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Reduced methanol kinetic mechanisms for combustion applications

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Abstract

Reduced chemical kinetic mechanisms for methanol combustion were investigated by evaluating ignition delay magnitudes and combustion in a continuously stirred reactor. Unsteady computations were made to study the characteristics of the kinetic mechanisms proposed in the literature and to compare the dependence of various parameters on methanol combustion. All computations were done under isobaric conditions, and, to capture the influence of all the reactions involved in the mechanism, a very small time step was used. Finite-difference methods were used to solve the coupled differential equations. The five-step mechanism developed by C.M. Mueller and N. Peters [in: N. Peters, B. Rogg (Eds.), Reduced Kinetic Mechanisms for Applications in Combustion Systems, Springer-Verlag, New York, 1993, pp. 143–155] for premixed flames and both the five-step mechanism and the four-step mechanisms developed by C.M. Mueller, K. Seshadri, J.Y. Chen [ibid, pp. 284–307] for non-premixed flames were considered. It was found that the Mueller et al. five-step mechanism, with some modifications, best supported the spontaneous ignition and continuous stirred reactor combustion. The results were validated by comparing calculated ignition delays with available experimental data of C.T. Bowman [Combust. Flame 25 (1975) 343–354], and calculated final steady-state concentrations with chemical equilibrium calculations [J.-Y. Chen, Combust. Sci. Technol. 78 (1991) 127]. Initial temperature and concentration and the operating pressure of the system have a major effect on the delay of methanol ignition. The residence time of the continuous stirred reactor affects ignition delay and also changes the transient characteristic of chemical composition of the fuel–vapor mixture. The computations are intended to guide and explain many combustion studies that require a methanol kinetic mechanism.

Keywords: Methanol kinetics; Ignition; Stirred reactor

1. Introduction

Reduced mechanisms are useful for practical computations in which many complexities exist and more than one independent variable is used. Three well-known four- and five-step methanol oxidation reduced kinetic schemes have been advanced by Mueller and Peters [1] for established premixed flames (MP5) and by Mueller et al. [2] for established diffusion flames (MSC4 and MSC5). The formulation of the five-step mechanism (MSC5) introduced steady-state approximations to the following species: CH_2OH, CHO, OH, O, HO_2, and H_2O_2 [2]. This work extends the methanol reduced kinetic model to be valid for ig-

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nition, developing flames, and established steady or unsteady flames. It also improves the ability of the model to predict the equilibrium composition and temperature downstream of a premixed flame, using a modified MSC5 mechanism built on an understanding of all of the known important elementary reactions. Some more recent mechanisms might have updated kinetic constants for the elementary reactions, but the structure of the mechanism is not different. Other articles on methanol reduced kinetics either address only the steady state [3], postulate a mechanism [4], or require at least 14 steps for the unsteady initiation process [5].

For one portion of our modified model development, spontaneous ignition and homogeneous oxidation were considered. We studied temporal behavior in a constant-pressure, adiabatic, spatially uniform situation: volume changed with time. A second unsteady configuration was also studied wherein the fresh premixed combustible gas was continuously introduced into a high-temperature environment with available chemical radicals. An ideal, continuous, stirred reactor achieves perfect mixing of reactants and products inside the control volume. The continuous stirred reactor (CSR) case was chosen to test the accuracy of the kinetic model when solving a combusting-flow process with a residence time. Under the infinite mixing rate assumption, the outflow temperature and concentrations are taken to be identical to those inside the control volume. On exiting the volume after a finite residence time, the mixture is assumed to cease reacting; combustion need not be complete and chemical equilibrium need not exist in the exit flow. Both inflow properties and initial properties within the volume are prescribed, and then properties within the volume (and equivalently in the exit flow) are determined as functions of time. The mass inflow rate is held constant throughout the operation. The implication of a constant pressure, a constant volume, and a constant mass inflow rate with temporally varying temperature and concentration is that the outflow rate must change with time in a controlled manner. Variable exit area can be used to maintain the desired constant pressure. The constant ratio of the chamber volume to the volumetric inflow rate is called the "residence time," although differences between inflow density and chamber density and/or unsteadiness cause this ratio to differ somewhat from a true time-dependent travel time.

2. Kinetic models

Our computations showed that the MSC4, MSC5, and MP5 kinetic models did not support the ignition delay characteristics. This was not surprising as the models were designed to describe established flame structures after the ignition delay period. Hence, these mechanisms had to be modified by the addition of Reaction 96, an initiation reaction. So, we created modified mechanisms $MMSC_{96}4$, $MMSC_{96}5$, and $MMP_{96}5$ (see Appendix A). The rate of Reaction 96 was high prior to ignition and approximately zero after ignition; therefore, it is very important to model ignition delay characteristics. However, the modified five-step mechanism (MMP5) still did not support the ignition delay characteristics, even though it was sufficient to describe premixed flames. MMP5 predicted negative values for the mass fraction of the hydrogen molecule. Further, the mechanism did not predict the correct characteristic temporal curves for all of the major species. It was concluded that MMP5 was not robust enough to predict ignition delay. Furthermore, $MMSC_{96}5$ overestimated the final adiabatic temperature (calculated following Ref. [9]) by almost 600 K. Because of the absence of a backward reaction for Reaction 17, CO_2, CO, and O_2 were not at equilibrium after complete combustion. Hence, it overestimated the final concentration of CO_2 and underestimated the final O_2 and CO concentrations. So, $MMSC_{96}5$ was further modified by the addition of a backward reaction for Reaction 17. See Appendix A; Reactions 1 and 18 [1] produce the equilibrium balance for CO_2, CO, and O_2.

In our calculations, CH_2O did not reach steady state, and, hence, $MMSC_{96}4$, which assumes steady state for CH_2O, should not be used.

MMP5 implicitly contains a backward reaction for Reaction 17 (Appendix A). As this model also includes the steady-state balance for the intermediate species CH, CH_2, and CH_3, combinations of a few reactions (Reactions 1, 2, 19, and 20 from Ref. [1]) provide the backward reaction for Reaction 17. However, due to the problems mentioned earlier, the model was still not robust enough to predict spontaneous ignition characteristics. MMSC5, MMSC4, and MMP5 predict the same final adiabatic temperature when the above-mentioned modifications are made.

3. Governing equations and numerical method

The independent variables considered are the major species mass fractions and the temperature of the system. A system of quasi-linear ordinary differential equations is developed to govern the mass fractions of the eight major species CH_3OH, O_2, H_2O, CO_2, CO, H_2, H, and CH_2O, and temperature T. The intermediate species were assumed to be at steady state, and simple algebraic equations were developed.

For both spontaneous ignition and CSR computations, constant pressure and perfect gases were con-