

Development of Reaction Kinetics for Diesel-Based Fuel Cell Reformers

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Objectives

Develop reaction kinetics, predictive models, and test methods for diesel fuel reforming and provide necessary tools and information to fuel reforming developers and fuel cell system integrators for technology development, performance optimization, and system control.

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:

- M. Fuel Processor System Integration and Efficiency

Approach

- Conduct process optimization study for the diesel autothermal reforming.
- Carry out kinetic measurements of representative model compounds.
- Develop a level-1 kinetic model with a benchmark fuel (diesel).
- Build liquid hydrocarbon characterization capability.

Accomplishments

- Tested three model compounds from the major representative functional groups in diesel fuel.
- Developed surface response maps for steam reforming, partial oxidation and autothermal reforming (ATR) using Pt/ γ -alumina catalysts for n-tetradecane, 1-methylnaphthalene, and decalin.
- Built liquid hydrocarbon characterization capability.

Future Directions

- Evaluate other fuel compounds within a classification to examine if similar reforming behavior exists.
- Conduct combinatorial fuel compound studies.
- From response mapping, develop intrinsic reaction models for particular catalyst types.
- Collaborate with Las Alamos National Laboratory to provide carbon deactivation kinetics.
- Collaborate with Argonne National Laboratory to obtain experimental reactor performance data to validate reaction models and provide for fuel reactant mixing modeling capability suitable for computational fluid dynamic (CFD) modeling codes.
- Develop a detailed kinetic model that incorporates CFD.

Introduction

The fuel processor is a critical component of fuel cell systems. The processor must be able to provide a clean, tailored synthesis gas to the fuel cell stack for long-term operation. Key characteristics desired for the processor (and the system) include low cost, high efficiency, maximum thermal integration, low maintenance intervals, and acceptable startup and transient response. There are also several barrier issues that must be overcome to achieve these characteristics. Carbon formation, particularly upon startup, must be minimized to avoid coking of the catalysts in the reformer and downstream fuel cell. Fuels containing sulfur can poison both the reforming catalysts and the fuel cell anode. High thermal mass components (some of which may have heat-ramp restrictions) can limit startup times and transient response. And finally, cost targets must be achieved to ensure commercial success.

Fundamental understanding for design and operation of reformers is important for successful technology development. One of the most fundamental engineering design parameters that can be measured in the laboratory is the intrinsic kinetics of a catalyst system. Once established for a particular feedstock and catalyst system, it can be coupled with computational fluid dynamics (CFD) code to effectively design, optimize, and minimize hydrocarbon slip in autothermal reformer systems. In principle, the kinetics of NO_x formation, sulfur poisoning, carbon formation and catalyst aging can be added to allow for a complete predictive model for reformer performance and operation.

However, modeling of reforming systems is extremely complicated. Diesel fuel consists of a complex variable mixture of hundreds of hydrocarbon compounds containing mainly olefins, saturates and aromatics. Empirical expressions for space velocity or simple power law-type models are typically used to design reformers. Unfortunately, these tend to be limited to a specific catalyst, fuel composition, and operating point. Therefore, the development of validated predictive models that can account for variations in these parameters is necessary.

For the autothermal reforming of diesel with steam and oxygen, a complex reaction network is expected. Elucidation of this network and the development of a generalized complex network model for platinum catalysts will be the initial focus of this project. The overall kinetic approach employed will balance the level of detail that can accurately be accommodated by CFD code with the ability to easily update kinetic parameters for a new catalyst system.

Approach

To select an appropriate model, it is necessary to understand the reaction mechanisms and pathways for the chemical system. One approach to gaining that understanding is surface response mapping. This is a statistical technique used to map characteristic responses (e.g. yield, conversion, carbon buildup, etc.) to input variables (O_2/C , $\text{H}_2\text{O}/\text{C}$, temperature, space velocity, etc.) over a defined region. It identifies the significance of parameters and their interactions. Also, it provides data that can lead to validation of kinetic models and can test the statistical significance of proposed reaction pathways. As the most important mechanisms and reaction pathways are defined, appropriate models will be selected to develop the model. Kinetic measurements of single component or individual reaction systems will be developed and used to validate the model. This will initially be done for a platinum catalyst and extended to other catalyst systems as needed to complete the model.

A fixed bed reactor system was used to conduct the experiments. The reactor was operated continuously at steady state. γ -Alumina supported platinum (0.611 wt%) catalyst (surface area $103 \text{ m}^2/\text{g}$) was used in this study as a base catalyst. A summary of reaction conditions is given in Table 1.

