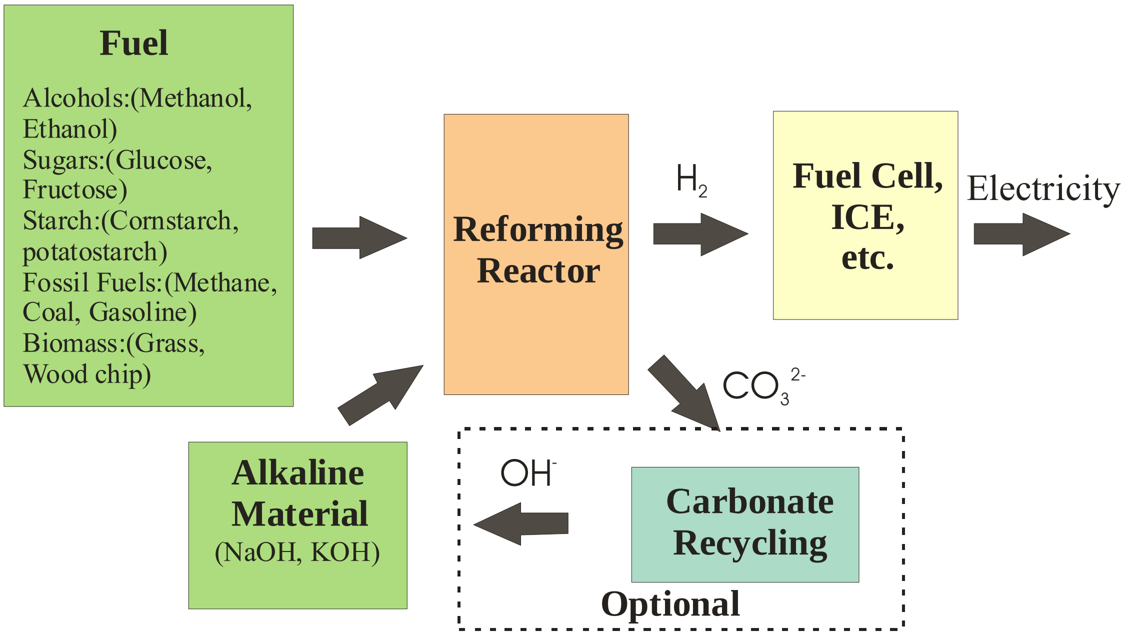
Final Report

A New Method for the Production of Hydrogen from Bioethanol/Biomethanol



Renewable Development Fund Grant Contract RD-22

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By

Energy Conversion Devices, Inc.,
Rochester Hills, MI

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Table of Contents

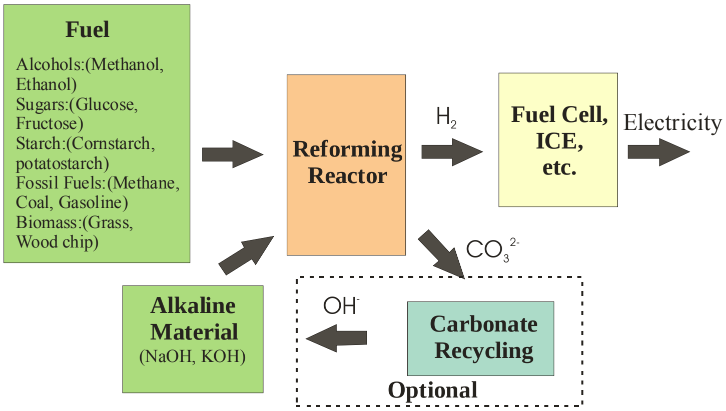
Executive Summary:

