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PARTIAL OXIDATION REFORMING OF METHANOL

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PARTIAL OXIDATION REFORMING OF METHANOL

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Introduction

Methanol is an attractive fuel for fuel cell-powered vehicles because it has a fairly high energy density, can be pumped into the tank of a vehicle much like gasoline, and is relatively easy to reform. For on-board reforming, the reformer must be compact and lightweight, and have rapid start-up and good dynamic response. (fig.1).

Steam reforming reactors with the tube-and-shell geometry that was used on the prototype fuel cell-powered buses are heat transfer limited. To reach their normal operating temperature, these types of reactors need 45 minutes from ambient temperature start-up. The dynamic response is poor due to temperature control problems.

To overcome the limitations of steam reforming, ANL explored the partial oxidation concept used in the petroleum industry to process crude oils. In contrast to the endothermic steam reforming reaction, partial oxidation is exothermic (fig. 2). Fuel and air are passed together over a catalyst or reacted thermally, yielding a hydrogen-rich gas (fig. 3). Since the operating temperature of such a reactor can be controlled by the oxygen-to-methanol ratio, the rates of reaction are not heat transfer limited. Start-up and transient response should be rapid, and the mass and volume are expected to be small by comparison.

Theoretical Considerations

The partial oxidation reaction of methanol is given in fig. 2. Assuming adiabatic conditions and liquid methanol feed at 25°C and the stoichiometric amount of air, model calculations indicate that at equilibrium the reaction product would contain 38.5 mol % nitrogen, 28.1 % hydrogen, 12.9% water, 12.9% carbon monoxide, and 7.6% carbon dioxide. The reaction temperature would be 784°C. The equilibrium composition is largely controlled by the water-gas shift reaction (fig. 4). To maximize the yield of hydrogen and minimize CO, it is advisable to decrease the reaction temperature.

By decreasing the oxygen-to-methanol ratio and by adding liquid water to the inlet gas, the temperature can be decreased substantially. Figure 5 shows a calculated thermoneutral line illustrating oxygen-to-methanol ratios and water-to-methanol ratios that will result in an enthalpy of reaction of zero. Figure 6 illustrates the adiabatic exit gas temperature versus oxygen-to-methanol ratio. Greater than 50% hydrogen is expected at oxygen-to-methanol ratios of less than 0.34.

Experimental Results

An experimental reactor was built and tested. It consisted of a 7.5-cm-dia stainless steel pipe, 40 cm long, and employed a copper/zinc oxide catalyst (fig. 7). A liquid methanol/water mixture was injected at the top through a nozzle into a swirling air stream. The mixture was initially ignited with an electrically heated wire.

Figure 8 shows the exit gas temperature and gas composition versus time, beginning with a cold start. In a little more than two minutes after ignition, the hydrogen content is already at 40%. We anticipate that even shorter start-up times will be achieved with the help of an automated start-up protocol that provides the optimum feed proportions as a function of temperature distribution in the reactor.

Figure 9 shows hydrogen, CO, and CO₂ concentrations over a 50-hour operating period for an oxygen-to-methanol ratio of 0.26-0.31, a water-to-methanol ratio of 0.2-0.36, and a space velocity of 3400-5400 hr⁻¹. The amount of hydrogen being generated in this small and simple prototype reactor would be sufficient to operate a 18-kW fuel cell.

Conclusions

The results (fig. 10) confirm that partial oxidation reforming of methanol is feasible in a small reactor (5 by 40 cm) that has rapid start-up capability.