Individual model compounds representing each organic class in diesel were subjected to autothermal, partial oxidation, and steam reforming at the temperatures and space velocities given in Table 1. Tetradecane, decalin, and 1-methylnaphthalene were identified as model compounds to represent

paraffins, naphthenes, and aromatics, respectively, found in diesel.

Table 1. Experimental conditions

		Paraffin	Aromatic	Naphthene
Model Compound		n-Tetradecane	1-methyl naphthalene	Decalin
O ₂ /C	POX	0.5	0.5	0.5
	SR	0	0	0
	ATR	0.3	0.3	0.3
H ₂ O/C	POX	0	0	0
	SR	3.0	3.0	3.0
	ATR	1.5	1.5	1.5
T (°C)		750 - 900	750 - 850	750 - 850
GHSV (h ⁻¹)		50,000 - 200,000	22,000 - 66,000	50,000 - 150,000

Gas chromatography was used to identify and separate the reaction products. The gases (N₂, O₂, CO, CO₂, and CH₄) were analyzed using a thermal conductivity detector (TCD), and the gaseous hydrocarbons were analyzed using a flame ionization detector (FID). Gas chromatography (Perkin Elmer's AutoSystem XL) coupled with mass spectrometry (Perkin Elmer's TurboMass Gold) was used to quantify and identify the complex liquid hydrocarbon product mixture that formed at various hydrocarbon conversions. Product yield is reported as a percentage of the theoretical yield based on moles of carbon in hydrocarbon fed to the reactor. For example, the yield of product A (H₂, CO, and CO₂) can be defined as

$$\text{Yield of A (\%)} = \frac{\text{Moles of A produced}}{N \times \text{moles of hydrocarbon fed to the reactor}} * 100$$

where N is the number of carbons in hydrocarbon fuel used in this study. In some cases, H₂ yields may be higher than 100% since steam reforming and the water gas shift reaction also contribute to H₂ production apart from hydrocarbons.

Results

Statistical Analysis of Reforming Process

The yields of individual species from hydrocarbon reforming, z, which depend on the space velocity (x) and reaction temperature (y), can be described by the equation

$$z = b_0 + b_1x + b_2y + b_{11}x^2 + b_{22}y^2 + b_{12}xy \quad (1)$$

where z = the yield of individual species after completion of the reaction, x = gas hourly space velocity (hr⁻¹), y = temperature (°C), and b₀...b₂₂ are the coefficients of the model. The coefficients of Equation 1 were estimated by making use of the responses of experiments for the standardized values of x and y which varied in the range given in Table 1. A relationship between yields (z) and two quantitative variables x (space velocity) and y (reaction temperature) is represented by response surface curves as shown in Figures 1-5. Coefficients of quadratic Equation 1 are summarized in Table 2 for H₂ and CO yields from autothermal reforming of various types of raw materials used in this study. Quadratic fit of data from response surface mapping was excellent (>90%).

Analysis of a response surface curve can be helpful in establishing the hypothetical kinetic schemes of the process. The effect of different parameters on the course of a process may vary from one organic class to another. That is why we decided to study each organic class separately.

Model compounds representing each homologous series present in diesel were evaluated to develop surface response maps for steam reforming, partial oxidation and autothermal reforming over Pt catalysts. Each model compound behaved differently upon reforming under the same conditions. Aromatics were less active than aliphatics and required relatively higher contact time to convert into synthesis gas. The hydrogen production rates at the same conditions were observed in this order: Aromatics << Naphthenes < Paraffins.

Table 2. Coefficients of Quadratic Equations for Autothermal Reforming of Model Components