Base-Facilitated Reforming has been developed from a concept in preliminary laboratory experiments to a commercially viable technology where a liquid phase prototype device has generated hydrogen at a rate 100 gram per day (50 liters/hr) from methanol and ethanol (bioethanol) fuels. Cost analysis has shown the process has favorable economics. Demonstrating a Base-Facilitated Reforming (BFR) reactor which generates 100 gram H_2 per day (corresponds to 100 watts of electricity) and showing economic viability was the goal of our project. To accomplish this goal, we attained a series of milestones throughout the project allowing us to understand the reaction mechanisms and characteristics of the Base-Facilitated Reforming (BFR) process in both liquid phase and gas phase reaction modes. We gained understanding of the effects of process parameters on reaction rate. Low cost catalyst materials exhibiting excellent rate characteristics were identified. Effects of temperature, pressure, fuel composition, type of base material used and its concentration were quantified. Optimized parameters were applied to the design and operation of the prototype reactor. The liquid phase reaction showed favorable characteristics with respect to reforming rates and temperature of operation and therefore a prototype reactor based on the liquid phase reforming was selected for the demonstration of the BFR technology. Economic analysis projected very competitive hydrogen production costs using the BFR reactor. The reactor is simpler in design and lower in cost compared to conventional steam reforming reactors and produces high purity hydrogen which can be used for production of electricity.

Technology Background:

Three years ago, we developed the concept of a base-facilitated reforming and conducted laboratory experimentation showing the addition of base material (alkaline) to an organic fuel, produces hydrogen gas at significantly milder conditions (temperature and pressure) compared to conventional steam reforming. Moreover, a reformer based on this Base-Facilitated concept is simpler in design and can be constructed at lower cost because gases such as CO and CO_2 are not formed. Therefore, water gas shift (WGS) reactor to react CO gas and pressure swing absorption (PSA) reactor to scrub CO_2 gas are not needed as with conventional steam reforming reactors. Figure 1 is a schematic diagram describing the Base-Facilitated process.

Figure 1. Schematic diagram of a Base-Facilitated Reforming process



The Base-Facilitated concept is also described by equation (1) for methanol reformation:

$$(1)\ CH_3OH + 2NaOH \leftrightarrow 3H_2 + Na_2CO_3$$

No other gases are formed besides H_2 and therefore WGS and PSA units are not needed unlike steam reforming of methanol where CO and CO_2 gases are formed as described in equation (2)-(4)

$$\begin{array}{rl}
(2)\ CH_3OH \leftrightarrow 2H_2 + CO & \\
\underline{(3) CO + H_2O \leftrightarrow H_2 + CO_2} & \text{WGS} \\
(4)\ CH_3OH + H_2O \leftrightarrow 3H_2 + CO_2 & \text{net}
\end{array}$$

The BFR reaction (1) is also thermodynamically more favorable and operates at lower temperatures and with lower heat requirements than conventional steam reforming. In the BFR process a solid carbonate (Na_2CO_3) is formed rather than gases by-products. The carbonate can be removed and recycled back to the base material (i.e. NaOH) to be fed back to the reactor.

Our goal in this project was to develop the BFR concept and to demonstrate its feasibility via a prototype reactor operating in a continuous flow mode and generating >100 gram H_2 per day (50 liters/hr) corresponding to 100 watts of electrical energy and be economically viable. This goal was achieved. A prototype continuous flow liquid phase reactor was built and tested to generate 100 grams H_2 per day from methanol and ethanol (bioethanol). Economic analysis showed the BFR reformer, in a scaled up version, will generate hydrogen at a competitive cost to hydrogen produced by conventional reforming and to other liquid petroleum fuels. The use of generated hydrogen as a fuel to produce electrical power was demonstrated. An electrical generator was fed hydrogen produced in the prototype reformer creating electricity which powered a 100 watts lamp and portable TV.

Technology development:

To advance the technology from concept to a prototype device showing continuous operation and having economic benefit, different steps of research and development have been undertaken. First, we developed two types of reforming reactors:

- Liquid phase reactor where the fuels are in the liquid phase reacting with dissolved base materials. The BFR process allows reaction in the liquid phase due to lower temperatures required for operation.

- Gas phase reactor where higher operating temperatures are applied and fuels in gas phase react with solid base materials to produce hydrogen.