Acknowledgment

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Requirements for Reformers in Fuel Cell Systems for Light-Duty Vehicles

- Rapid Start

- | |
|---|
| <ul style="list-style-type: none">- low thermal mass- low operating temperature- direct heat transfer |
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- Dynamic Response

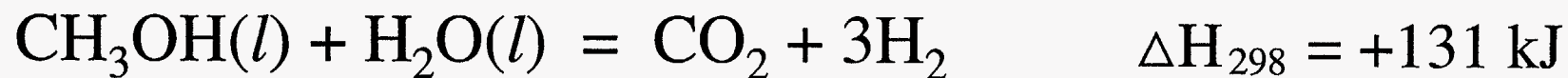
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| <ul style="list-style-type: none">- direct heat transfer- absence of recycle loops |
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- Compact and Lightweight

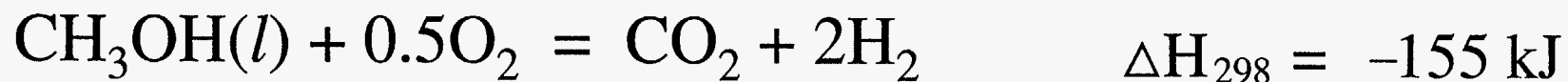
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| <ul style="list-style-type: none">- fast reactions- simple design |
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There are two major reforming pathways

