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Hydrogen Fuel Reformation System

Facilitating a Hydrogen Infrastructure in Support of Fuel Cell Power Generation

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Typical Hydrogen Production

- A process called “reforming” can be used to produce hydrogen from various materials.
- Steam Reformation is the most commonly used today. This process typically uses nonrenewable natural gas as its feedstock and is energy intensive.
- The hydrogen produced is typically only 70% pure, requiring additional processing for many applications.
- Steam Reformation produces CO_2. For every ton of hydrogen, 11 tons of CO_2 are produced.
- By using a non-renewable feed stocks and producing greenhouse gas, the hydrogen produced by Steam Reformation is often referred to as “brown hydrogen”.
- States are now starting to mandate that 33% of all H_2 production be from renewable sources. This hydrogen is referred to as “green hydrogen”

Hydrogen Infrastructure

• The existing hydrogen infrastructure in developed countries is minimal and nearly non-existent in less developed countries.

• Steam Reformer plants are usually large, stationary facilities to keep the cost per kilogram down. They are typically located near the largest users, i.e. steel and chemical industries.

• The majority of hydrogen users do not use enough to justify the large capital expense associated with the Steam Reformer. This multitude of smaller hydrogen users comprise the merchant market. To serve this market, the hydrogen is typically liquefied and put in specialized tanker trucks. At depots, the hydrogen is then returned to the gaseous state at various pressures, put into cylinders and delivered by other trucks.

• All of this results in the hydrogen delivered to the merchant market having its cost increased 2-5 times.

Hydrogen Production From Multiple Feedstock Categories

• ETI and its collaborators have developed a new reformation process that allows the use of a multiple of feedstocks including renewables to produce hydrogen.

• ETI's modular and scalable Hydrogen Fuel Reformation System™ (HFRS) will allow the production of hydrogen at or near the point of use, reducing or avoiding the transport costs.

• The HFRS typically produces 98-99% pure hydrogen avoiding any additional clean up processes.

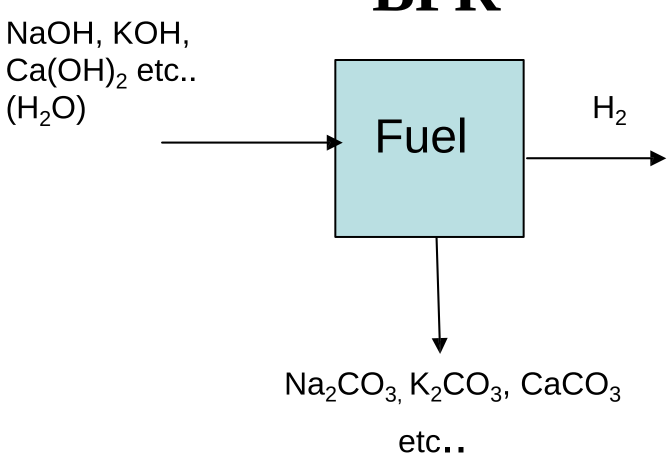
• The HFRS reaction does not produce or release CO or CO_2 to the atmosphere.

• For all of these reasons, the hydrogen produced by this process is truly "green hydrogen".

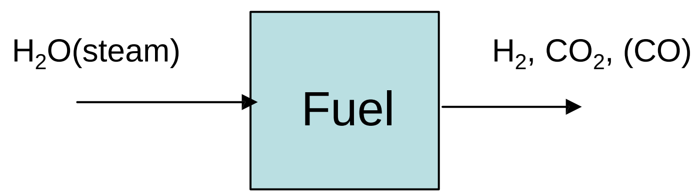
What is Base-Facilitated Reforming (BFR)?