The advantage of the liquid phase reactor is in the lower operating temperatures and simplicity in reactor design and construction. The advantage of the gas phase reactor is that higher temperatures can be applied to further increase hydrogen generation rate and utilize other potential starting fuels such as biomass. Research has focused on the effect of process parameters on the rate of the reforming reaction. The study was conducted in stainless steel batch reactors as shown in the figures below:

Figure 2: Laboratory batch test reactors: left 1.0 liter with accumulator, right 100 cc reactor

Parameters studied were: Catalyst type and quantity, alkaline material type, operating temperature, operating pressure and fuel composition. It was found the reforming reactions are strongly dependant on catalyst type. The best catalysts for methanol and ethanol were identified. The reforming rates are also strongly dependent on operation temperatures with an increase in rate of two upon increase of temperature by 10°C in the liquid reforming for both methanol and ethanol and by a factor of 1.2-1.5 in the gas phase reforming. For a given catalyst, equations describing the dependence of rate of hydrogen generation on fuel composition in the liquid phase reforming have been developed as shown below:

Reformation rate of methanol in liquid phase

$$\textbf{Rate(cc/hr.g-catalyst)) = } \mathbf{R_0^M} + \mathbf{a^M} A_f + \mathbf{b^M} C_{OH}$$

(where M designates methanol)

Optimum composition: A_f=100%; C_{OH}=0.22g/cc

Reformation rate of ethanol in liquid phase

$$\textbf{Rate (cc/hr.g-catalyst) = } \mathbf{R_0^E} + \mathbf{a^E} Af + \mathbf{b^E} C_{OH} + \mathbf{c^E} A_f{*}C_{OH}$$

(where E designates ethanol)

Optimum composition: A_f=100%; C_{OH}=0.074g/cc

Where $R_{0,}$ a, b, c are constants and the parameters A_f and C_{OH} are:

A_f – fuel activity (0-100%)
C_{OH} – hydroxide concentration (g/cc)
$A_f{*}C_{OH}$ – term of interaction between A_f and C_{OH}

The constants in the above equations are:

For Metahnol:

R_0^M(cc/hr.g-catalyst) - -997
a^M (cc/hr.g./(100%-fuel)) – 18
b^M (cc/hr.g-catalyst/(g/cc-OH^-)) – 8498

For Ethanol:

R_0^E(cc/hr.g) - -3544

a^E (cc/hr.g.100%) – 74
b^E (cc/hr.g-catalyst/(g/cc-OH^-)) – 19146
c^E (cc/hr.g-catalyst/(100% -fuel)/(g/cc-OH^-) - -253

For the gas phase reforming, the reforming rate depends also on the pressure and activity (fuel/water). Equations describing this dependence were derived as shown below:

R (cc/hr.gr-catalyst) = $R_0 * P$

Where P is the fuel pressure.

Process parameters were optimized using JMP statistical software program for highest hydrogen production rate for both methanol and ethanol fuels and for liquid phase and gas phase reactions. Selection of parameters was subjected to system limitations however with the temperature limited by the maximum pressure allowed (150 psi) in our system. Selected parameters for highest production rate subjected to pressure limitation are shown in tables I-III below:

(A) Liquid phase

Table I: Selected optimum parameters for methanol reformation

Parameter	Optimized selection
Catalyst	Catalyst A
Specific catalytic rate	1.8 liter H_2/hr.gr-catalyst
Base material	NaOH
Temperature	140°C
Operating Pressure	150 psi
Fuel activity	1
Base concentration (C_{OH^-})	0.22 g/cc

Table II: Selected optimum parameters for ethanol reformation

Parameter	Optimized selection
Catalyst	Catalyst B
Specific catalytic rate	2.7 liter H_2/hr.gr-catalyst
Base material	NaOH
Temperature	140°C
Operating Pressure	150 psi
Fuel activity	1
Base concentration (C_{OH^-})	0.074 g/cc

(B) Gas Phase

Table III: Selected optimum parameters for methanol and for ethanol gas phase reformation

Parameter	Optimized selection
Catalyst	Catalyst C
Specific catalytic rate (methanol)	1.5 liter H_2/hr.gr-catalyst
Specific catalytic rate (ethanol)	2.0 liter H_2/hr.gr-catalyst
Base material	NaOH
Temperature	220°C
Fuel Pressure	150 psi
Fuel activity	1

