ASYMPTOTIC ANALYSIS FOR COUPLED HYDROGEN, CARBON MONOXIDE, METHANOL AND ETHANOL REDUCED KINETIC MECHANISMS

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***Abstract*— Based on a mechanism composed by 372 reversible chemical reactions among 56 reactive species for the oxidation of ethanol, we propose a reduction strategy to obtain a six-step kinetic mechanism for the methanol and a seven-step mechanism for the ethanol. A three-step kinetic mechanism results for the carbon monoxide and two-step for the hydrogen. The reduction strategy consists of four steps: 1) estimate the order of magnitude of the rates of chemical reaction, 2) define the main chain, 3) apply the steady-state and partial equilibrium assumptions and 4) justify the assumptions by asymptotic analysis. The main advantage of the obtained reduced mechanisms is the decrease of the work needed to solve the system of chemical equations. Such decrease is proportional to the order of the number of elementary reactions present in the complete mechanism.**

***Keywords*— Hydrogen, carbon monoxide, methanol, ethanol, reduced mechanisms.**

I. INTRODUCTION

Methanol is commonly used in biodiesel production for its reactivity, and can be employed as one possible replacement for conventional motor fuels (Demirbas, 2007). Methanol has advantages over traditional hydrocarbon fuels derived from mineral oil, because it can be produced from biological sources.

Ethanol can be used as an oxygen additive fuel extender, octane enhancer, or as an alternative fuel to replace reformulated gasoline. Although most ethanol is currently generated by fermentation, recent developments suggest that the ethanol fuel can be derived more efficiently from other types of biomass, thus offering the potential to reduce dependence on fossil-fuel energy resources (Li *et al.*, 2004).

Some mechanisms were obtained and published in the mid-1980s for premixed and nonpremixed flames (Peters and Rogg, 1993). For the oxidation of the hydrogen it is used about 10 chemical species and 20 elementary reactions while for the oxidation of the ethanol it is used about 350 elementary reactions among 50 chemical species (Marinov, 1999).

The computational simulations with detailed mechanisms turn complicated by the existence of highly reactive radicals which induces significant stiffness to the governing equations. Consequently, there exists the need to develop reduced mechanisms of fewer variables and moderate stiffness, while maintaining the accuracy of the detailed mechanism (Lu and Law, 2006).

Kinetic mechanisms for methanol combustion were proposed by Westbrook and Dryer (1980), Dove and Warnatz (1983), Norton and Dryer (1990) and a reduced mechanism based on these works was derived by Paczko *et al.* (1988). The chemical kinetics of ethanol combustion has been studied by Marinov (1999), Li *et al.* (2004), Saxena and Williams (2007), Seiser *et al.* (2007), among others.

Hydrogen is an important intermediate species in the principal path of oxidation of methanol (Seiser *et al.*, 2007). The principal species in the oxidation of methanol (Yalamanchili *et al.*, 2005) and of ethanol are H_2O, CO_2, CO, H_2, O_2 and CH_2O.

In what follows, we propose a strategy to obtain reduced kinetic mechanisms using the hypotheses of partial equilibrium and of steady-state; we check the reduced mechanisms using an asymptotic analysis and compare some numerical values with data found in the literature.

II. STRATEGY TO OBTAIN REDUCED KINETIC MECHANISMS

The reduction strategy proposed here is to:

- Estimate the order of magnitude for rates of reaction;
- Define the main chain;
- Apply the assumptions of steady-state and of partial equilibrium;
- Justify the assumptions by asymptotic analysis.