

**Reforming Petroleum Based Fuels for Fuel Cell Vehicles: Composition –
Performance Relationships***

John P. Kopasz, Laura E. Miller, and Shabbir Ahmed
Electrochemical Technology Program
Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Peter Devlin* and Manuel Pacheco**

*U. S. Department of Energy, **Petro'leos de Venezuela, PDVSA

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Reforming Petroleum-Based Fuels for Fuel Cell Vehicles: Composition-Performance Relationships

John P. Kopasz, Laura E. Miller, and Shabbir Ahmed

Argonne National Laboratory

Peter Devlin* and Manuel Pacheco**

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ABSTRACT

Onboard reforming of petroleum-based fuels, such as gasoline, may help ease the introduction of fuel cell vehicles to the marketplace. Although gasoline can be reformed, it is optimized to meet the demands of ICEs. This optimization includes blending to increase the octane number and addition of oxygenates and detergents to control emissions. The requirements for a fuel for onboard reforming to hydrogen are quite different than those for combustion. Factors such as octane number and flame speed are not important; however, factors such as hydrogen density, catalyst-fuel interactions, and possible catalyst poisoning become paramount. In order to identify what factors are important in a hydrocarbon fuel for reforming to hydrogen and what factors are detrimental, we have begun a program to test various components of gasoline and blends of components under autothermal reforming conditions. The results indicate that fuel composition can have a large effect on reforming behavior. Components which may be beneficial for ICEs for their octane enhancing value were detrimental to reforming. Fuels with high aromatic and naphthenic content were more difficult to reform. Aromatics were also found to have an impact on the kinetics for reforming of paraffins. The effects of sulfur impurities were dependent on the catalyst. Sulfur was detrimental for Ni, Co, and Ru catalysts. Sulfur was beneficial for reforming with Pt catalysts, however, the effect was dependent on the sulfur concentration.

INTRODUCTION

Onboard reforming of petroleum-based fuels, such as gasoline, may help ease the introduction of fuel cell vehicles to the marketplace. The use of gasoline negates problems associated with putting a refueling infrastructure in place and provides a fuel with high hydrogen storage capacities, proven consumer acceptance, and low cost.¹⁻³

However, while gasoline has been reformed,^{4,5} gasoline formulations have been optimized to meet the demands of today's internal combustion engines (ICEs). The requirements for a fuel for onboard reforming to hydrogen are quite different than those for combustion, and a fuel optimized for combustion will not be optimized for reforming. Combustion is a series of gas-phase reactions, controlled by free radical chemistry. Reforming is generally performed catalytically, (although partial oxidation can be performed non-catalytically) and is controlled by reactions occurring on the catalyst surface. Factors such as octane number, which are correlated to performance in ICEs, are not expected to be relevant for reforming. The change from gas-phase combustion chemistry to surface-catalyzed reactions suggests a whole new set of factors will control the reactivity and determine what makes a good fuel for reforming. Catalyst-fuel interactions and possible catalyst poisoning are expected to be paramount. In addition, factors such as hydrogen density of the fuel assume new importance.

For onboard reforming of hydrocarbons to hydrogen, autothermal reforming is thought to be the method of choice.⁶ The net autothermal reforming reaction can be written as:



The O_2/C (x/n) and H_2O/C ($(2n-2x-p)/n$) ratios can be chosen such that the overall reaction has an overall heat of reaction close to zero (autothermal). In practice, the reaction is run with conditions so that the net reaction is slightly exothermic.

In order to identify what factors are important in a hydrocarbon fuel for reforming to hydrogen and what factors are detrimental, we have begun a program to test various components of gasoline and blends of components under autothermal reforming conditions. One area where fuel formulations have been found to have an impact is in the formation of coke and the positions of the

coke-forming regime.⁷ Differences in composition are also expected to affect other factors related to reformer performance, such as hydrogen production and hydrocarbon conversion.