The tables above show temperatures required for the gas phase reforming process are significantly higher than the liquid phase process for similar hydrogen production rates. In addition, we found moving the solid alkaline material through a catalytic bed required in a continuous gas flow reactor is a difficult task. Mixing of catalyst with the solid alkaline material is needed and design of this task is complicated. A fluidized bed design was found to be the best design for mixing the solid alkaline with catalyst and the fuel vapors. Construction of a small scale fluidized bed reactor is difficult and therefore larger reactor, capable of generating >2kg/day, was built. Design and construction of such a reactor required expertise from an outside engineering vendor. This reactor is shown in figure 3. A liquid phase reactor required significantly lower operating temperatures. Transferring liquid through a catalyst bed is a relatively easy task and a design and construction of such a reactor is simpler and has a lower cost. It was concluded that for methanol and ethanol reforming, a continuous flow liquid phase reactor will be economically more feasible due to lower capital and operating costs and therefore a decision was made to demonstrate the feasibility of the BFR technology developed in this project via a liquid phase prototype reactor. A description of the prototype liquid reactor and test results are given in the next section.

Figure 3. Fluidized bed gas phase test reactor at ECD

Prototype reactor design and test:

A schematic diagram describing the liquid phase prototype reactor is shown in figure 4. The reactor is a tubular cylinder made out of stainless steel. Catalyst powder fills the reactor between two porous plugs. The plugs allow liquid to flow through the catalyst while keeping the catalyst fixed in the reactor. The liquid (fuel with dissolved hydroxide) is pumped through the catalyst where the reforming reaction takes place. The reactor is heated to the desired temperature by heating bands. The hydrogen gas formed in the reactor is separated from the liquid fuel in the gas/liquid separator at the top of the reactor. The gas is delivered to an accumulator at a predetermined pressure (70-150 psi) and the unreacted liquid fuel return to the fuel storage tank. A picture of the prototype liquid phase reactor is shown in figure 5.

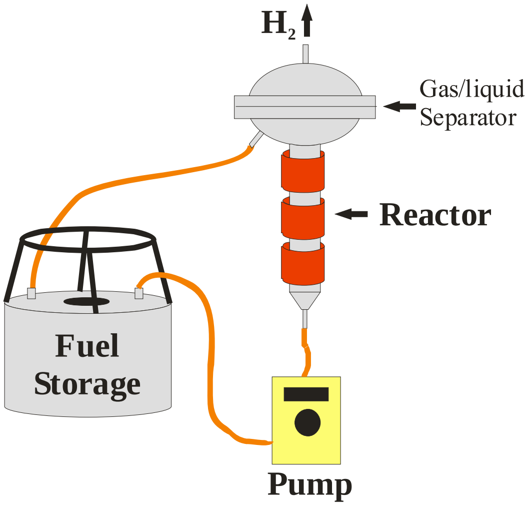


Figure 4. Schematic diagram of a liquid phase continuous reactor

Figure 5. Liquid-phase continuous prototype reactor

In the continuous flow reactor the rate of the reforming reaction depends on the flow rate of the liquid fuel through the catalyst bed. Characteristics curve showing the dependency of hydrogen production rate on flow rate in the prototype reactor is shown in figure 6.

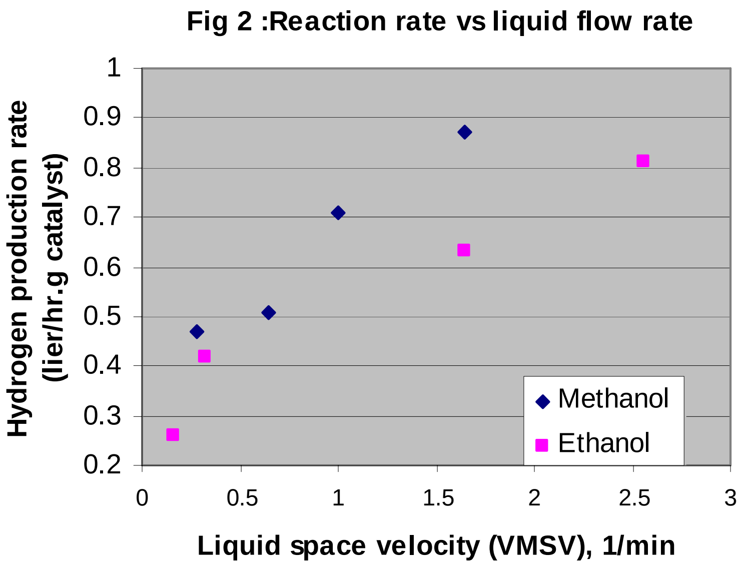


Figure 6. Dependence of hydrogen production rate on liquid flow rate in prototype reactor. Catalyst A

