Gas-to-Liquids Synthetic Fuels for use in Fuel Cells: Reformability, Energy Density, and Infrastructure Compatibility

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GAS-TO-LIQUIDS SYNTHETIC FUELS FOR USE IN FUEL CELLS: REFORMABILITY, ENERGY DENSITY, AND INFRASTRUCTURE COMPATIBILITY

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ABSTRACT

The fuel cell has many potential applications, from power sources for electric hybrid vehicles to small power plants for commercial buildings. The choice of fuel will be critical to the pace of its commercialization. This paper reviews the various liquid fuels being considered as an alternative to direct hydrogen gas for the fuel cell application, presents calculations of the hydrogen and carbon dioxide yields from autothermal reforming of candidate liquid fuels, and reports the product gas composition measured from the autothermal reforming of a synthetic fuel in a micro-reactor. The hydrogen yield for a synthetic paraffin fuel produced by a cobalt-based Fischer-Tropsch process was found to be similar to that of retail gasoline. The advantages of the synthetic fuel are that it contains no contaminants that would poison the fuel cell catalyst, is relatively benign to the environment, and could be transported in the existing fuel distribution system.

FUEL CHOICE

Fuel cell commercialization is dependent on advances in fuel reformation, which directly relates to fuel choice. Reformer design is driven by the application of the fuel cell engine (transportation, land-based, etc.) and fuel choice. If a fuel cell is stationary and has access to a natural gas source, the choice is simple. If the fuel cell application is mobile, other fuels must also be considered, including compressed natural gas (CNG), liquefied natural gas (LNG), liquefied petroleum gas (LPG), methanol, ethanol, gasoline, and diesel.

Except for methanol and LNG, these fuels typically require sulfur removal prior to reforming. Also, LNG, LPG, and CNG require a fuel distribution system separate from the present conventional gasoline/middle-distillate system. Because LNG is cryogenic and LPG is a compressed liquid, both are highly volatile. At present, LNG requires more investment and attention than other fuels. Fleet bus tests identified possible reliability issues for LNG as an alternative fuel [1]. Efforts to establish a nationwide CNG fuel infrastructure available to the public continue to be unsuccessful [2].

Perhaps the most publicized candidate fuel-cell fuel to date is methanol. Methanol can be made from abundant natural gas or coal, is liquid at room temperature, and contains no sulfur or other complex organic compounds such as aromatics. Above all else, methanol's apparent advantage is that it requires a lower temperature to reform than the non-oxygenate fuels with present technology. Thus, it is viewed to have the potential to satisfy the "instant on and go" properties perceived necessary to compete with internal combustion engines or batteries. Methanol also has other characteristics that continue to discourage its widespread acceptance as a commercial transportation fuel. It is relatively volatile at room temperature, is highly toxic to the human nervous system, and because methanol fires are very difficult to see, it will probably require additives to make flames visible. Its solubility in water is viewed as an advantage for fire fighting and a concern for contaminating water sources.

Gasoline continues to be of interest to both industry and government as a potential fuel for fuel cells because of its wide refueling network. Unfortunately, gasoline sold in the U.S. is a generally difficult fuel to use in a fuel cell. The American Petroleum Institute reports that the average sulfur content of U.S. gasoline is 347 ppm (by weight) [3] with 25% containing greater than 500 ppm. Fuel cell processor manufacturers indicate that using gasoline containing >50 ppm sulfur will require

significant additional technology and expense. Typical gasoline is also challenging to fuel reformers because it contains significant amounts of undersaturated compounds, including aromatics and olefins. These hydrogen-poor hydrocarbons reduce the processor conversion efficiency and, thus, hydrogen deliverability to a fuel cell.

The best petroleum-derived fuel for automotive fuel cells is suggested to be a simple distillation cut (without additives) from which sulfur has been removed at the refinery. What if a 100% liquid synthetic paraffin fuel were available for cell fuel applications? Sulfur- and aromatic-free fuel in the boiling range of natural gasoline has not been considered for fuel cells because it has not been a commonly available product of the oil and gas industry. However, with recent advancement in some GTL technologies, such a fuel is viable.