Reformer performance, as defined by hydrogen production and hydrocarbon conversion, has been studied as a function of fuel composition. These studies focus on reformer performance in regimes where coke formation should not occur and is generally not observed. Earlier we compared performance data for several individual components of gasoline-type fuels. This work found that trimethylbenzene required the most severe reforming conditions of the components tested, requiring both high temperature and low space velocities to reform. Isooctane and n-octane could be reformed at lower temperatures, while methylcyclohexane, methylcyclopentane, and 1-octene could be reformed at higher space velocities than trimethylbenzene.⁸ The current work looks at mixtures to gain more insight into composition/performance relationships for autothermal reforming. This should help determine what an optimum fuel for onboard reforming would be and help determine what the penalties in reforming efficiency would be using current gasoline formulations.

EXPERIMENTAL

Effects of composition were investigated by testing fuels prepared from refinery streams and by testing mixtures of isooctane with different components. Three different fuels were prepared using readily available refinery streams and systematically varying the concentration of aromatics and naphthenes. The fuels compositions, as determined by PIONA analyses, are shown in Table I. To further investigate performance-composition effects, mixtures of isooctane with xylene, methylcyclohexane, benzothiophene and isobutyl amine were reformed.

Volume %	Fuel A	Fuel B	Fuel C
n-paraffins	10.48	26.08	15.79
isoparaffins	89.27	46.95	57.86
olefins	0.20	0.48	0.76
naphthenes	0.05	19.84	5.19
aromatics	0.00	6.65	20.39
sulfur (wppm)	26.9	12.0	18.5
Calculated mol. Wt.	104.6	96.6	100.1

Table I. Fuel compositions

The fuels were tested at Argonne National Laboratory (ANL) facilities under autothermal reforming conditions to measure fuel reformability, including hydrogen yield and hydrocarbon conversion. The reforming temperature was in the range of 650-800°C with gas hourly space velocities (GHSV) ranging between 15,000 and 150,000 h⁻¹. This

corresponds to residence times in the reformer of approximately 200 to 20 milliseconds. The catalyst particle mean diameter was 0.5-0.75 mm. Reforming was performed with a constant H₂O:C ratio of 1.43 and an O₂:C ratio of 0.42, for reforming conditions which are near autothermal reforming conditions but are slightly exothermic.

Experiments were conducted in a microreactor system consisting of a 1/4-in. O.D. reactor tube housed in a temperature-controlled furnace. The reactor tube contains four sampling ports that allow gas samples to be withdrawn during the course of the experiment and injected directly into a mass analyzer. One benefit of this sampling arrangement is that it allows gas samples that have differing contact times to be analyzed without having to change the reactant feed rate. Approximately 2 g of catalyst was loaded into the reactor tube and located such that only two of the four sampling ports are located within the catalyst bed. Of the remaining two sampling ports, one was located above the catalyst bed, to analyze the feed composition, and the other was located below the catalyst bed, to analyze the product gas. A small portion (<1%) of the gas stream was diverted through one of these ports to the residual gas analyzer for analysis. The remainder of the gas stream continued through the reactor bed to the exit stream. Unless noted otherwise, the ATR catalyst used in these tests was developed by ANL and consisted of a group VIII metal on an oxide ion conductor. To provide a baseline for comparison between the different chemical compounds and catalysts tested, constant molar feed ratios were employed (O₂/C=0.42 and H₂O/C=1.4). A high-pressure liquid chromatographic (HPLC) pump was used to inject fuel and water into a heated zone, where they were vaporized prior to being introduced into the reactor tube. Gas flow rates were controlled by mass flow controllers.

Long-term tests (>1000h) were performed in a separate reactor utilizing a 1/2-in. reactor tube and containing approximately 20 g of catalyst. This reactor was equipped with a solid-state on-line hydrogen sensor and infrared carbon monoxide and carbon dioxide detectors. Batch sampling was performed at the exit stream, and the gas analyzed using a HP 5890 GC with the effluent stream split and sent to a TCD and an HP 5970 MSD. This system allowed us to determine the durability of the autothermal reforming catalyst and to determine if there were any long-term problems (poisoning, coking) caused by the fuel components.