- Steam Reforming

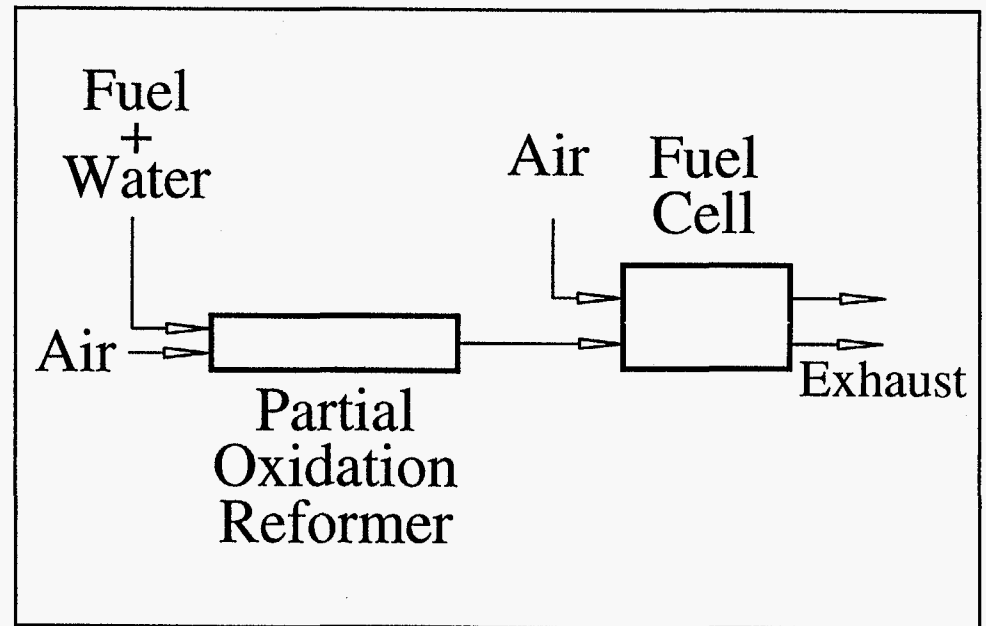


- Partial Oxidation

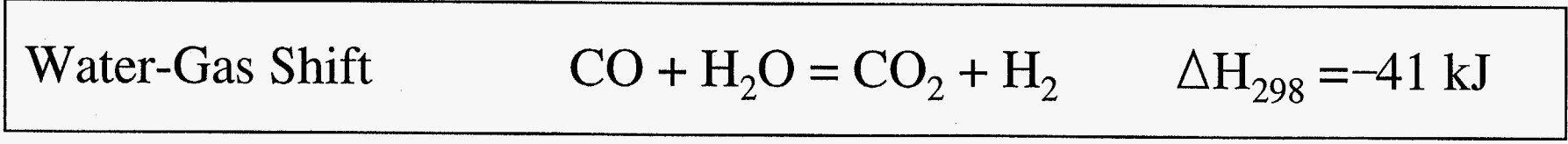
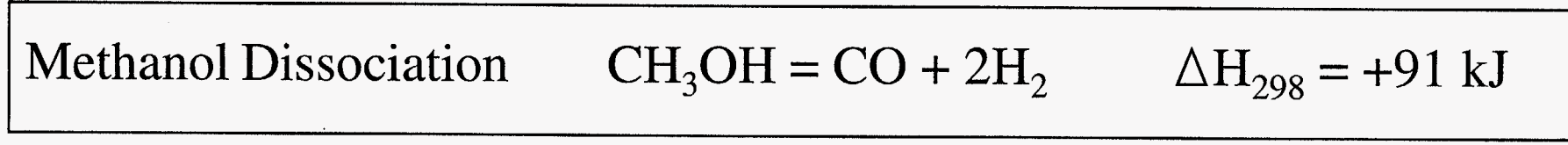
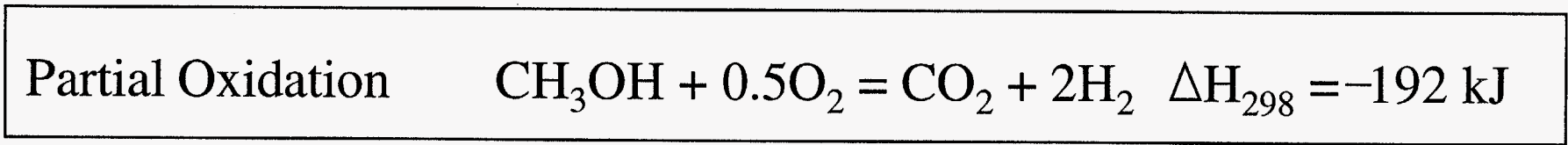