A maximum space velocity of 2.5 min^{-1} (~70cc/minute) was applied in operation of the prototype reactor and using the optimum process parameters selected as described earlier in tables I and II, the amount of catalyst in the bed needed to obtain a hydrogen production rate of 100 g H_2/ day is 85g for methanol and 75gr for ethanol fuel. Testing of the reactors demonstrated a capability for continuous operation as shown in figure 7 for the case of ethanol. The reformer produced hydrogen at a rate of 100 grams/day (100 watts of electricity) in a continuous way. Operation for extended length of time will require continuous removal of the carbonate salt (Na_2CO_3) and this operation has not been implemented in this project. The hydrogen produced in the reactors was analyzed by gas chromatograph and was found to be highly pure (>99.5%).

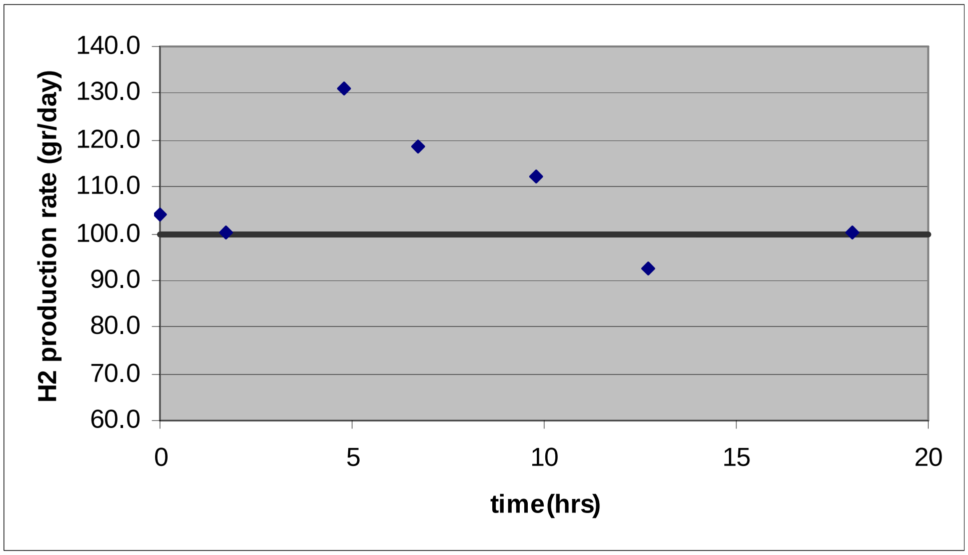


Figure 7. Hydrogen production rate as a function of operation time in a prototype liquid phase reformer using ethanol (bioethanol) fuel

To demonstrate the application of using the hydrogen for energy production, we delivered the hydrogen to a portable electrical generator which was modified to operate with hydrogen. Electricity was produced and used to operate a 100 watts electrical bulb or a portable colored TV as shown in figure 8.

Figure 8: Operation of 100 watts light bulb and portable TV from portable generator fed by hydrogen generated in BFR prototype reformer

Economic Benefit:

