HYDROCARBON FUELS FOR FUTURE AUTOMOTIVE ENGINES

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In response to a need for transportation vehicles with less environmental impact, automakers around the world have been exploring a variety of novel advanced vehicle engine technologies. Fuel cells, devices that electrochemically oxidize fuels, have emerged as the focus of long range vehicle engine research: at least thirteen major auto makers now are exploring their use in light duty vehicle applications.

The Polymer Electrolyte Membrane (PEM) fuel cell has been the focus of most vehicle fuel cell research. It produces power at near ambient temperature, and thus offers advantages vs. other fuel cells that require preheating to 200°C or above before they can generate electric power. Rapid startup, with minimum power input, is a critical requirement for any vehicular application of fuel cells.

Figure 1 describes the operational principles of a PEM fuel cell. Hydrogen fuel dissociates at the anode catalyst to hydrogen ions and electrons. Hydrogen ions migrate across the electrolyte to the cathode side. At the cathode, oxygen from the air combines with electrons from the anode and hydrogen ions traversing the membrane to form water. The flow of electrons from the anode to the cathode, and the production of water generates electric power. Advanced fuel cell stacks, such as those produced by Ballard Power Systems, have achieved power density levels of 1 kW/liter. These figures exceed targets set by the US PNGV program for fuel cells aimed at light duty vehicle applications.

Fuel cells offer potential for step-out changes in vehicle emissions and efficiency. The H_2/air fuel cell produces no CO, NO_x, or particulate matter emissions. However, H_2 production may lead to emissions of one or more of these air pollutants, depending on how it is produced. Peak steady-state efficiencies of H_2 PEM fuel cells approach 60% when operated at the low end of their maximum load, while compression-ignition or spark-ignition engines achieve peak efficiencies (up to 45%) near the higher end of their peak load. Net efficiency credits for fuel cell vehicle systems will again depend on how the H_2 fuel is produced and distributed, as well as the way fuel cells or internal combustion engines are incorporated into a vehicle power train, e.g. as a stand-alone power source, or as an electric generator in a hybrid vehicle.

Net Efficiency Estimates

Higher energy efficiency in transportation is a major factor driving efforts to develop fuel cell vehicles. Here we use a method to compare net efficiencies of fuel and fuel cell vehicle systems that considers energy losses in the fuel cycle (fuel production, refining, distribution) and in operation of the vehicle. We compare systems for vehicles that store H_2 produced at a retail station from natural gas, methanol produced from natural gas, and gasoline produced from petroleum.

The first option considers hydrogen production at a retail-refueling site by steam reforming of natural gas. We chose natural gas steam reforming because it is currently the lowest cost method to produce hydrogen. Currently 97% of the world's hydrogen is produced by this process, but it is possible that long term, technology advances will reduce cost of H_2 from renewable resources to economically competitive levels (1,2). Natural gas is widely distributed in many developed countries, so fuel availability is not an issue (where it is not available, one could instead steam reform or partially oxidize fuels like gasoline, diesel, alcohols, etc).

Steam reforming is an endothermic process that generates H_2 and CO_2 from methane and water: $CH_4 + 2\ H_2O + \text{heat} = CO_2 + 4\ H_2$. The heat requirement is substantial, over 253 kJ/mole methane, or about 31% of methane's lower heating value. After the reforming step, there is a purification train to remove CO_2 and CO, followed by two-stage compressors and high pressure storage tanks. Overall thermal efficiency (heating value of H_2/heating value of methane fuel) of the process is 70-80%, depending on the level of plant heat integration and the final H_2 storage pressure (2). Assuming 90% efficiency in delivering natural gas wellhead to retail station, we obtain a net 63-72% efficiency for H_2 production.

The second fuel option considered is methanol produced from natural gas. Nearly all methanol is now produced from natural gas, usually near large, remote gas fields where distance from population centers makes pipeline distribution/sale of the gas impractical. This low-cost gas is instead converted to methanol near the production site, which is then shipped to the market by liquid tankers.

Methanol is produced from natural gas in a multi-step process. Gas is first processed to remove impurities such as H_2S, and then converted to synthesis gas (a mixture of H_2, CO, and CO_2) by steam reforming (or partial oxidation) followed by water-gas shift reactions. This is fed to a methanol synthesis reactor where CO and CO_2 are catalytically hydrogenated to CH_3OH. The crude product is distilled and dehydrated to remove water, hydrocarbon, and alcohol impurities. The thermal efficiency of methanol production is typically 68-72% (3). Energy losses in transportation range from 1-2%, yielding a net fuel production efficiency of 67-71%.

The third option is a petroleum-based fuel (e.g. gasoline or diesel) stored and converted to an H_2-rich gas by partial oxidation on-board the vehicle. Gasoline delivered at the pump in a retail station typically carries 85-90% of the heating value available from petroleum produced at the wellhead.