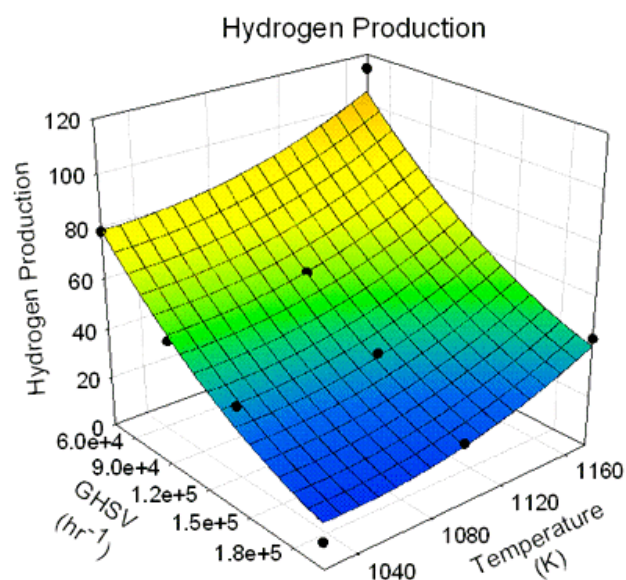
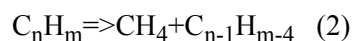
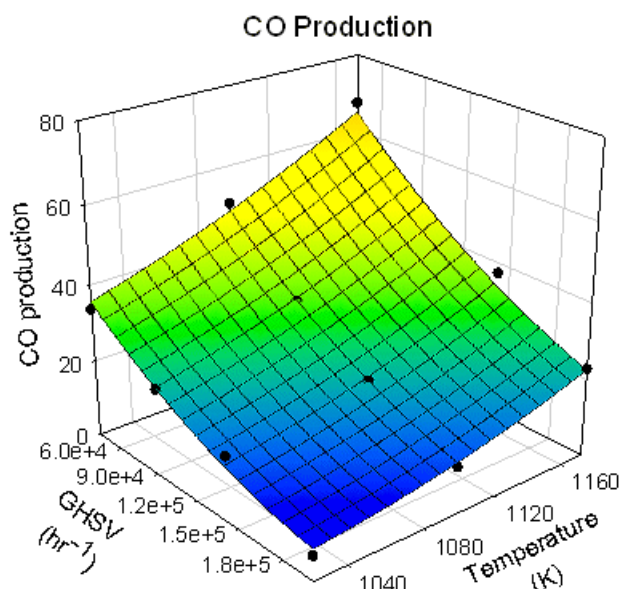
Fuel	X	Coefficients						R ²
		b ₀	b ₁	b ₂	b ₁₁	b ₁₂	b ₂₂	
Tetradecane	H ₂	1313.8	-6.0e ⁻⁴	-2.36	1.4e ⁻⁹	-1.4e ⁻⁷	1.2e ⁻³	0.96
	CO	283.8	2.9e ⁻⁴	-0.62	7.4e ⁻¹⁰	-6.3e ⁻⁷	3.9e ⁻⁴	0.98
1-Methylnaphthalene	H ₂	1155.9	1.9e ⁻³	-2.36	4.7e ⁻⁹	-2.4e ⁻⁶	1.2e ⁻³	0.98
	CO	521.8	1.7e ⁻³	-1.14	-6.1e ⁻¹⁰	-1.6e ⁻⁶	6.2e ⁻⁴	0.96
Decalin	H ₂	627.4	-2.6e ⁻⁴	-1.47	2.7e ⁻⁹	-4.2e ⁻⁷	8.7e ⁻⁴	0.97
	CO	1975.2	-1.2e ⁻³	-3.67	1.7e ⁻⁹	-6.7e ⁻⁷	1.7e ⁻³	0.87

Hydrocarbon product distributions depended greatly on the model compound, the type of reforming performed, and the process parameters (space velocity and reaction temperature). Generally, in addition to desired products (H₂ and CO), the gas product streams also include CO₂, C1 to C7 n-alkanes, ethylene, propylene, iso-butane, iso-pentane, and benzene. Methane and CO₂ were the major by-products present in significant amounts in the gas product streams. Furthermore, a series of oxygenated products such as aldehydes and ketones were observed in liquid product from partial oxidation of n-tetradecane, particularly at higher space velocities and lower temperatures.

Figures 1-3 show the effect of temperature and space velocity on the yields of H₂, CO, and CO₂ from the autothermal reforming of n-tetradecane (paraffin). Figures 4-5 show the yields of H₂ from the autothermal reforming of 1-methylnaphthalene

(aromatic) and decalin (naphthene), respectively. Generally, the yields of H₂ and CO increased with increasing reaction temperature and decreasing space velocity. However, the yields of CO₂ from autothermal reforming of n-tetradecane and decalin decreased with increasing temperature because the lower temperatures favor the water-gas-shift reaction, while the reverse of water-gas-shift reaction is facilitated at higher temperatures.