RESULTS AND DISCUSSION

We have investigated the effects of reforming three fuel blends; a blend which is mainly paraffinic (fuel A), a blend which is mainly paraffinic with ~20% naphthenes added (fuel B), and a blend which is mainly paraffinic with ~20% aromatics added (fuel C). The fuels were reformed at temperatures of 650, 700, 750, and 800°C and GHSVs of

15,000, 25,000, 30,000, 50,000, 75,000 and 150,000 h^{-1} to determine the temperature-space velocity parameter space where these fuels may be useable. Fig. 1 shows a 3D plot of the hydrogen yield after water gas shift (WGS), shown as the percentage of the maximum theoretical hydrogen yield, versus temperature and GHSV for fuel A.

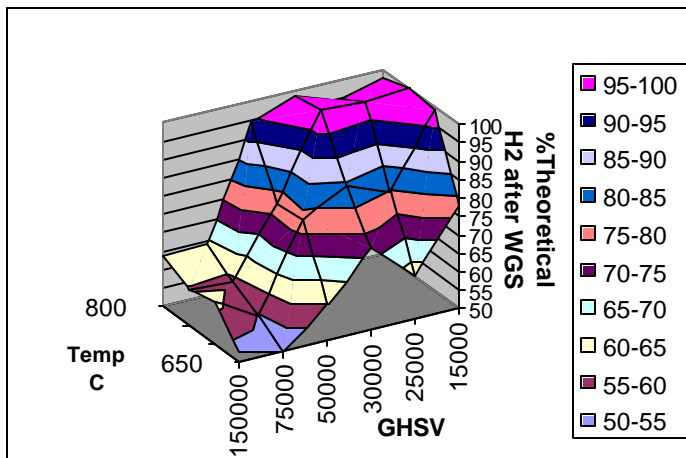


Figure 1. Hydrogen yield from fuel A, a > 99% paraffinic fuel.

This fuel shows what we consider to be acceptable H_2 yields (>95% of the theoretical H_2 after WGS) over a fairly wide range of temperatures and space velocities. Good performance was obtained at 800 and 750°C for GHSVs below 50,000 h^{-1} . At a GHSV of 15,000 h^{-1} , acceptable behavior could be obtained at temperatures down to 700°C.

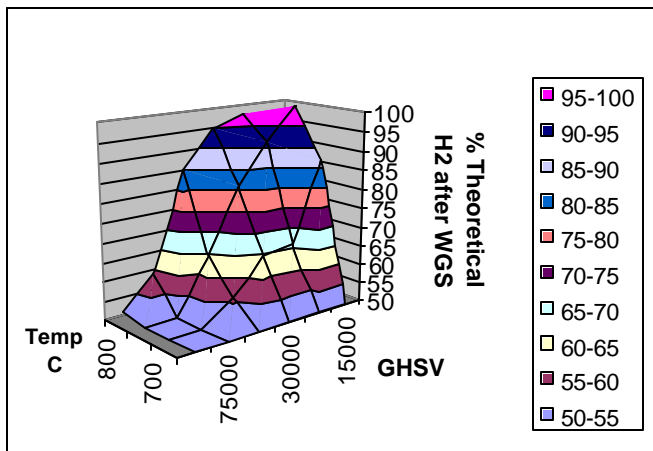


Figure 2. Hydrogen yield from fuel B, a fuel with ~20% naphthenes.

To examine the effects of naphthenic components, we investigated the reforming of fuel B, which contains ~20 naphthenes in the blend. This fuel provides acceptable hydrogen yields over a much smaller parameter space than fuel A (see Fig. 2). The acceptable parameter space is narrowed in terms of temperature and space velocity. Hydrogen yields are acceptable at GHSVs <30,000 h^{-1} for temperatures of 800°C. At 750°C, acceptable

performance is only obtained at a GHSV of 15,000 h^{-1} . This indicates the addition of naphthenes is detrimental to reformer performance. The changes in the temperature dependence upon addition of naphthenes is consistent with previous work on the individual components of gasoline, which indicated the reforming of methylcyclohexane showed a greater dependence on temperature than the reforming of isooctane or n-octane.⁸