- Alkaline material is used as a reactant in the reformation process
- Carbonate is formed as a by-product instead of CO_2

BFR



SR



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Hydrogen Fuel Reformation System

Example – Methane (CH_4)

Base-Facilitated Reforming

$$CH_4 + 2NaOH + H_2O \leftrightarrow Na_2CO_3 + 4H_2$$

Steam Reforming

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$$

$CH_4 + H_2O \leftrightarrow CO + 3H_2$

$CO + H_2O \leftrightarrow CO_2 + H_2$ Gas Shift

$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$

Example – Methanol (CH_3OH)

Base-Facilitated Reforming

$$CH_3OH + 2NaOH \leftrightarrow Na_2CO_3 + 3H_2$$

Steam Reforming

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2$$

$CH_3OH \leftrightarrow CO + 2H_2$

$CO + H_2O \leftrightarrow CO_2 + H_2$ Gas Shift

$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2$

Example – Ethanol (C_2H_5OH)

Base-Facilitated Reforming

$$C_2H_5OH + 4NaOH + H_2O \leftrightarrow 2Na_2CO_3 + 6H_2$$

Steam Reforming

$$C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2$$

$C_2H_5OH + H_2O \leftrightarrow 2CO + 4H_2$

$2CO + 2H_2O \leftrightarrow 2CO_2 + 2H_2$ Gas Shift

$C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2$

Example – Glycerol ($C_3H_5(OH)_3$)

Base-Facilitated Reforming

$$C_3H_5(OH)_3 + 6NaOH \leftrightarrow 3Na_2CO_3 + 7H_2$$

Steam Reforming

$$C_3H_5(OH)_3 + 3H_2O \leftrightarrow 3CO_2 + 7H_2$$

$C_3H_5\,(OH)_3 \leftrightarrow 3CO + 4H_2$

$3CO + 3H_2O \leftrightarrow 3CO_2 + 3H_2$ Gas Shift

$C_3H_5(OH)_3 + 3H_2O \leftrightarrow 2CO_2 + 6H_2$

Example – Glucose ($(C_6H_{12}O)_6)$)

Base-Facilitated Reforming

$$C_6H_{12}O_6 + 12NaOH \leftrightarrow 6Na_2CO_3 + 12H_2$$

Steam Reforming

$$C_6H_{12}O_6 + 6\ H_2O \leftrightarrow 6CO_2 + 12H_2$$

$C_6H_{12}\ O_6 \leftrightarrow 6CO + 6H_2$

$6CO + 6H_2O \leftrightarrow 6CO_2 + 6H_2$ Gas Shift

$C_6H_{12}O_6 + 6H_2O \leftrightarrow 6CO_2 + 6H_2$

Example – Cellulose $(C_6H_{10}O_5)_n$

Base-Facilitated Reforming

$(C_6H_{10}O_5)_n + 12nNaOH + nH_2O \leftrightarrow 6nNa_2CO_3 + 12nH_2$

Steam Reforming

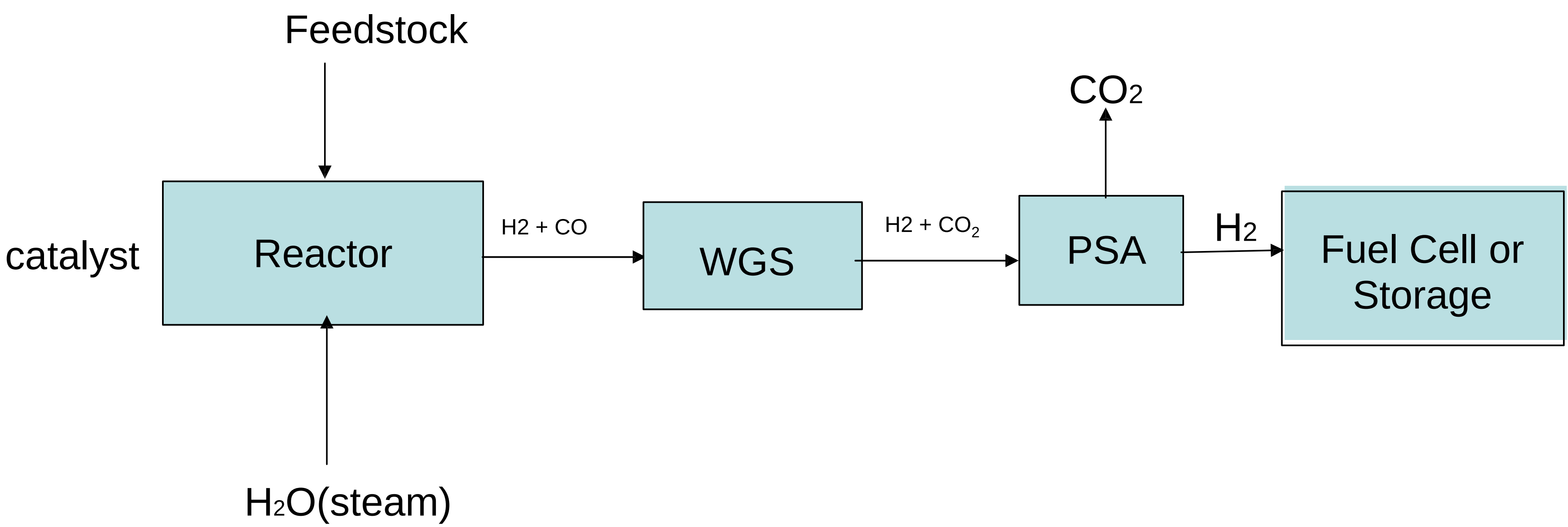
$(C_6H_{10}O_5)_n + 7nH_2O \leftrightarrow 6nCO_2 + 12nH_2$