Partial Oxidation Reformer provides rapid start and dynamic response

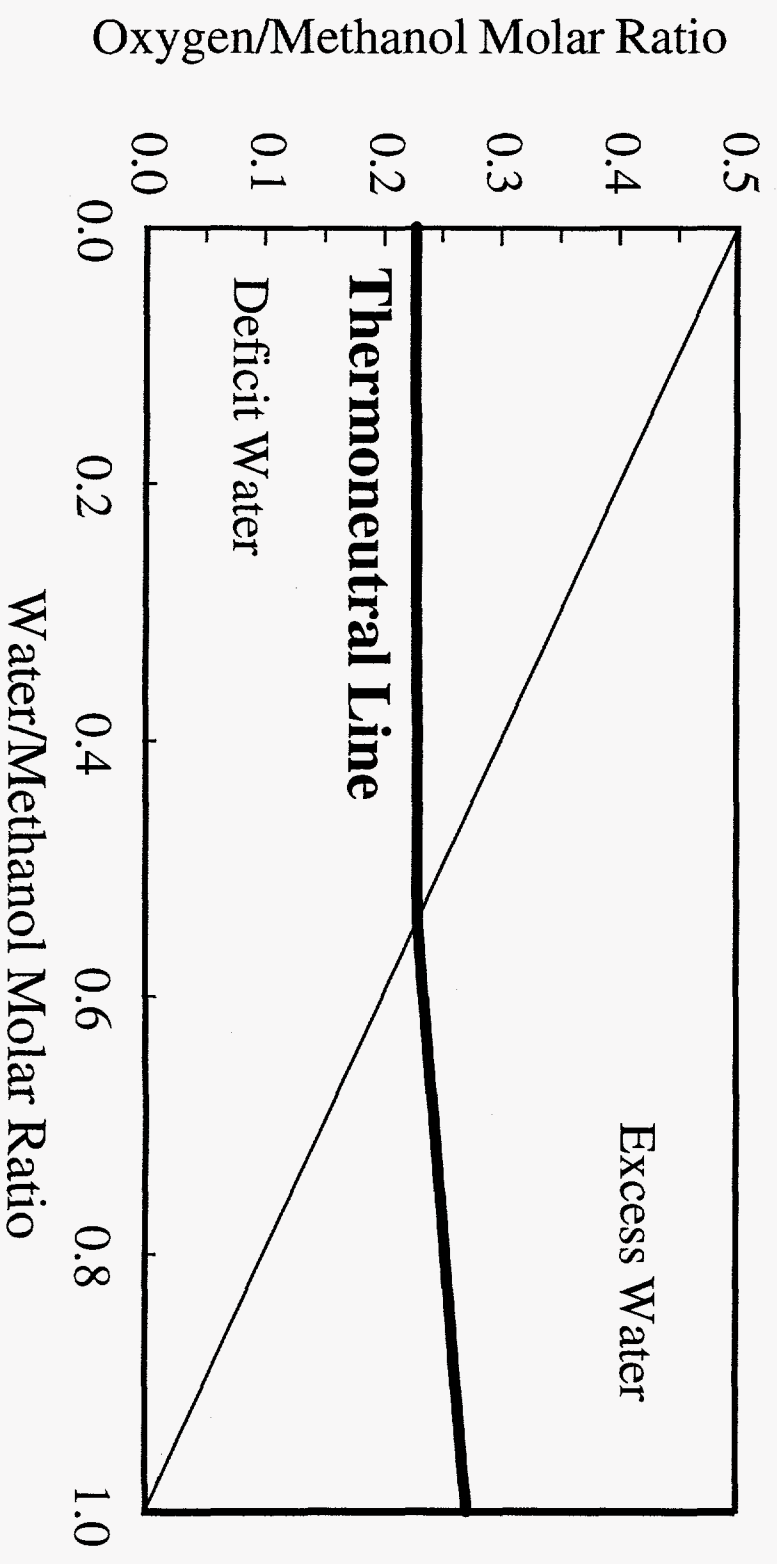
- Exothermic reaction
- Direct heat transfer (simple reactor)
- Once through flow



