Gas Phase Simulation of an Ethanol Autothermal Reforming Reactor for Hydrogen Production for Fuel Cell Vehicles

Gregory A. Buck
Associate Professor, Mechanical Engineering Department
South Dakota School of Mines and Technology
501 E. St. Joseph Street, Rapid City, SD USA 57701
E-mail: gregory.buck@sdsmt.edu

Extended Abstract

Chemical processes involving the reforming of hydrocarbon fuels (including alcohols) to produce hydrogen have been extensively studied. Among the most promising processes for mobile applications are those which involve the partial oxidation (POX) of the fuel in combination with the well known steam reforming process, both reactions typically supported by some simultaneous (local) total oxidation to provide the heat necessary for the endothermic steam reforming reaction, in a process usually referred to as autothermal reforming. The partial oxidation and steam reforming reactions may be carried out at high temperatures (>1200 ºC) without a catalyst, but in addition to higher material costs, this approach presents operational difficulties that render impractical for mobile applications. Catalyzed partial oxidation (CPO) of various fuels has however, seen much development, as the required temperatures are typically much lower, reaction rates much faster, and specific catalysts can be employed to promote desirable reactions.

Although the literature appears to show that considerable effort has been directed to the CPO reforming of methanol and other hydrocarbons, ethanol reforming has apparently seen much less attention. However, the existing infrastructure within the United States is currently geared to produce nearly 3 billion gallons/year of ethanol from fermented biomass, at a cost quite competitive with petroleum fuels. In a recent study at the University of Minnesota, Deluga and Schmidt et al (2004), report experimental results for the CPO of pure ethanol and ethanol-water mixtures with 25% ethanol (mole basis) on Rh-ceria catalysts. They varied the ratio of carbon to oxygen in the reactant stream (referred to as the C/O ratio, which is basically a measure of the fuel/air ratio) and examined the selectivity (yield) of various products as a function of this ratio. They define the selectivity of \( H_2 \) as the fraction of \( H_2 \) atoms in the ethanol molecule converted into \( H_2 \). Because some of the \( H_2 \) in the products comes from \( H_2O \) in the ethanol-water mixtures that they studied, selectivities greater than 100% were observed. In fact their findings show a clear maximum in \( H_2 \) selectivity of about 80% at a C/O ratio of 0.7 for pure ethanol and about 110% at a C/O ratio of 0.65 for the ethanol-water mixture. Because these findings appear to offer great promise in utilizing ethanol as an onboard fuel source for PEM hydrogen fuel cells, additional validation of these results is certainly warranted. This research attempts to study the physics of the reacting flow through a simplified first principal model, which includes only the most significant species present and the dominant chemical reactions, with a simple model of the chemical kinetics.

The chemical reactions associated with the partial oxidation of any hydrocarbon or alcohol fuel are complicated by the large number of highly reactive (often short lived, but essential to the reaction mechanism) radicals and other intermediate species that are known to exist within the reaction vessel. Marinov (1999) reports a detailed kinetic mechanism for ethanol oxidation involving 57 species and over 200 chemical reactions. The chemistry is further
complicated by the presence of catalysts that are typically employed to enhance the reaction rates for those reactions that produce the desired species. Large spatial variations in temperature and the attendant effect on reaction rate and radical formation provide additional complication, as convective fluid motion (which may be laminar or turbulent) transports and mixes reacting and product species together, which may enhance or inhibit certain reactions locally. Despite this complexity, much can be learned from simple models that include only the principal species of interest and their most significant reactions, and that invoke simplifying assumptions with regard to the reaction kinetics. Most fuels (including alcohols) are fast burning, and if the reacting flow is turbulent, the overall rate of reaction is controlled by the slower rate of convective mixing necessary to place reactants together for a successful molecular collision (i.e. one that results in reaction). When the turbulence transports reactants together, the reaction is assumed to occur instantaneously; such flows are said to be mixing limited, and provide a reasonably good first approximation for separate turbulent streams of fuel and oxidizer brought together within a reforming reactor.

In order to gain some initial insight into the physics of the chemically reacting flow associated with the partial oxidation of the ethanol fuel, a simple numerical model was constructed using the commercially available Fluent CFD package. The reactor simulated here is comprised of a cylinder with a small fuel inlet opening at one end and a 15° angled air inlet opening, located near the fuel inlet end. Products were allowed to exit the reactor through a center opening at the opposite end of the cylindrical vessel. All reactants and products were assumed to be in the gaseous state and the inlet ethanol and air flow rates were adjusted to give 6 different air/fuel ratios on a mass basis (AF), i.e. AF=9 (corresponds to the total oxidation of reaction 3), AF=5, AF=2.78 (corresponds to the C/O of 0.7 for maximum H₂ yield observed by Deluga and Schmidt), AF=1.5 (corresponds to the partial oxidation of reaction 1), AF=1 and AF=0.5. In all six cases, the total gaseous product outflow was held constant at 0.002 kg/sec, and both the air and fuel flow rates were chosen to give the desired ratio while maintaining this total outflow. Although in practice, it is difficult to provide the proper air-fuel ratios for the rich mixtures studied here (i.e., AF = 2.78, 1.5, 1 and 0.5), as the evaporation of ethanol into air will be limited by a saturated condition, oxidation of liquid ethanol has been studied and reported in a companion study. The fuel and air were each assumed to enter the reactor at 300 K, and all reactor walls were assumed to be adiabatic. A species transport model was enabled within the Fluent software to account for the seven major species involved, i.e. O₂, N₂, C₂H₅OH, H₂O, CO₂, CO and H₂, subject to a simplified system of 4 chemical reactions. The flow was assumed to be turbulent with closure obtained by invoking a realizable k-ε model for the turbulence. Reaction rates were dictated by the turbulent mixing as discussed above.

Figures 1 and 2 show contours of H₂ mass fraction and temperature throughout the reactor for the 2 of the 6 air-fuel ratios studied. As this ratio is varied from rich (small AF) to lean (large AF), the H₂ production at the outflow is observed to first increase and then decrease, clearly indicating the prediction of a maximum at an AF of approximately 2.8, corresponding to the same C/O ratio as that observed in the experiments of Deluga and Schmidt, et al (2004). Note that a C/O of 0.7 corresponds to an AF of 2.78 on a mass basis:

Figure 3a provides additional confirmation by showing plots of H₂ mass fraction variation across the 0.03175 m diameter gas outlet opening for the various AF ratios, and Figure 3b shows the average H₂ mass fraction at the outflow plane, plotted as a function of the air-fuel ratio. In remarkable agreement with the experiment cited, the maximum between AF=2 and AF=3 is clearly shown.
Figure 1  Contours of $\text{H}_2$ mass fraction and temperature for AF = 9

Figure 2  Contours of $\text{H}_2$ mass fraction and temperature for AF = 2.78

Figure 3  Variations of $\text{H}_2$ mass fraction a) across the gas outlet and b) with AF