$(C_6H_{10}O_5)_n + nH_2O \leftrightarrow 6nCO + 6nH_2$

$6nCO + 6nH_2O \leftrightarrow 6nCO_2 + 6nH_2$ Gas Shift

$(C_6H_{10}O_5)_n + 7nH_2O \leftrightarrow 6nCO_2 + 12nH_2$

Steam Reforming Process



WGS – Water Gas Shift
PSA – Pressure Swing Absorption

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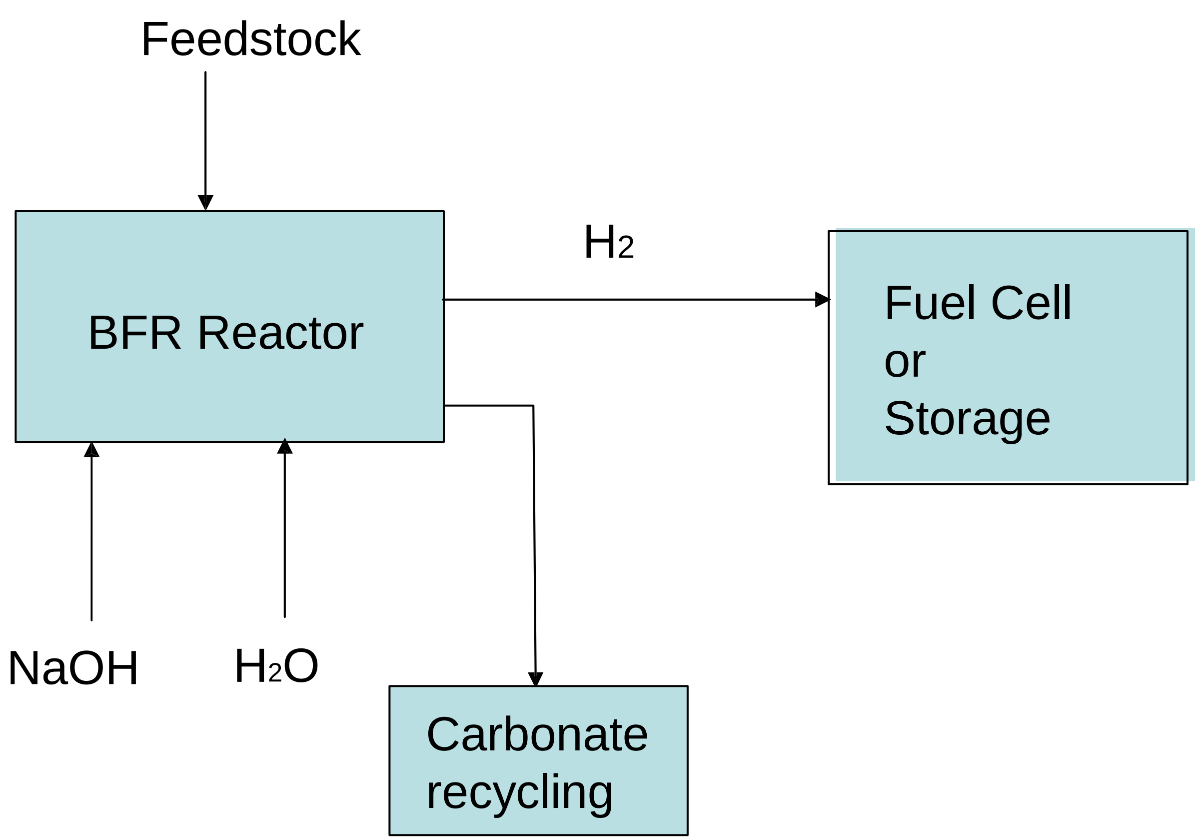
Base-Facilitated Reformation Process
Simple One Step Reaction
to High Purity Hydrogen