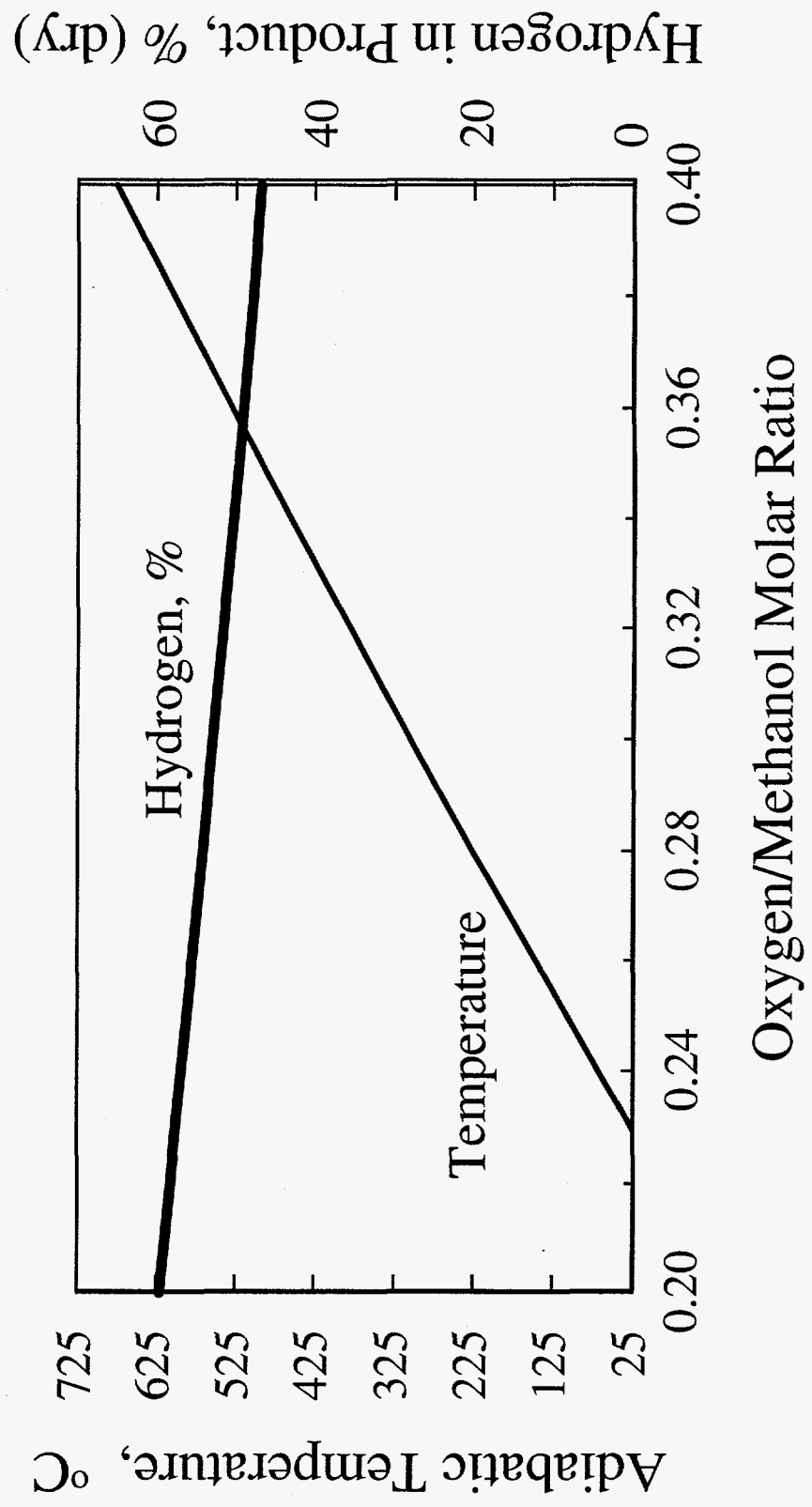
The reformer process can be represented with three reactions