Economic feasibility of the new reactor was analyzed using the H2A cost analysis model developed by the United States Department of Energy (DOE). The model was developed in order to obtain uniformity and objectivity between different manufacturers or laboratories. The analysis uses net present value with internal rate of return (IRR) of 10%. It assumes 20 year depreciation on facility equipment and 10 year depreciation on the reactor. For the analysis we took the cost of feedstock and electricity from Energy Information Administration (EIA) annual energy outlook report. We present here economic analysis for production of 1,500 Kg-H_2/day. The capital cost for the scale-up (1,500 Kg-H_2/day) BFR reformer was calculated using the cost of similar size conventional steam reformer as reported in DOE's report minus the cost of WGS unit (~ 30% of the total cost of the conventional reformer) and that of the PSA unit (also ~30% of the total cost of the conventional reformer) which are not needed in the case of the BFR reactor. The cost of equipment to recycle the carbonate salt (Na_2CO_3) back to the alkaline (NaOH) was then added (equal to ~30% of the total reactor cost). Taking this in consideration the cost of BFR reformer is about 70% of a conventional steam reformer. Estimation of capital cost for a scale up reactor (1,500 kg- H_2/day) was also conducted by using the cost of the prototype reactor we built and applying engineering scale-up factor ($cost2 = cost1(size2/size1)^{0.6}$). Capital cost estimation was similar to the cost obtained by method described earlier. In calculating the operating cost of the reformer, energy used for the reforming process and for recycling the carbonate salt was taken into consideration. Figure 9 shows the cost and cost structure projected for hydrogen produced by BFR reformer for rate of production of 1,500 Kg/day. The cost projected for the BFR reforming of methanol and ethanol is \$3.5/Kg H_2 and \$2.5/Kg H_2 respectively. This cost is ~ 10%-15% lower than the cost projected for production of hydrogen using conventional steam reforming mainly from these fuels due to the lower (~40%) capital cost of the BFR process and it is within the cost range required by DOE ($2-3/kg H_2) for applying H_2 fuel for transportation purposes. If a biomass such as a switchgrass were used as starting fuel, the hydrogen production cost is calculated to be less than $2 per kg.

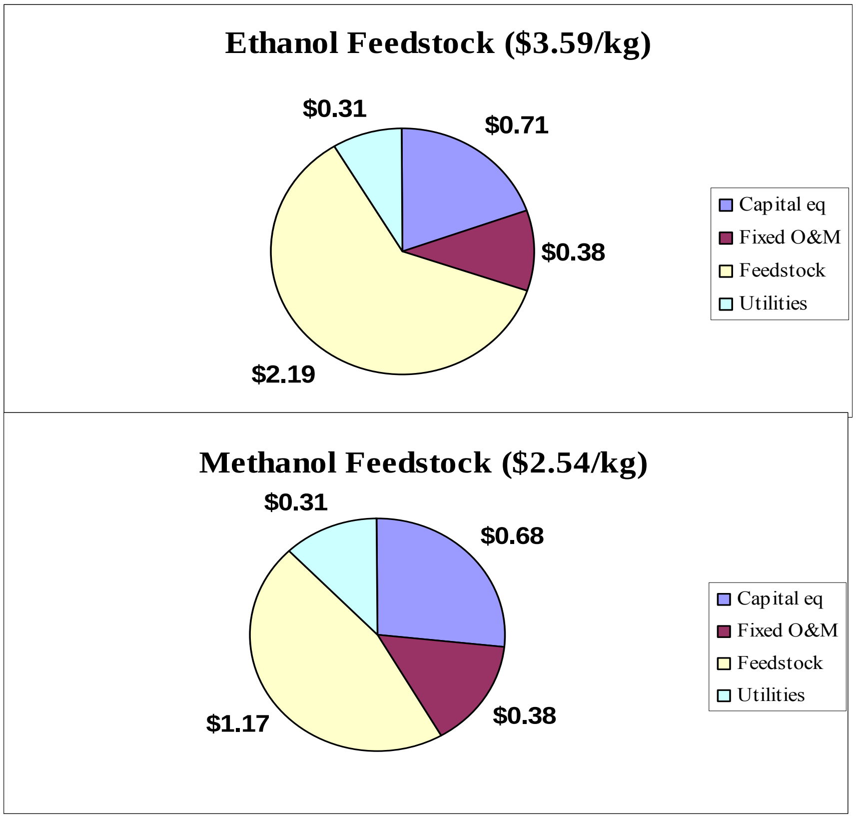


Figure 9: Cost structure for hydrogen production projected for BFR process using methanol and ethanol (bioethanol) feedstocks

As one can see from figure 9 the cost of hydrogen production is significantly affected by the cost of the feedstock used. The fuel cost account for ~45% and ~60% of the total cost for methanol and ethanol (bioethanol) respectively. It should be noted that the hydrogen production cost as calculated here is estimated to be ~+/-30% accurate due to the uncertainty in the estimation of capital equipment cost (estimated to within +/-40%), energy cost (estimated to within +/-30%) and feedstock cost (estimated to within +/- 20%). For a more accurate cost calculation a larger pilot line reactor has to be built and tested.