Hydrogen Fuel Reformation System

Base-Facilitated Reforming
More Favorable Thermodynamics
Lower Operating Temperatures

Gibbs free energies ΔG° are significantly lower in the BFR process compared to Steam Reforming – Lower reaction temperatures

Fuel	Δ G° (Kcal/mole)	Reaction temperature (°C)
CH_4 (SR)	+31.2	900
CH_4 (BFR)	+0.55	300
CH_3OH (SR)	+2.2	350
CH_3OH (BFR)	-28.5	120
C_2H_5OH (SR)	+23.3	800
C_2H_5OH (BFR)	-38.3	130
$C_6H_{12}O_6$ (SR)	-8.2	900
$C_6H_{12}O_6$ (BFR)	-192	220

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Hydrogen Fuel Reformation System

Base-Facilitated Reforming
More Favorable Thermodynamics
Lower Heat Requirement

Enthalpies ΔH° are significantly lower in the BFR process compared to Steam Reforming – Lower heat of reaction and higher efficiencies

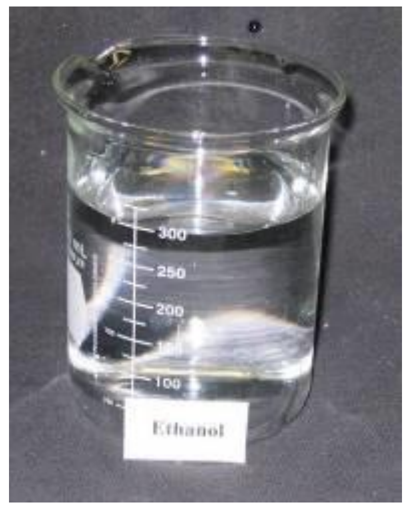
	Fuel	ΔH°(Kcal/mole)	Efficiency(%)
CH_4 (SR)	Methane	+60.5	92
CH_4 (BFR)	Methane	+12.9	113
CH_3OH (SR)	Methanol	+31.5	94
CH_3OH (BFR)	Methanol	-9.7	114-121
C_2H_5OH (SR)	Ethanol	+83.3	92
C_2H_5OH (BFR)	Ethanol	+1.0	117
$C_6H_{12}O_6$ (SR)	Glucose	+150.2	92
$C_6H_{12}O_6$ (BFR)	Glucose	-96.8	114-136
$C_{12}H_{22}O_{11}$ (SR)	Sucrose	+213.4	91
$C_{12}H_{22}O_{11}$(BFR)	Sucrose	-291.3	112-136
$C_6H_{10}O_5$ (SR)	Cellulose	+146.1	90
$C_6H_{10}O_5$ (BFR)	Cellulose	-169.3	112-153

Advantages of BFR Process

- One step reaction – making reformer design simpler
- No CO or CO_2 gases formed – Water gas shift and PSA not necessary.
- Pure hydrogen is formed.
- Greener process – CO_2 sequestered as a carbonate (i.e. Na_2CO_3)
- Lower operating temperatures.
- Operation in liquid phase is possible.
- Batch or continuous operation possible
- Lower heat ($\Delta H°$) required for reforming so more efficient and less expensive operation
- Can be used to reform variety of fuels. Reforming renewable fuels a major advantage.