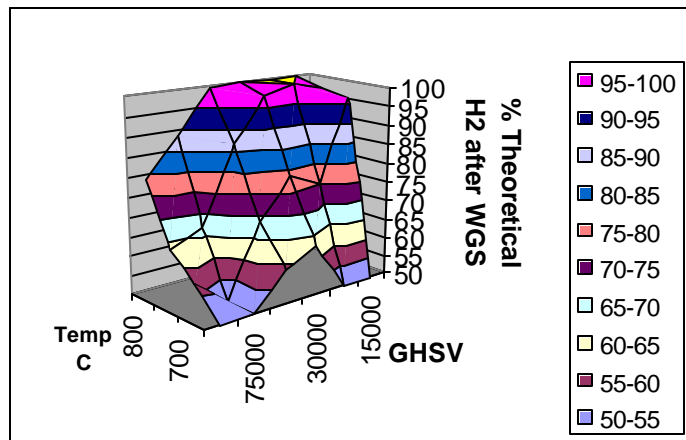


Figure 3. Hydrogen yield from fuel C, a fuel containing ~20% aromatics.

Next, we examined fuel C, with ~20% aromatics in the blend. A plot of hydrogen production, represented as the percentage of the maximum theoretical hydrogen yield obtained after water gas shift, as a function of temperature and GHSV is shown in Fig. 3. Two changes from the paraffinic fuel are apparent. First, the gradient in H_2 yield with temperature is much steeper for the fuel with aromatics than for the paraffinic fuel. Fuel C achieved 45-50% of the maximum theoretical hydrogen yield at 650°C and a GHSV of 15000 h^{-1} , while fuel A achieved 75-80% of the maximum hydrogen yield under the same conditions. Again, the temperature results are consistent with tests performed on individual components of gasoline, where trimethylbenzene and toluene reforming were found to decrease more dramatically with decreasing temperature than did isooctane reforming.⁸ The more aromatic fuel will need higher operating temperatures, probably to overcome the higher bond dissociation energies (BDE) needed for the dissociation of aromatic C-C and C-H bonds. Secondly, at high temperature (800°C), the gradient in H_2 production with GHSV is less steep for the fuel with aromatics present than for the paraffinic fuel. Our earlier work found that the dependence of reforming of the aromatic components with space velocity depended on the level of substitution of the aromatic ring. Toluene reforming was less dependent on variations in GHSV than isooctane, while trimethylbenzene was more dependent on GHSV changes than isooctane.⁸ This suggests the GHSV dependence of mixtures of aromatics will depend on the distribution of aromatics in the fuel.

In order to understand more fully the effects of adding aromatics and naphthenes to the paraffinic fuel, we have

looked at the kinetics of decay of the C4 species during the reforming of these fuel blends. The C4 decay was fit to a pseudo first-order rate law, and the rate constants extracted. These rate constants are plotted as a function of temperature in Fig. 4. For the fuels with naphthenes and aromatics, the rate of decay or disappearance of the C4 species at higher temperatures decreased compared to that for the most paraffinic fuel with no naphthenes and aromatics. This results in higher C4 species concentrations in the gas phase for the aromatic and naphthenic fuel at the outlet of the reactor (GHSV of 15,000 h⁻¹) than for the fully paraffinic fuel, even though more C4 species are present near the inlet (at GHSV of 150,000 h⁻¹) for the paraffinic fuel. For the aromatic fuel, this type of behavior can be explained by blocking or poisoning of the reactive metal sites by the aromatic species, which are adsorbed to the metal sites more strongly than the paraffinic species. This decreases the rate of reaction of the paraffinic species. Similar behavior has been observed in the oxidation of mixed fuels, where the rates of oxidation of other species are decreased by poisoning of the catalyst site by aromatics.^{9,10} We believe a similar mechanism is occurring with the naphthenic mixture with the additional step that the naphthenes are first dehydrogenated over the Pt sites to form aromatics, which then react much like the aromatic blends and poison the site for reaction with the paraffins.