Ultra clean (sulfur and aromatic-free) synthetic light paraffin can be reformed for fuel cell power generation. Buses, locomotives, and other vehicles using synthetic light paraffin could fill up at existing fuel stations and could maintain the driving ranges possible with gasoline. Perhaps one of the more subtle, but more significant advantages of synthetic fuel is that it can not only improve the performance of fuel cells as discussed above, but it can also contribute in so many other ways to improve the environment. For example, it can be produced from gas flared during oil production, which would immediately reduce world CO_2 emissions.

Analysis of a cobalt-based Fischer-Tropsch (FT) fuel equivalent to gasoline (see Table 1) showed that over 99% (by weight) of the sample consisted of saturated aliphatic hydrocarbons with chains containing four (C_4) through ten (C_{10}) carbons. Straight-chained hydrocarbons (not distinguished in the table) constituted 96.5% of the mixture. The balance was primarily branched aliphatics with a single methyl group. The FT-gasoline contained 87% saturated C_6 through C_9 paraffins, indicating a much more uniform composition than the typical gasoline from crude. The average formula for the fuel was calculated to be $C_{7.01}H_{15.9}$. The hydrogen-to-carbon ratio for this fuel was 2.27.

A similar analysis of a retail gasoline sample (premium) showed its average composition to be $C_{7.3}H_{14.8}O_{0.1}$ and its sulfur content, 120 ppm. The gasoline sample contained 62% paraffins, 23% aromatics, 6% naphthenes, 8% methyl-tertiary-butyl-ether (MTBE), and 1% olefins. The right-hand side of Table 1 lists some of the principal components found in the petroleum-derived gasoline sample and their concentrations. Octanes (n- and iso-) constituted 34%, followed by 12% C_9 aromatics, and 8% MTBE – an oxygenate added at the refinery for improving emissions from gasoline engines. The gasoline sample had a hydrogen-to-carbon ratio of 2.03.

Table 1. Compositions of an FT-gasoline and retail gasoline

FT-Gasoline Components	Wt. %	Average Composition	Gasoline Components	Wt. %	Average Composition
C_4H_{10}	0.08		C_4H_{10}	0.7	
C_5H_{12}	3.81		C_5H_{12}	0.1	
C_6H_{14}	11.83		C_6H_{14}	4.9	
C_7H_{16}	21.18	$C_{7.01}H_{15.9}$	C_7H_{16}	7.5	
C_8H_{18}	27.20		C_8H_{18}	34.3	
C_9H_{20}	26.46		C_9H_{20}	5.6	$C_{7.3}H_{14.8}O_{0.1}$
$C_{10}H_{22}$	8.80		$C_{10}H_{22}$	1.4	
			$C_5H_{12}O$ (MTBE)	8.3	
			C_9H_{12}	12.4	
Others	0.62		Others	24.8	

HYDROGEN YIELDS OF CANDIDATE FUELS

The hydrogen carrying/yield capacity of a fuel is a function of the hydrogen percentage of the fuel's elemental composition, its energy content, and its density. Let us consider the idealized autothermal reforming reaction of a fuel,

$$C_nH_mO_p + x(O_2+3.76N_2) + (2n-2x-p)H_2O = nCO_2 + (2n-2x-p+m/2)H_2 + 3.76xN_2, \qquad (1)$$

where all the carbon in the fuel is converted to carbon dioxide, the H is released as H_2, and the oxygen-to-fuel ratio (x) is adjusted such that the heat of reaction is zero. This idealized reaction produces the maximum amount of hydrogen and defines the theoretical limiting efficiency. Table 2 shows the lower heating value (LHV), the maximum efficiency, and the hydrogen and carbon dioxide yields per liter and per kilogram of fuel achievable from methanol, ethanol, gasoline (retail premium in U.S.), and FT-gasoline (Syntroleum, SLP-2). Since these calculations are for idealized conditions where the conversion process is most efficient, the values listed for the hydrogen and carbon dioxide yields are the maximum and minimum possible, respectively. The actual conversion efficiency for the reforming process will be lower than the theoretical values shown in the table and, therefore, will result in correspondingly lower hydrogen yields and higher carbon dioxide yields.