Reformation Fuels Demonstrated

Examples of Fuels Reformed by ETI's Base-Facilitated Reformation



Alcohols: Methanol, Ethanol, Crude Ethanol, E95, Ethylene Glycol, Glycerol (from bio-diesel plant)

Sugars, Starches: Glucose, Fructose, Starch (Corn starch, Potato starch) , Food wastes

Fossil Fuels: Methane (Natural Gas, Landfill Gas, Bio-Gas), Coal

Biomass: Grass, Sawdust, Woodchips, Corn, Potato Peels, Cellulose, Hemicelluloses (Xylan from Beachwood), Lignin (Organosolv), Fryer Oils

Municipal Solid Waste (MSW): Paper

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Reactors For Base-Facilitated Reformation

Batch

Lab Batch reactor 100 ml open volume (rate: 3L H_2/hr for 0.5hrs)

Semi-Continuous

Semi-Continuous reactor with storage tank 4L open volume (rate: 10L H_2/hr for 8 hrs)

Continuous

Continuous reactor producing H_2 (rate: 100L/hr as long as needed)

Prototype 10 kg H_2/day Base-Facilitated Solid Biomass Fluidized Bed Reactor

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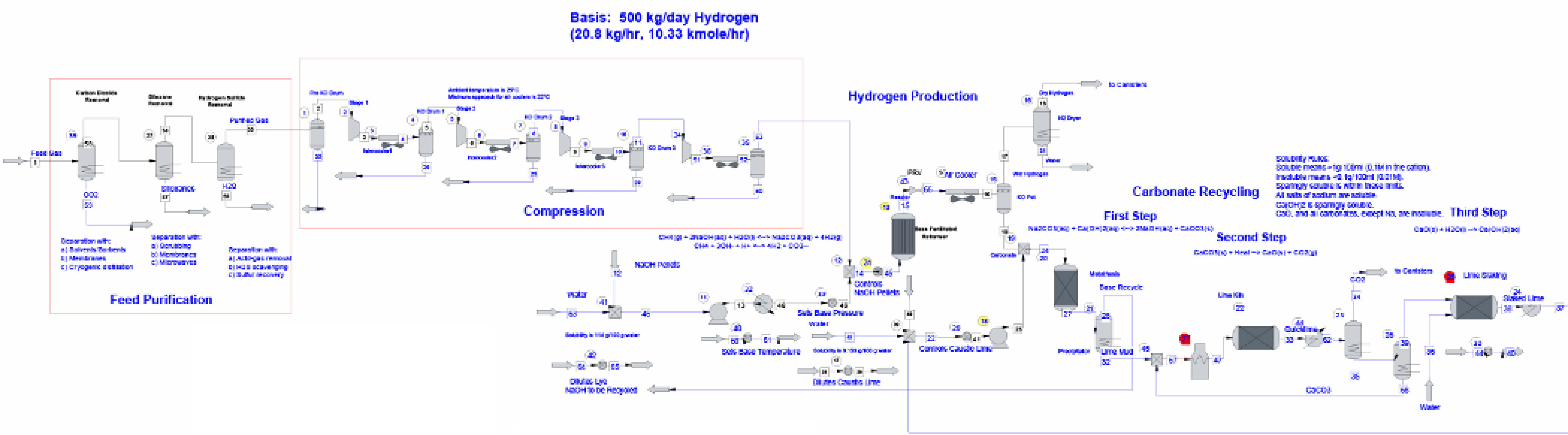