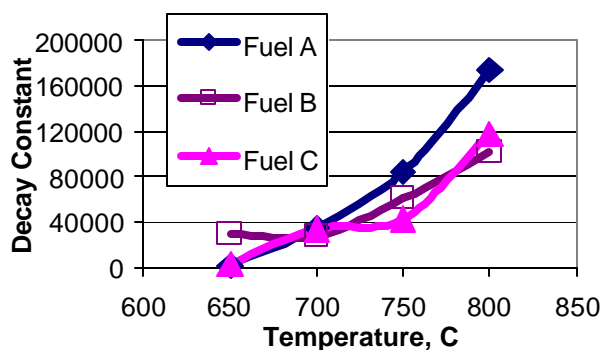


Figure 4. Comparison of rate constants for disappearance of butane species for the blended fuels.

To further test this hypothesis, we reformed pure isooctane and a mixture of isooctane with 20 volume % of xylene added at 700°C. The product gas was analyzed to look for butane fragments, which are the major species obtained from isooctane cracking. The results are shown in Fig. 5.

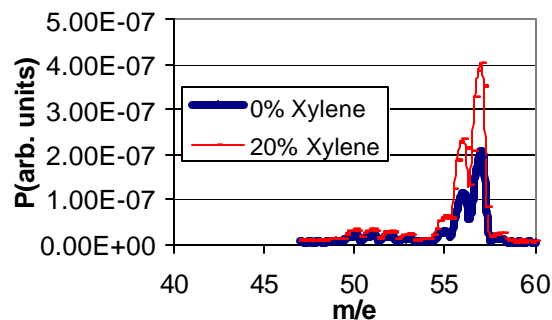


Figure 5. Comparison of butane in product gas from reforming isooctane and isooctane+20% xylene.

The product gas from the blend with 20% xylene added contained higher butane concentrations in the exit stream, even though the fuel contained less isooctane, the precursor for butane. Tests with xylene at 700°C showed no butane in the exit stream. This suggests that the xylene is interfering with the conversion of alkanes to CO₂ and hydrogen, or poisoning the reforming of the alkanes.

A similar test was performed on a mixture of isooctane and 20% methylcyclohexane. Again, more butanes were observed in the product gas stream for the mixture than for pure isooctane, suggesting a poisoning effect from the methylcyclohexane on isooctane reforming.

Sulfur Effects

The effect of sulfur impurities on isooctane reforming was determined by reforming isooctane doped with benzothiophene to provide solutions with 50 wppm sulfur. The short-term effect on hydrogen yield at a GHSV of 15,000 h⁻¹ and a temperature of 800°C is shown in Fig. 6. Hydrogen yields dropped for Ni-, Co-, and Ru-doped ceria catalysts, but increased for the Pt-doped ceria catalyst. This suggests that sulfur is detrimental to reforming over Ni, Co, and Ru catalysts, but that the Pt catalyst appears to benefit slightly from S.

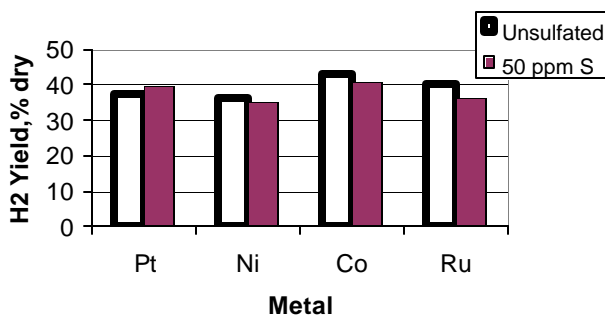


Figure 6. Comparison of hydrogen yield from reforming isooctane and isooctane+50 wppm S over several different catalysts (T=800°C, GHSV 15,000 h⁻¹).

Long-term tests were also performed to determine the long-term effect of sulfur on reforming. The fuel for these tests was a mixture representative of gasoline (74 wt% isooctane, 20 wt% xylenes, 5 wt% methylcyclohexane, 1

wt% pentene) doped with benzothiophene to provide 50 wppm S. Results for reforming over Pt-doped ceria and Co-doped ceria are shown in Fig. 7. The Co catalyst activity decreased rapidly. The catalyst was regenerated and the test resumed, however, activity again died off. After several regeneration-reaction cycles, the original activity could no longer be achieved and the test was stopped. In contrast, the Pt catalyst activity remained high throughout the test, and degradation over the length of the test was similar to that for sulfur-free fuel.