Table 1 lists compares net efficiencies of the three fuel options, considering energy efficiency of fuel production, fuel processing on-board the vehicle, and the fuel cell. The previous paragraphs outline assumptions used in estimating fuel production efficiencies. On-board fuel processing and fuel cell efficiencies estimates reflect ranges cited by others (4,5). Net efficiencies of all the options are significant improvements over current gasoline-fueled IC engines. On highway drive cycles (which are closest to the steady-state fuel cell system efficiencies cited above), these engines are 20 % efficient in delivering power to the wheels (6), yielding a net efficiency of 17-18% when gasoline production/delivery is included.

The data used to construct Table 1 contain some uncertainties. Fuel production efficiency figures are fairly solid, relying on many years of commercial experience in production of gasoline, methanol, and hydrogen in large scale. Fuel cell and fuel processor efficiencies are less certain. These rely on models and limited hardware data measured under steady-state operating conditions. Still, the exercise is valuable in that it shows that the fuel cell options have potential to significantly improve efficiency vs. current generation ICE vehicles. Overlapping ranges of the gasoline and compressed H_2 fuel option efficiencies illustrates the need to determine efficiencies and emissions of these systems in vehicles under realistic drive cycles.

Fuels from Natural Gas

The equivalent of over 800 billion barrels of oil currently lies dormant in natural gas reserves largely inaccessible by pipeline. These previously untapped resources along with underutilized light hydrocarbons associated with crude oil production could become energy sources for gas-to-liquids conversion technologies emerging from research and development efforts.

Chemical conversion of natural gas is a relatively newer route for preparing liquid hydrocarbons for transport to markets. Although current conversion processes have lower thermal efficiencies than LNG processing, under some circumstances this debit can be largely offset by higher value liquids which can range from ultrahigh quality refinery and petrochemical feed stocks to finished products. Moreover, these streams can be shipped and stored in conventional facilities obviating the need for dedicated cryogenic transportation equipment and tankage.

Natural gas can be converted to zero sulfur, zero aromatic hydrocarbons and also to methanol and methanol derivatives like dimethyl ether. The table below lists the potential of the various products for natural gas as fuels for advanced automotive power plants.

	Fuel Cell	Compressor Ignition Combustion
Methanol	X	
Dimethylether	X	X
Fischer Tropsch Naphtha	X	
Fischer Tropsch Diesel		X

The process for producing methanol from natural gas was described earlier. Process schemes to convert natural gas to Fischer-Tropsch hydrocarbon products all start with the partial oxidation or steam reforming of natural gas to a mixture of carbon monoxide and hydrogen. Various process schemes have been developed and demonstrated ranging from fluidized to packed bed reactors. All depend to varying degrees on the thermal combustion of the hydrocarbon and the reforming of the hydrocarbon with steam. The product is generally a synthesis gas with a ratio of hydrogen to carbon monoxide slightly above 2.0. This mixture is then converted at 25-40 atmospheres to a hydrocarbon mixture with a carbon distribution determined by a Schultz-Flory distribution. The product of the Fischer Tropsch reaction is in most cases further processed to adjust the product distribution according to market opportunities. The product options range from waxes, lubricant basestocks, specialty solvents, diesel fuel, naphthas and liquefied petroleum gas (7).

The transportation fuel market is by far the largest since worldwide consumption is on the order of 40 million barrels a day versus less than one million barrels for lubricant basestocks. The diesel product from Fischer Tropsch synthesis is particularly attractive since it has a very high cetane number, above 75, and essentially no sulfur or aromatics. The naphthas from Fischer Tropsch is not a very attractive gasoline component due to its low octane number (less than 50) however it is a very attractive fuel for the generation of hydrogen for fuel cell powered vehicles.

The Next Steps

At the present time there are many organizations, including Exxon, actively involved in evaluating the performance of a broad range of hydrocarbons and alcohols in fuel cell and internal combustion automotive power plants. The amount of data available is limited since research on these fuel/engine combinations are at the exploratory stage. In the next two years the results will begin to emerge and the assessment of their potential can begin under a sound footing of facts. The assessment process will not be easy since it will be necessary to balance complex factors like energy efficiency, emissions, vehicle and fuel cost and infrastructure costs. In the final analysis the public acceptance of the vehicle/fuel system will determine its market impact.

References

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Table 1: Comparison of Net System Efficiencies

	Efficiencies			
Fuel	Fuel Production	Fuel Processor	Fuel Cell	Net Efficiency
Gasoline	0.85-0.90	0.75-0.83	0.45-0.50	0.29-0.37
Methanol	0.67-0.71	0.78-0.85	0.50-0.55	0.26-0.33
5000 psi H_2	0.63-0.72	NA	0.55-0.60	0.35-0.43

Figure 1: Operational Principles of an H_2 PEM Fuel Cell