One-Step Chemistry Model For Methane Post-Oxidation In Gas-/Biogas Engines

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Introduction

Unburnt hydrocarbon (UHC) emission can be a significant greenhouse gas contribution for gas engines. Flame-wall quenching, crevices and valve-overlap are the major sources of UHCs. To predict the emissions quantitatively, the information regarding the local thermodynamic and flow conditions are necessary, these can be obtained from 3D-CFD in a RANS or LES context. The post-flame oxidation requires detailed chemistry, which even in the context of RANS 3D-CFD for engine simulations is computationally expensive on the industrial scale. The UHC emissions can be solved as additional transport equations for individual sources with a proper source term, in order to consider post-flame oxidation.

Mathematical formulation

The present work deals with the development of a one-step post-flame oxidation model of methane with an accuracy of detailed GRI 3.0 Mechanism [1] for the transient gas engine conditions. An approach similar to Kwon et al. [2] is adopted, leading to a new one step methane oxidation mechanism for gas engine conditions. However, in this work, the reaction rate constants are dynamically varying according to the rapid changing conditions in the engine. A pressure range of 2 – 200 bar, temperature: 900 – 2600 K, phi: 0.4 – 1, EGR: 10 – 30% and residence time 200 ms is considered. This broad range is considered in order to take the post-oxidation into account, for gas engines of varying sizes and operating rotational speed.

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

The methane oxidation rate is described in terms of the Arrhenius equation for the rate constant

$$\frac{d[CH_4]}{dt} = A \cdot T^n \cdot e^{\left(-\frac{Ea}{RT}\right)} \cdot [CH_4]^a \cdot [O_2]^b \cdot R^*$$

Where A is the pre-exponential factor, n is the temperature exponent, Ea (kcal/mol) is the activation energy, a and b are the reaction orders and R^* accounts for the effect of intermediate radicals (explained in the further section). Initially the rate constants were used from the rate coefficients provided by Westbrook and Dryer [3], however the coefficients are not valid for the gas engine conditions. The rate of methane oxidation is strongly dependent on the local pressure, temperature, gas composition and the intermediate radicals (when the unburned fuel comes in contact with hot bulk gases in the cylinder). Hence it is necessary to optimize the rate constants dynamically as a function of pressure, temperature, equivalent ratio, exhaust gas recirculation and burnt gas products, to predict the 95% methane oxidation times $(\tau_{95\%,GRI\,3.0})$. Zero dimensional (perfectly stirred reactor [PSR]) simulations using GRI 3.0 Mechanism are performed using the chemical kinetic code Cantera [4]. An adaptive time stepping method is used to accelerate the calculation process (especially for points at low temperatures and low pressures), a starting time-step of 0.01 Sec is taken and is in process multiplied with a factor of 0.1 till a convergence criteria of 1e-4 for the 95% methane oxidation is obtained. A database containing more than 19,450 Points is generated. The data is generated in two categories:

1. $\{\phi\} \cdot \{EGR = 0\%\} \cdot \{p\} \cdot \{T\} \cdot \{\xi\}$
2. $\{\phi = 1\} \cdot \{EGR\} \cdot \{p\} \cdot \{T\} \cdot \{\xi\}$

This generated data base is used to calibrate the Arrhenius rate coefficients of the single step mechanism. PSR Simulations are performed using the single step mechanism, where the Arrhenius constants are adjusted per point according to the criteria:

$$\tau_{95\%,GRI\,3.0} - \tau_{95\%,1-step} \le 1e-15$$

This optimization is done using the optimization code Dakota [5], using the NL2SOL Fortran library based on an adaptive nonlinear least-squares algorithm. At the completion of the optimization process, the Arrhenius coefficients are described as follows:

Temp Range [K]	**A**	**n**	**Ea [cal/mol]**	**a**	**b**
900-1400	A_1	0	Ea=40000 $(EGR = 0)$	0.09	0.15
1400-2600	A_2		Ea=44000 $(EGR = 0)$ Ea=46000 $(EGR \neq 0)$		

$$A_1(\phi, EGR, p) = \left(\frac{p}{p_0}\right)^{1.7} [19.85 \cdot e^{(-0.9 \cdot EGR)} \cdot EGR^{0.001}$$

$$+ 473.5 \cdot e^{0.1 \cdot \phi} \cdot (1 - EGR)]$$

$$A_2(\phi, EGR, p) = \left(\frac{p}{p_0}\right)^{1.7} [1797 \cdot e^{(-1.407 \cdot EGR)} \cdot EGR^{0.001}$$

$$+1723 \cdot e^{0.1 \cdot \phi} \cdot (1 - EGR)]$$

Where, $p_0 = 1e+5$.