Post-test examination of the Co catalyst revealed extensive coke formation, with carbon levels of 10 to 14 wt% on the catalyst. A microscopic examination revealed the formation of carbon throughout the catalyst and the formation of carbon fibers extending into the void regions. However, very little sulfur was found on the catalyst (<50 wppm S). These tests suggest that sulfur promotes coking on the Co-doped ceria catalysts.

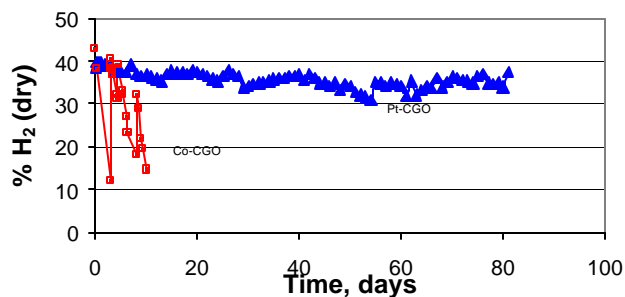
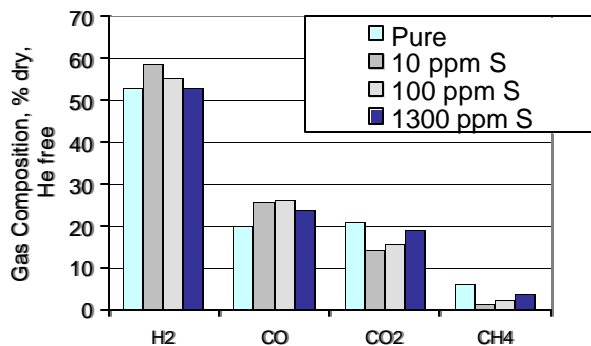


Figure 7. Long-term effects of reforming fuel with 50 wppm S over Pt-ceria and Co-ceria catalysts (T=800°C, GHSV 5,200 h⁻¹).

To provide further insight into the effects of sulfur on the Pt catalyst, isooctane solutions doped with benzothiophene to provide S levels of 0, 10, 100, and 1000 wppm were investigated. The product gas composition for reforming these solutions at 800°C and a GHSV of 15,000 h⁻¹ is shown in Fig. 8. The hydrogen Figure 8. Effect of



S level on product gas from reforming isooctane over Pt-ceria catalyst.

and CO yields increase when going from pure isooctane to isooctane plus 10 wppm S, but then decrease as the sulfur content is increased to 100 and 1300 wppm.

Conversely, the methane and CO₂ levels decrease when the sulfur level is increased from 0 to 10 wppm, then increase as the sulfur level is increased to 100 and 1300 wppm. These tests indicate that the effect of sulfur impurities on reforming depends on the catalyst, and can vary from a negative effect for Ni, Co, and Ru catalysts to a positive effect for the Pt catalyst. With the Pt catalyst, the effect of sulfur impurities is also dependent on the sulfur content of the fuel.

CONCLUSION

The results indicate that fuel composition can have a large effect on reforming behavior. Fuels with high aromatic content and high naphthenic content were more difficult to reform. Both the naphthenic and aromatic fuels were more sensitive to temperature than the paraffinic fuel. Aromatics and naphthenes were also found to have an impact on the reforming of paraffins in the blend, and decrease the efficiency for paraffin conversion. The effects of sulfur impurities were dependent on the catalyst. Sulfur was detrimental for Ni, Co, and Ru catalysts. Sulfur was beneficial for reforming with Pt catalysts; however, the effect was dependent on the sulfur concentration.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

GHSV: Gas hourly space velocity

Piona: paraffin, isoparaffin, naphthene, aromatic

wppm: weight part per million.

TCD : thermal conductivity detector

MSD: mass selective detector

CONTACT

John P. Kopasz,
Chemical Technology Division, Bldg 205
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
e-mail Kopasz@cmt.anl.gov