Of the fuels, methanol has the lowest and the synthetic gasoline has the highest heating value on a molar basis. The heating values of the gasolines are nearly seven times higher than that of methanol. On a mass basis, that factor is reduced to approximately 2 because of the division by their respective molecular weights. As such, the lower heating values range from 19,940 kJ/kg for methanol, to 44,600 kJ/kg for FT-gasoline. The maximum theoretical efficiency achievable is highest for methanol (96.3%), and lowest for gasoline (90.8%). The trend in the efficiency values correlates with the hydrogen-to-carbon ratio in the fuel, which is 4 for methanol and 2.27 for the gasoline.

The hydrogen and carbon dioxide yields from the fuels are dependent on fuel properties (e.g., density, energy content) as well on the reaction stoichiometry. The resultant values shown here indicate that on a volumetric basis, the FT-gasoline will provide the highest amount of hydrogen 0.235 kg/L, which is 88% higher than that from methanol, which is the lowest at 0.125 kg/L. The carbon dioxide yield will also be least for methanol, 1.1 kg/L, while the gasolines will produce 2.2 kg/L. Similar trends are also seen for the yields on a mass basis, where the heavier fuels produce more hydrogen and carbon dioxide. Note that the theoretical ratios of hydrogen to carbon dioxide yield for methanol (0.114) and FT-gasoline (0.107) are essentially equivalent because the FT-gasoline reforming extracts more hydrogen from water ($H_2O/C=1.27$) than does methanol ($H_2O/C=0.54$).

Table 2. Hydrogen and carbon dioxide yields achievable from the reforming of fuels

Fuel	Formula	LHV kJ/gmol	Efficiency[1] % (max.)	H$_2$ Yield (max.) kg/L	H$_2$ Yield (max.) kg/kg	CO$_2$ Yield (min.) kg/L	CO$_2$ Yield (min.) kg/kg
Methanol	CH$_3$OH	638	96.3	0.125	0.159	1.08	1.38
Ethanol	C$_2$H$_5$OH	1236	93.6	0.159	0.204	1.47	1.87
Gasoline	C$_{7.3}$H$_{14.8}$O$_{0.1}$	4440	90.8	0.224	0.321	2.16	3.09
FT-Gasoline	C$_{7.01}$H$_{15.9}$	4460	91.2	0.235	0.336	2.16	3.08

Due to the complex kinetics of the reforming reaction, the actual efficiency of the fuel processor varies with the fuel. Let us say that current fuel processors for methanol and gasoline operate at 85% and 75% efficiency, respectively. Taking these efficiency values into account, the yields from methanol become 0.106 kg/L (0.135 kg/kg) of hydrogen, and 1.27 kg/L (1.62 kg/kg) of carbon dioxide. In comparison, FT-gasoline will yield 0.176 kg/L (0.252 kg/kg) of hydrogen, and 2.88 kg/L (4.11 kg/kg) of carbon dioxide.

Fuels are valued with regard to their energy content. As such, it is appropriate to also compare them on the basis of their heating value. Table 3 shows the calculated hydrogen and carbon dioxide

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[1] Efficiency is defined as the lower heating value (LHV) of the hydrogen produced as a percentage of the LHV of the fuel.

yields on the basis of grams per megajoule. Methanol yields 8.0 g/MJ of H_2 and 689 g/MJ of CO_2, while the FT-gasoline yields 7.5 g/MJ and 692 g/MJ of hydrogen and carbon dioxide, respectively. Methanol produces 6.7% more H_2 than the FT-gasoline, while the difference in the CO_2 yield is negligible.