Higher yields of methane (1-10%) were observed in the product gas from autothermal reforming of different feedstocks. Methane is not thought to be produced from the methanation reactions because those reactions are not thermodynamically favored at the temperature studied. It is probable that CH₄ is formed by successive α -scission of the hydrocarbons on the metal catalysts,

**Figure 1.** Yield of H₂ from ATR of n-Tetradecane (O₂/C = 0.3 and S/C = 1.5)**Figure 2.** Yield of CO from ATR of n-Tetradecane (O₂/C = 0.3 and S/C = 1.5)

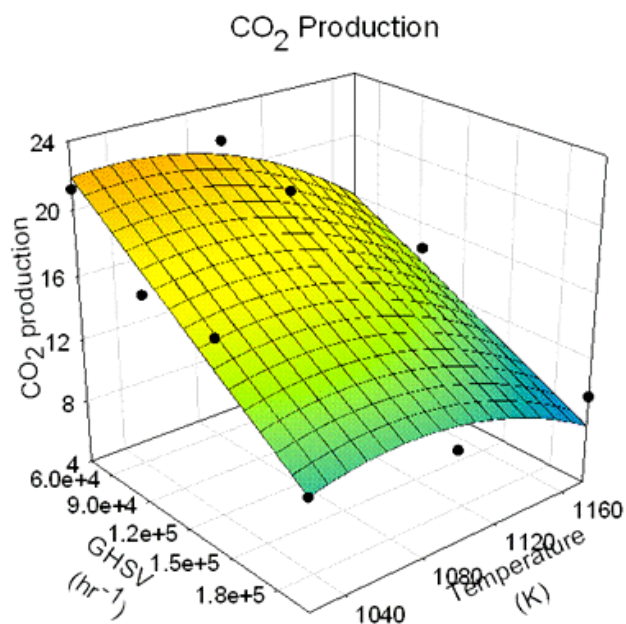


Figure 3. Yield of CO₂ from ATR of n-Tetradecane (O₂/C = 0.3 and S/C = 1.5)

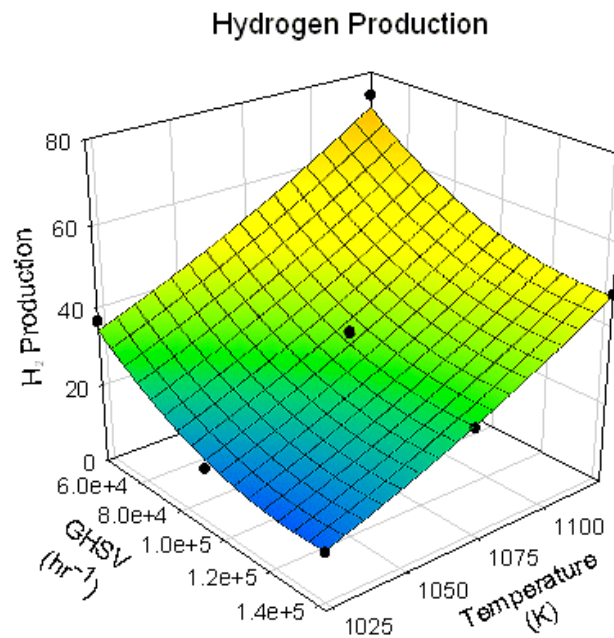


Figure 5. Yield of H₂ from ATR of Decalin (O₂/C = 0.3 and S/C = 1.5)

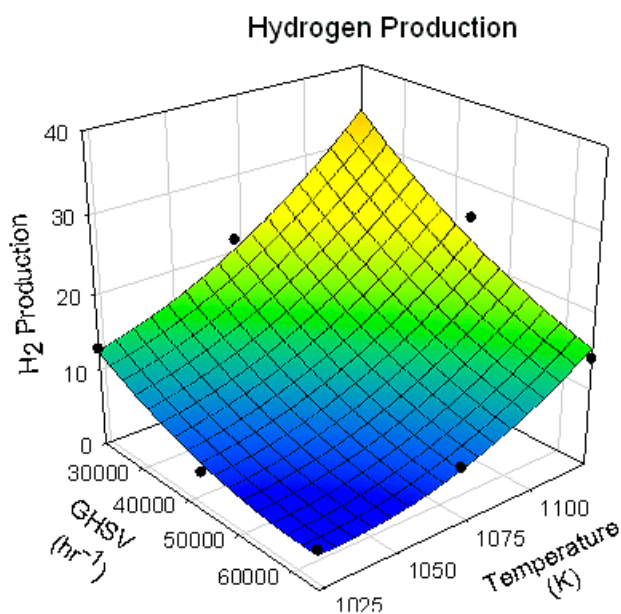


Figure 4. Yield of H₂ from ATR of 1-Methylnaphthalene (O₂/C = 0.3 and S/C = 1.5)

Higher yields of methane compared to negligible other hydrocarbons coupled with the significant concentrations of naphthalene in the product stream from autothermal reforming of 1-methylnaphthalene suggests that the reforming of aromatics starts with a dealkylation reaction.