The partial oxidation reformer should operate above the thermoneutral line

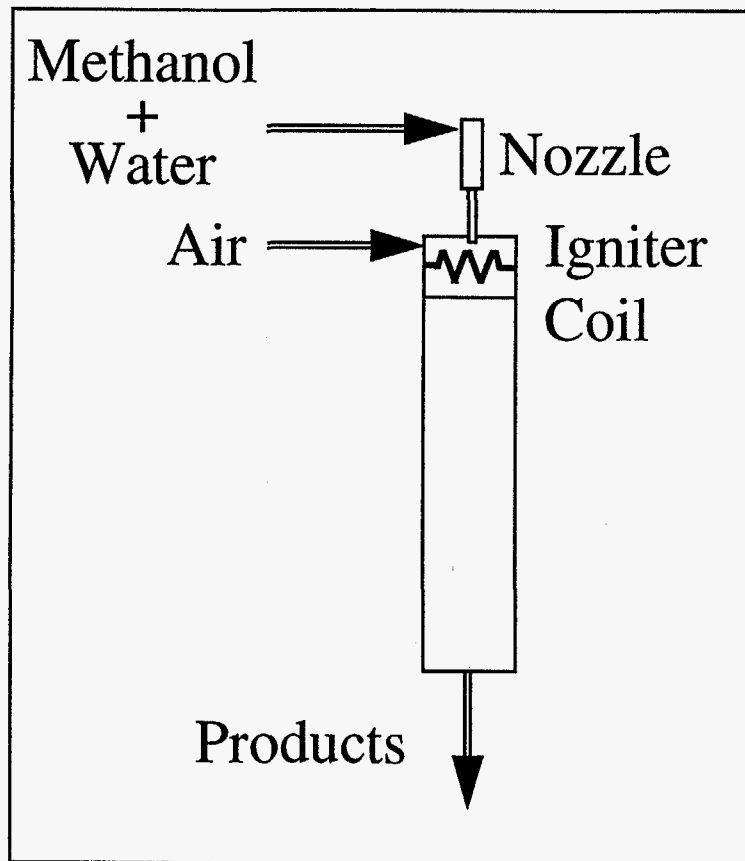


The reactor temperatures and H₂ content are sensitive to oxygen/methanol ratio



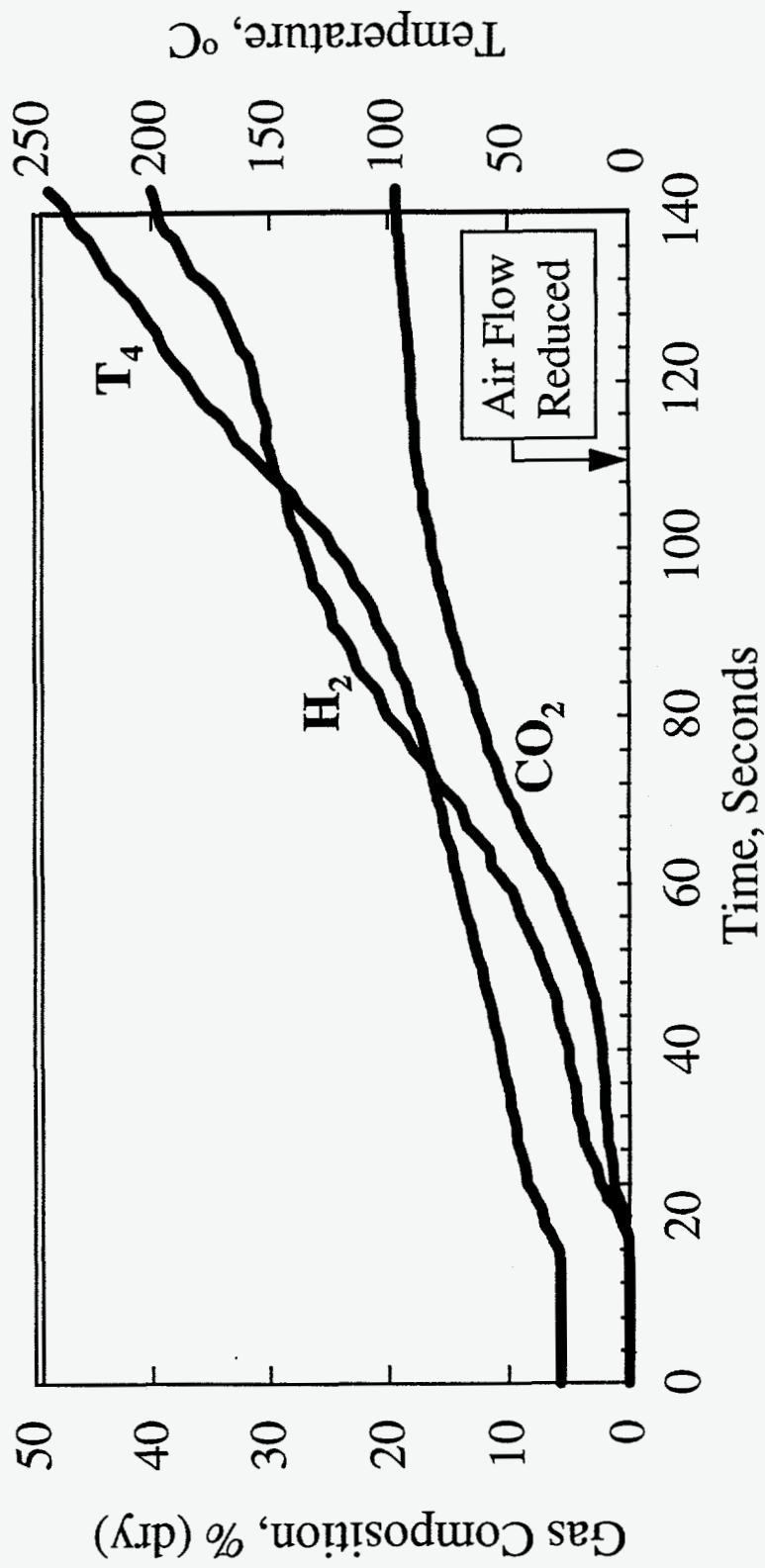
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The Argonne Partial Oxidation Reformer is simple and compact