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A sensitivity analysis is performed by varying A, n, Ea, a and b systematically, it is observed, that the pre-exponential factor is the most sensitive term among all the terms in the Arrhenius equation.

Fig. 1 shows that the modified single step mechanism shows a good agreement with the detailed GRI 3.0, especially in the fuel lean region, which is the normal operating condition in gas engines, with a maximum deviation of 20%. This maximum deviation is however, in regions (Fig. 1 shaded elliptical region) near stoichiometric conditions and higher temperatures. Since Gas-engines are mainly operated in lean conditions, the obtained results are satisfactory.

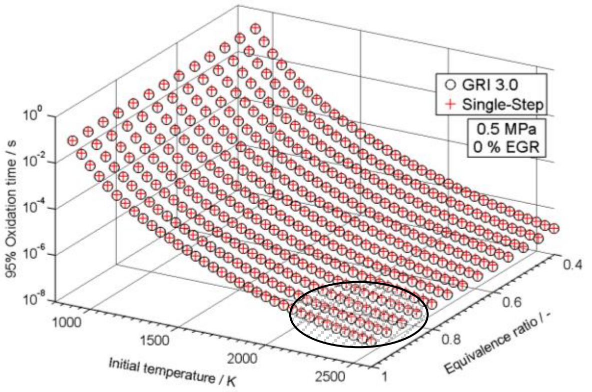

Fig. 1: Oxidation time of methane (95%). Comparison between GRI 3.0 and one step mechanism.

The unburned gas from the quenched layer on the cylinder wall or crevices comes in contact with the hot bulk gases due to convection and diffusion (turbulent Schmidt number = 0.7). The intermediate species in the burnt gases supply chain branching reactions in the methane oxidation, this effects the oxidation rate of methane. It is necessary to consider the effect of these intermediate species, mostly, OH, O, CO, H, NO_x along with other radicals. The effects of the specific radicals vary complexly with varying engine conditions. Hence in this study, all the possible resulting species (GRI 3.0) are taken into account, the product species are varied from 0-100%. PSR Simulations using the GRI 3.0 are carried out for entire operating range and a factor function is derived. This factor function R^* is combined to the modified single step mechanism to consider the effect of the intermediate species. This factor function R^* is a function of pressure, temperature, equivalence ratio, intermediate species mass fraction (all product species in GRI 3.0) and EGR. The equivalence ratio and EGR are known from the gas composition, pressure and temperature are the local cell values, and the intermediate species mass fraction is calculated from the local cell center value for UHC and O_2 scalar as shown below,

$$\xi = 1 - ([UHC] + [O_2])$$

Once these values are determined for a cell at a time step, then the factor function R^* is obtained from a look up table, hence the reaction rate for [UHC] scalar is obtained. Fig. 2 shows a good agreement in the 95% oxidation rate values between the modified single step mechanism and GRI 3.0 with the effect of all the product species.

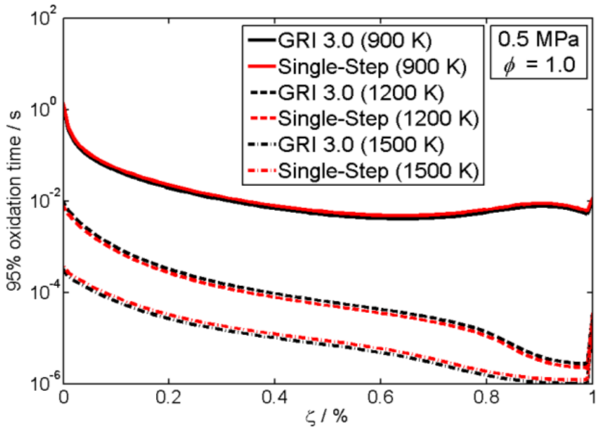

Fig. 2: Oxidation time of methane (95%). Comparison between GRI 3.0 and one step mechanism with the effect of intermediate species.

Conclusions

In this work, a single step chemistry model for methane post-flame oxidation is proposed. The Arrhenius constants are dynamic in nature and are functions of local pressure, equivalence ratio, exhaust gas recirculation and intermediate species. The presented model is validated for varying gas engine conditions with GRI 3.0. The pre-exponential factor is found to be the most sensitive parameter for the modelling of the reaction rate. The main purpose of this work is to incorporate this reaction rate as a source term to the UHC emissions scalar in the 3D-CFD Engine simulations.

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