The cost projected for hydrogen production via the BFR process from methanol was compared with the cost of different liquid and gaseous fuels as shown in table IV below:

Table IV: Comparison of cost of hydrogen produced by the BFR process with other fuels

	High Heating Value (Btu)	Cost($)	Cost/mmBtu
Gasoline(gallon)- w/taxes	125000	2.80	22.40
Diesel (gallon)- w/taxes	130500	2.80	21.46
Ethanol(gallon)	84000	1.37	16.30
Methanol (gallon)	65200	0.55	8.45
Natural Gas (mmBtu)	1000000	6.72	6.72
Hydrogen (1kg)- ECD's Process	134438	2.54	18.95

The table shows the heating values of the different fuels (Btu) and their 2007 cost per million Btu (mmBtu) of energy. As the table shows the cost of hydrogen compares favorably with cost of gasoline and diesel. Hydrogen can be used as a fuel to produce electricity via microturbine or a fuel cell. Table V below shows the projected cost of distributed electricity using hydrogen fuel in a microturbine or in a fuel cell device in comparison to cost of electricity produced by some other selected fuels. In all cases the combined heat and power (CHP) technologies for producing electricity were considered. Calculations for the cost of electricity for the various technologies were based on methodology and data from publications by congressional budget office (CBO) of United State Congress "Prospects for Distributed Electricity Generation" (2003). Capital cost of equipment, operating cost, process efficiency and fuel cost ($/kWh) were considered in calculating the cost of electricity. As the table shows, the cost of electricity produced by hydrogen compared favorably with majority of the fuels. Analysis shows the cost of electricity from hydrogen can be further reduced to $0.11/Kwh using biomass material in the reformation process. It should be noted that since the cost of hydrogen is only an estimate which is accurate to within +/-30%, the cost calculated for electricity is also subjected to the same accuracy range.

Table V: Calculated Cost of Distributed Electricity Produced
by Different Technologies and Fuels

Technology-CHP (Fuel)	Cost of Electricity ($/KWh)
Microturbine-CHP (Diesel)	0.17
Microturbine-CHP (Ethanol)	0.136
Microturbine-CHP (Methanol)	0.087
Microturbine-CHP (Natural Gas)	0.086
Microturbine-CHP (Hydrogen ECD's process)	0.152
Fuel Cell – CHP (Hydrogen ECD's process)	0.148

Summary:

The goal of the project was to develop the Base-Facilitated Reforming (BFR) concept and to demonstrate its technological and economic benefits. We have been successful in achieving this goal and demonstrated the feasibility of the technology via a prototype liquid phase continuous flow reactor reforming methanol and ethanol (bioethanol) fuels. The reactor operated at a production rate of 100 gram H_2 per day (100 watts of electricity) and is capable of operating in a continuous way. Scale up of the reactor to larger sizes should be straightforward. We have shown the technological advantages of BFR reforming over conventional steam reforming. The BFR reformer operates without the need of a water gas shift (WGS) and pressure swing absorption (PSA) units in contrast to the conventional steam reformer. The elimination of these units make the reactor simpler in design and lower in cost compared to conventional steam reformer. The hydrogen gas which is formed in the BFR process is also higher in purity. In the BFR process solid carbonate salt (i.e. Na_2CO_3) is formed. The solid can be removed from the system, sold as a useful chemical or recycled back to the starting base material (i.e NaOH) using recausticizing process. This project did not deal with the handling of the carbonate by-product. The recycling process is a known economical industrial process and can be implemented in future work. Economic benefit was shown when comparing our process to conventional hydrogen production method and the projected cost of hydrogen fuel competes well with cost of liquid petroleum fuels. In the economic analysis of the reformer we added the recycling cost of carbonate to the total cost of producing hydrogen and got a favorable hydrogen cost projection. The cost of hydrogen production was found to be very sensitive to the cost of the feedstock used. Using biomass feedstocks instead of methanol or ethanol could significantly lower the cost of hydrogen produced by the Base-Facilitated Reforming process to $1.50 per Kg of H_2 which corresponding to electricity cost of $0.11/KWh. Using the BFR process to reform biomass materials should be a subject of another project.