Reforming of Diesel Fuel for Transportation Applications

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Objectives

- Verify feasibility of diesel autothermal reforming (ATR) in engineering-scale reformer
- Demonstrate operation with liquid fuel injection
- Reduce H_2O:C ratio needed to prevent coking

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- J. Durability
- M. Fuel Processor Integration and Efficiency
- N. Cost

Approach

- Perform computational fluid dynamics (CFD) modeling of reactors to guide reactor design
- Investigate reforming chemistry to determine how diesel fuel formulations, H_2O:C ratio, and O_2:C ratio affect reforming efficiency, coking, and catalyst lifetime
- Optimize reactor engineering based on results from modeling and reforming chemistry

Accomplishments

- Demonstrated successful operation of liquid fuel injector
- Determined effect of O_2:C and H_2O:C ratios on reforming efficiency for several different diesel components
- Demonstrated that di-aromatic components are more difficult to reform than mono-aromatics

Future Directions

- Determine how fuel composition affects catalyst durability
- Investigate reforming under partial oxidation (POX) conditions and in low H_2O:C regimes
- Provide data for National Energy Technology Laboratory (NETL) model development and validation

Introduction

Diesel fuel is widely distributed and has a high energy density. This makes diesel reforming an attractive option for hydrogen production on-board vehicles. The hydrogen-rich reformate gas produced from diesel reforming can be used to produce power with fuel cells or used to reduce NO_x emissions from combustion engines using reformate feed to selective catalytic reduction units. Diesel reforming poses several unique technical challenges, however. These challenges result from the physical and chemical properties of diesel fuel. To better understand diesel reforming and the chemistry involved, we have investigated the autothermal reforming of several major diesel constituents in a kilowatt-scale reactor.

Major technical challenges in reforming diesel fuel include preventing coking while maintaining high reforming efficiencies and extending the catalyst lifetime/durability. We have found that delivering the fuel and obtaining a well-mixed stream of fuel, steam, and air before the fuel begins to decompose thermally can affect catalyst durability and coking. Due to the high boiling point of diesel fuel, vaporizing the fuel and using gas-phase mixing prior to the reactor is not a viable option. Poor mixing leads to oxygen-starved regions, regions where the reactant ratios favor coke formation, and hot spots that accelerate catalyst degradation. To overcome this problem, we developed and tested an injection nozzle of a new design. This injector design led to well-mixed reactants that allowed us to reform diesel surrogates and obtain reformate compositions that closely match those predicted by equilibrium thermodynamic calculations. In addition to the reactant vaporization and mixing issues, the complex nature of diesel fuel also leads to several challenges in reforming. To understand better the chemistry of diesel reforming, we have investigated the reforming of representative compounds from the different classes of hydrocarbons present. Experiments were performed at gas hourly space velocities (GHSV) of 10,000 to 100,000 h^{-1} with varying oxygen-to-carbon ($0.15<O_2/C<0.5$) and steam-to-carbon ($1<H_2O/C<3$) ratios to determine the influence of these parameters on product gas composition and on reformer efficiency.

Approach

Computational fluid dynamics (CFD) modeling was utilized to study mixing of reactants and to guide improvements in a liquid injector system to deliver fuel to the reactor. The spray behavior of the new liquid injector nozzle was characterized with the help of a nonintrusive, laser-based phase Doppler particle analyzer (PDPA). After testing, the injector was installed in an engineering-scale reactor for the reforming tests.

Model compounds of different types of hydrocarbon species found in diesel fuel were tested under autothermal reforming conditions in the engineering-scale reactor. No external heating was supplied to the reactor. The product gas compositions were determined with various steam-to-carbon and oxygen-to-carbon ratios.

Results

We have performed CFD modeling studies that indicate that mixing of reactants is critical in avoiding hot spots and cold spots. The results also indicate that substantial variations occur in the H_2O:C and O_2:C ratios across the catalyst. The H_2O:C ratio is critical in controlling coking. To address this problem and provide well-mixed reactants to the catalyst bed, we have developed an innovative injector nozzle that produces small droplets of diesel fuel with low air-side pressure drops. It intimately mixes the fuel, steam (or water at startup), and air prior to the catalyst bed. In tests with hexadecane, the corrected and fitted mass median diameter (MMD) determined from PDPA over the central 1.5" of the spray was 8.3±2.7 μm at high-flow conditions (10 ml/min hexadecane) and 8.0±2.3 μm at low-flow conditions (3 ml/min hexadecane).