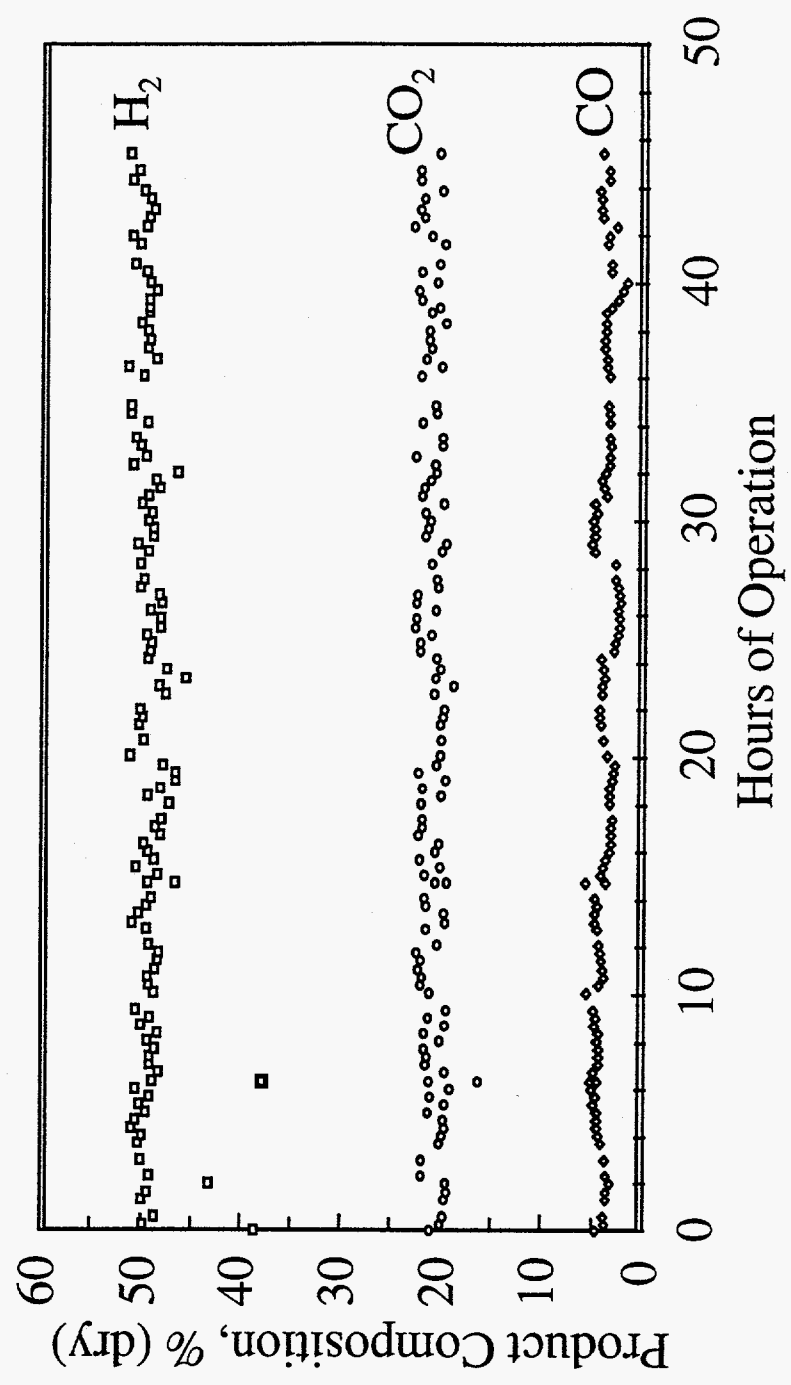


- Reactor: cylindrical
- Catalyst: copper zinc oxide
 - honeycomb, 64 channels/cm²
 - pellets
- Nozzle: 20-micron droplets
- Igniter: nichrome wire coil

The exothermic reaction aids rapid startup



Reformer products contained over 50% hydrogen



Summary

- The partial oxidation reformer is suitable for light-duty vehicles
- The reformer should operate above the thermoneutral line with sufficient water
- The Argonne reformer is simple, compact and operates with liquid feed
- The product contains over 50% hydrogen and less than 5% carbon monoxide