# 391a Hydrogen from Methanol in a Dual Membrane Atr Reactor

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Introduction Methanol is often considered as a fuel for on-board reforming to produce hydrogen for PEM fuel cell vehicles. Challenges to overcome include (i) the supply of heat to the reforming reactor, and (ii) Removal of CO from the reformate to the ppm levels necessary for the PEM fuel cell. The methanol steam reforming reaction, $CH3OH+H2O <-> CO2+3H2$, is endothermic and heat must be supplied to drive the reaction to produce hydrogen. Copper/Zinc/Alumina catalysts are excellent for this reaction at relatively mild temperatures of 200-250 °C. The heat may be supplied in a tubular reactor by burning a fuel and transferring heat to the reaction, but this results in a relatively bulky reactor design. In-situ combustion with air can supply the necessary heat, which is often referred to as autothermal reforming (ATR). Ideally, the reforming and combustion reactions would occur simultaneously, resulting in a flat temperature profile in an adiabatic reactor. In reality, the combustion reaction is much faster than the reforming reaction, and it is likely that the copper catalyst in the oxidizing environment is inactive for conducting the reforming reaction, which requires the copper to be in a reduced state. About 0.12 moles of oxygen per mole of methanol is required to supply the necessary heat of combustion to drive the endothermic reforming reaction. This amount of oxygen, if mixed with the methanol/steam feed to the catalyst bed, would create an exotherm of >300 °C in an adiabatic reactor, which would sinter the copper catalyst, quickly destroying its activity for reforming methanol to hydrogen. As an added complication, the reverse water gas shift reaction will convert some of the CO2 into CO, $CO2+H2 <-> CO+H2O$. Even small amounts of CO in the reformate will poison the Pt catalyst in the PEM fuel cell, and so CO must be removed to <20 ppm. These issues create challenges to the reaction engineer to design a reaction system that is compact, efficient, and will deliver hydrogen to the fuel cell on demand and free of poisons.

Materials and Methods Several options for the reactor design have been studied, and an adiabatic autothermal reforming reactor with distributed air introduction and in-situ hydrogen separation through Pd/Ag membranes was determined to offer the most compact design[1]. Figure 1 shows a schematic of this reactor configuration. The air is introduced to the catalyst bed through porous alumina tubes over the first 25% of the reactor length. By distributing the air introduction, the maximum temperature rise can be limited to ~100 °C, allowing the copper based catalyst systems to be utilized. The remaining 75% of the reactor length contains the dense Pd membrane coated over porous alumina tubes. The Pd/Ag membrane selectively removes hydrogen from the reaction mixture. Model predictions indicate that a 50kW fuel cell vehicle requires a reactor with a volume of 13 liters, and about 100 g of Pd forming a 10 micron-thick membrane with a surface area of 1.7 m2. By using ceramic fibers as the membrane support and reducing the Pd/Ag thickness to 5 microns, the reactor volume can be reduced to about 4 liters. The predicted fuel processor efficientcy is 81% (lower heating value basis).

Results and Discussion A prototype adiabatic ATR reactor has been built to test the model predictions and to demonstrate the feasibility of this reactor system. A typical internal temperature profile in the ATR mode (without membranes) is shown in Figure 2, along with the model prediction. The reactor was equipped with axial sample probes, allowing axial conversion and compositions profiles to be measured, as shown in Figure 3. These initial results indicate that the model provides a reasonable prediction of the actual results. We have found that the adiabatic reactor experiments has proven valuable in the development and validation of the kinetic model. For example, it was found that the oxidation rate from isothermal lab studies in the literature did not give a good prediction of the reaction exotherm. A model assuming the oxidation is rate-limited by oxygen supply achieved a much better fit of the adiabatic axial temperature profile.

Experiments with Pd/Ag membranes installed within the reactor are currently in progress. These experiments are expected to further validate the complete reactor model, allowing optimization of the reactor conditions and design parameters, including an estimate of the membrane surface area and the amount of Pd for a given power output.

Figure 1. Schematic of Adiabatic ATR Membrane Reactor

Figure 2. Temperature profile in adiabatic ATR reactor and comparison with prediction (GHSV = 8500 hr-1, O2:C =0.l2, H2O:C = 1.0, conversion = 92%)

Figure 2. Conversion and hydrogen composition profile in adiabatic ATR reactor and comparison with prediction (GHSV = 8500 hr-1, O2:C =0.l2, H2O:C = 1.0, conversion = 92%)

References 1. Lattner, J.R., and Harold, M.P. Appl. Catal. B: Env. (2005)