We have initiated a study of reforming of the various types of chemicals found in diesel fuel using liquid injection. Reforming of species found in diesel fuel indicate that there are differences in how the different species react. The product gas composition from reforming dodecane, hexadecane, and xylene as a function of O:C ratio (oxygen coming from O_2 in air) is shown in Figure 1. The hydrogen yield increases with increasing O:C to a

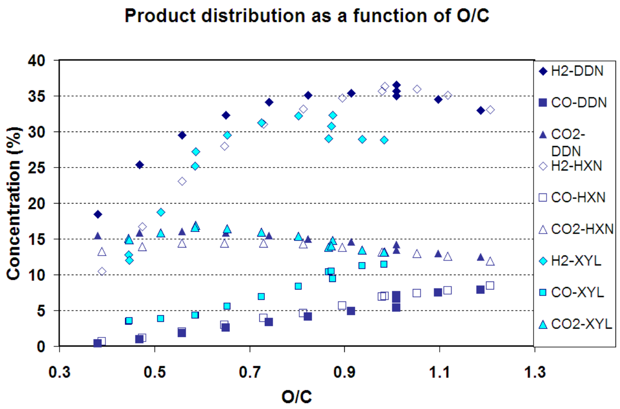

Figure 1. Effect of the O:C Ratio on the Product Gas Distribution from Autothermal Reforming of Dodecane (DDN), Hexadecane (HXN) and Xylene (XYL) in an Engineering Scale Reactor

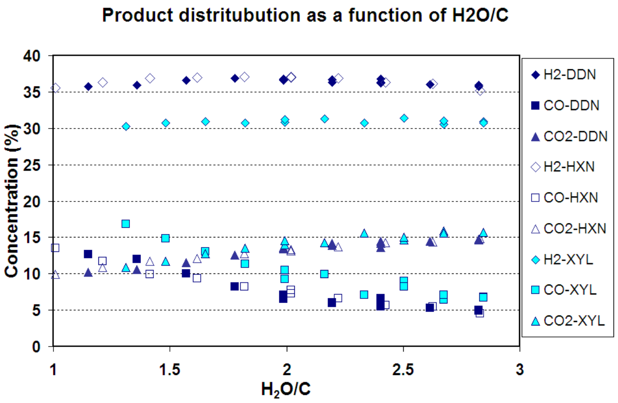

Figure 2. Effect of the H_2O:C Ratio on the Product Gas Distribution from Autothermal Reforming of Dodecane (DDN), Hexadecane (HXN) and Xylene (XYL) in an Engineering Scale Reactor

maximum at an O:C of approximately 1.0 for dodecane and hexadecane and 0.8 for xylene, then decreases. The increase occurs more rapidly for the shorter chain length dodecane than for hexadecane or xylene. Reforming efficiency also increases with O:C, reaching a maximum where the H_2 concentration maximizes, then levels off. Reforming efficiency is defined as:

$$\eta_{ref} = \{Ct_{H2}\Delta Hc_{H2} + Ct_{CO}\Delta Hc_{CO}\}/Ct_{fuel}\Delta Hc_{fuel}$$

$Ct_{,i}$ = Molar flow rate of i
ΔHc_i = *Heat of combustion of i*

The effect of the H_2O:C ratio on reforming is shown in Figure 2. As the H_2O:C ratio increases, the hydrogen content increases slightly, while the CO concentration decreases. This leads to an overall decrease in efficiency with increasing H_2O:C ratio. The decrease is likely the result of the increased thermal load from the additional steam, which results in lower reactor temperatures.

Xylene was more difficult to reform than the paraffinic species, providing lower hydrogen content and resulting in higher catalyst temperatures at similar O:C and H_2O:C ratios. Methylnaphthalene was reformed to determine how the multi-ring aromatic species present in diesel fuel react during reforming. Reforming of the methylnaphthalene was more difficult than the reforming of xylene. Reforming efficiencies were lower, and coke deposits were more likely to form.

Conclusions

- Proper delivery and mixing of reactants are needed to obtain high efficiencies and avoid hot spots and areas of non-uniform H_2O:C and O:C ratios.
- The new liquid injector nozzle provided small (<10 micron) droplets of fuel under relevant reactor operating conditions.
- Substantial differences were found and documented in how the major different diesel fuel constituents are reformed.
  - Aromatics result in higher maximum reforming temperatures and lower energy conversion efficiencies.
  - Di-aromatics are more difficult to reform than mono-aromatics.
- Increasing H_2O:C ratio reduces coking but decreases overall efficiency.

FY 2003 Publications/Presentations

1. "Characterization of Kilowatt Scale Diesel Autothermal Reformer With Surrogate Fuels", Di-Jia Liu, Hsiu-Kai Liao, Laura Miller and Shabbir Ahmed, presented at 2003 AIChE Spring National Meeting, New Orleans, LA, March 30 - April 3, 2003.

2. "Diesel Reforming for Fuel Cell Application in a 1- to 5-Kilowatt ATR Reformer", Di-Jia Liu, Hsiu-Kai Liao, Laura Miller and Shabbir Ahmed, presented at 18th North American Catalysis Society Meeting, Cancun, Mexico, June 2 - June 6, 2003.

3. "Diesel Reforming in a Kilowatt Scale Autothermal Reformer with Liquid Injection", Di-Jia Liu, Hsiu-Kai Liao, Laura Miller and Shabbir Ahmed, presented at 2003 Future Transportation Technology Conference, June 23-25, 2003, Hilton, Costa Mesa, California.

4. "Diesel Reforming in a Kilowatt Scale Autothermal Reformer with Liquid Injection", Di-Jia Liu, Hsiu-Kai Liao, Laura Miller and Shabbir Ahmed, SAE publication 03FTT-6.