both reactants, CO and O2, are present in the same location, we feel that EBU model does not capture the physics of flame for the CO oxidation step. To assure that these reactions are always in the kinetic mode, the coefficient “A” in EBU rate was set to 10×10^6 .
- The NO reaction rates are written for the expression $\text{N}_2 + \text{O}_2 \rightarrow 2 \times \text{NO}$: meaning that 2 molecules of NO formed in one reaction, e.g. $R_4 = d[2\text{NO}]/dt$. If rate for these reactions needs to be expressed as $R_{\text{NO}} = d[\text{NO}]/dt$, divide the pre-exponential factor by two.

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