Yields of cracking products, lower paraffins and olefins, decrease as temperature increases or space velocity decreases. Higher temperature facilitates the cracking reaction, but at the same time, it also increases the rate of reforming reaction. Increasing the residence time would increase the contact time between the catalyst and reactants, thereby increasing the conversion of cracking products into syngas and reducing the yield of cracking products.

Isoparaffins or branched olefins were not observed, which suggests that isomerization reactions are not taking place during reforming of diesel fuel components. Also, naphthenes were not detected from the autothermal reforming of paraffins or aromatics. However, a series of olefins (alkenes, dienes, trienes, alkynes, etc.) formed from reforming of n-tetradecane, particularly at higher space velocities and lower temperatures.

Production of olefins and aromatics was significant from autothermal reforming as well as partial oxidation of n-tetradecane at higher space velocity and temperature. Formation of compounds such as n-octyl benzene, but no naphthenic compounds from the paraffin reforming, suggests that the aromatics are produced primarily by cyclization reactions of poly-enes rather than

cyclization of paraffins to naphthenes and then dehydrogenation to aromatics. Reforming of decalin also produced significant concentration of aromatics, presumably via dehydrogenation reaction.

Reforming of 1-methylnaphthalene at elevated temperatures (~900°C) produced significant coking on the catalyst and resulted in higher pressure drops and eventually reactor plugging. Aromatics contribute significantly to the catalyst deactivation compared to paraffins and cycloparaffins present in the diesel fuel.

Conclusions

Single component reforming studies were conducted on tetradecane, decalin, and 1-methylnaphthalene. These model compounds represented the major organic classes found in diesel fuel (paraffins, naphthenes, and aromatics) and, studied individually, aided in analyzing the reforming characteristics and tendency of each species. Use of a surface response mapping technique was helpful in assessing the impact of space velocity (residence time) and temperature on reforming of the various compounds. Hydrogen, carbon monoxide, and carbon dioxide production were measured as a function of temperature, space velocity, and reforming type for a platinum-based catalyst. Intermediate species formation of various hydrocarbons including olefins and aromatics were observed during reforming. Carbon formation at various operating points and with certain fuel compounds point to the importance of understanding the mechanism or route for both reformer operation and catalyst design. Additional studies, including combinatorial fuel reforming, are needed to ensure successful development of this technology area.

FY 2003 Publications/Presentations

1. Rogers, W., Shi, S., Berry, D. A., Gardner, T. H., Shekhawat, D., "Modeling of Reformers for Fuel Cell Applications", First International Conference on Fuel Cell Science, Engineering and Technology, Rochester, NY, April 21-23, 2003.
2. Shi, S., Rogers, W., Berry, D. A., Gardner, T. H., Shekhawat, D., "Numerical Simulation of Partial Oxidization Processing of Diesel for Fuel Cells", Fourth ASME/JSME Joint Fluids Engineering Conference, Honolulu, HI, July 6-11, 2003.
3. Zinn, A. N., Gardner, T. H., Berry, D. A., James, R. E., Shekhawat, D., "Investigation of a Novel Reciprocating Compression Reformer for Use in Solid Oxide Fuel Cell Systems", First International Conference on Fuel Cell Science, Engineering and Technology, Rochester, NY, April 21-23, 2003.
4. Berry, D. A., James, R. E., Gardner, T. H., Shekhawat, D., "Systems Analysis of Diesel-Based Fuel Cells", First International Conference on Fuel Cell Science, Engineering and Technology, Rochester, NY, April 21-23, 2003.
5. Berry, D. A., Gardner, T. H., Shekhawat, D., "Development of Predictive Models for Diesel-Based Fuel Processors", 2003 Annual Merit Review Meeting of Hydrogen, Fuel Cells & Infrastructure Technologies Program, DOE Office of Energy Efficiency and Renewable Energy, Berkeley, CA, May 18 - 22, 2003.