Table 3. Hydrogen and carbon dioxide yields from fuels on the basis of their heating values

Fuel	Formula	H_2 Yield (max.) g/MJ	CO_2 Yield (min.) g/MJ
Methanol	CH_3OH	8.0	689
Ethanol	C_2H_5OH	7.7	712
Gasoline	$C_{7.3}H_{14.8}O_{0.1}$	7.5	723
FT-Gasoline	$C_{7.01}H_{15.9}$	7.5	692

From the perspective of environmental impact, it is desirable to lower the CO_2 yields. Such calculations for the carbon dioxide yield must include the well-to-wheel efficiency, which factors in all the energy losses including those accompanying the fuel production process. These calculations have shown that petroleum-derived gasoline is more efficient than methanol [4]. Production efficiencies of FT-gasoline are presently similar to methanol. However, new technology and plant design under development should boost production efficiency of FT-gasoline to near parity with petroleum-derived gasoline.

EXPERIMENTAL

Some limited experiments were performed to investigate the autothermal reforming of cobalt-based FT fuels in a microreactor using a reforming catalyst, developed at Argonne National Laboratory. These tests were conducted by passing a mixture of vaporized fuel, steam, and oxygen over 2 g of catalyst packed in a 12-mm dia reactor. The catalyst was maintained at the desired temperature by placing the reactor in a tube furnace. Although the feed mixture and temperature were not optimized for the synthetic fuel, the fuel performance was similar to that observed for gasoline, with the product gas containing up to 56% H_2 (dry, nitrogen-free basis) at 750°C. Significant amounts of methane were observed in the product gas, indicating that higher hydrogen content are obtainable if the reactor temperature is raised to convert more of the byproduct methane to hydrogen. Carbon monoxide is present in the product gas at levels close to 22%. If this product gas were passed through a water-gas shift reactor, the conversion of CO ($CO + H_2O = CO_2 + H_2$) would likely raise the hydrogen concentration to 64%.
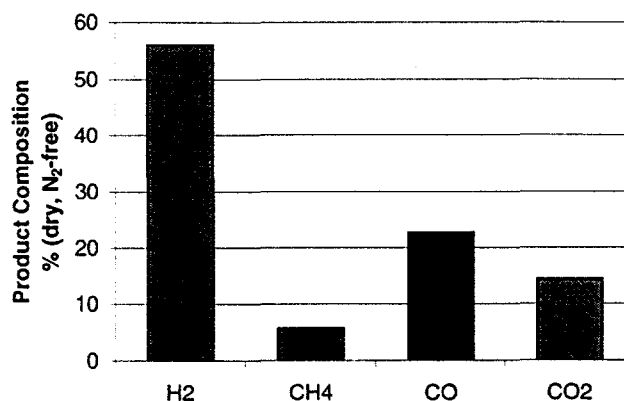

Figure 1. Product distribution obtained from the catalytic autothermal reforming of FT-gasoline in a micro-reactor at 750°C.

CONCLUSION

Increasing requirements for lower engine emissions are demanding changes in power generation, vehicle power trains, and appliance technologies. Fuel cells are already commercially viable in some stationary power applications, which could undergo explosive growth in the next decade. Also, fuel cells for vehicle propulsion should undergo large-scale commercialization in the next 10-20 years.

This fuel cell commercialization could be accelerated with the availability of synthetic light paraffin fuel. The potential environmental attributes of synthetic fuels are well documented. The absence of sulfur, aromatics, and metals (including halides) should simplify fuel reformer design, construction, and operation. If fuel storage and processing are simplified by using synthetic fuels, physical size of the fuel processor components would be reduced.

Cobalt-based FT-gasoline samples contain predominantly straight-chained paraffins, with a hydrogen yield that is 90% greater than that of methanol. The higher hydrogen-carrying capacity means that synthetic fuels permit greater utility and wider application of fuel cell power. Preliminary data indicate that these synthetic fuels can be converted in fuel processors designed for hydrocarbon fuels, with the added benefit that the fuel processor and fuel cell catalysts are less likely to be poisoned by sulfur and other contaminants present in petroleum-derived fuels.

Additionally, the present oil and gas industry is well suited to rapidly increase the production of synthetic fuels from natural gas. Synthetic fuel can simultaneously help reduce the emissions of today's vehicles while providing a fuel for tomorrow's power technologies, fuel cell or otherwise. No single fuel is a panacea for the world's ever-growing energy demands. However, synthetic fuel appears to be a big step forward, in the broad commercialization of fuel cells.

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