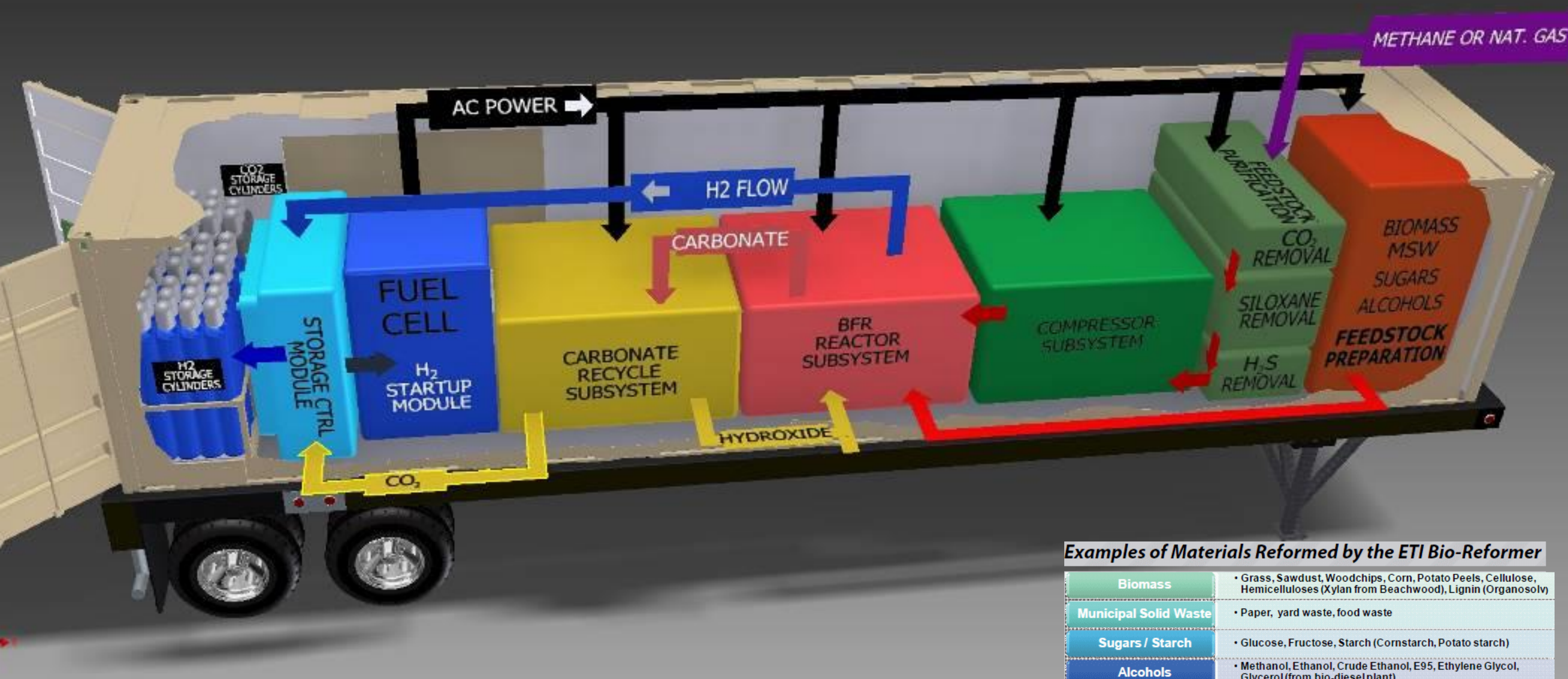
100 Kg, 500 Kg, 1500 Kg & 2000 Kg of H2 Per Day Line Drawing



Configured for recycle of Carbonate into Pure CO2 for market sale and Hydroxide returned to input as makeup. Module size and cost can be reduced if Carbonate is disposed as waste to landfill or sold.

Hydrogen Fuel Reformation System

Mobile HFRS Packaged System



Examples of Materials Reformed by the ETI Bio-Reformer

Biomass	• Grass, Sawdust, Woodchips, Corn, Potato Peels, Cellulose, Hemicelluloses (Xylan from Beachwood), Lignin (Organosolv)
Municipal Solid Waste	• Paper, yard waste, food waste
Sugars / Starch	• Glucose, Fructose, Starch (Cornstarch, Potato starch)
Alcohols	• Methanol, Ethanol, Crude Ethanol, E95, Ethylene Glycol, Glycerol (from bio-diesel plant)
Fossil Fuels	• Methane, Coal

Containerized HFRS Packaged System

Scalable up to 2000 kg of H_2 Per Day

Modules can operate in parallel for greater capacity.

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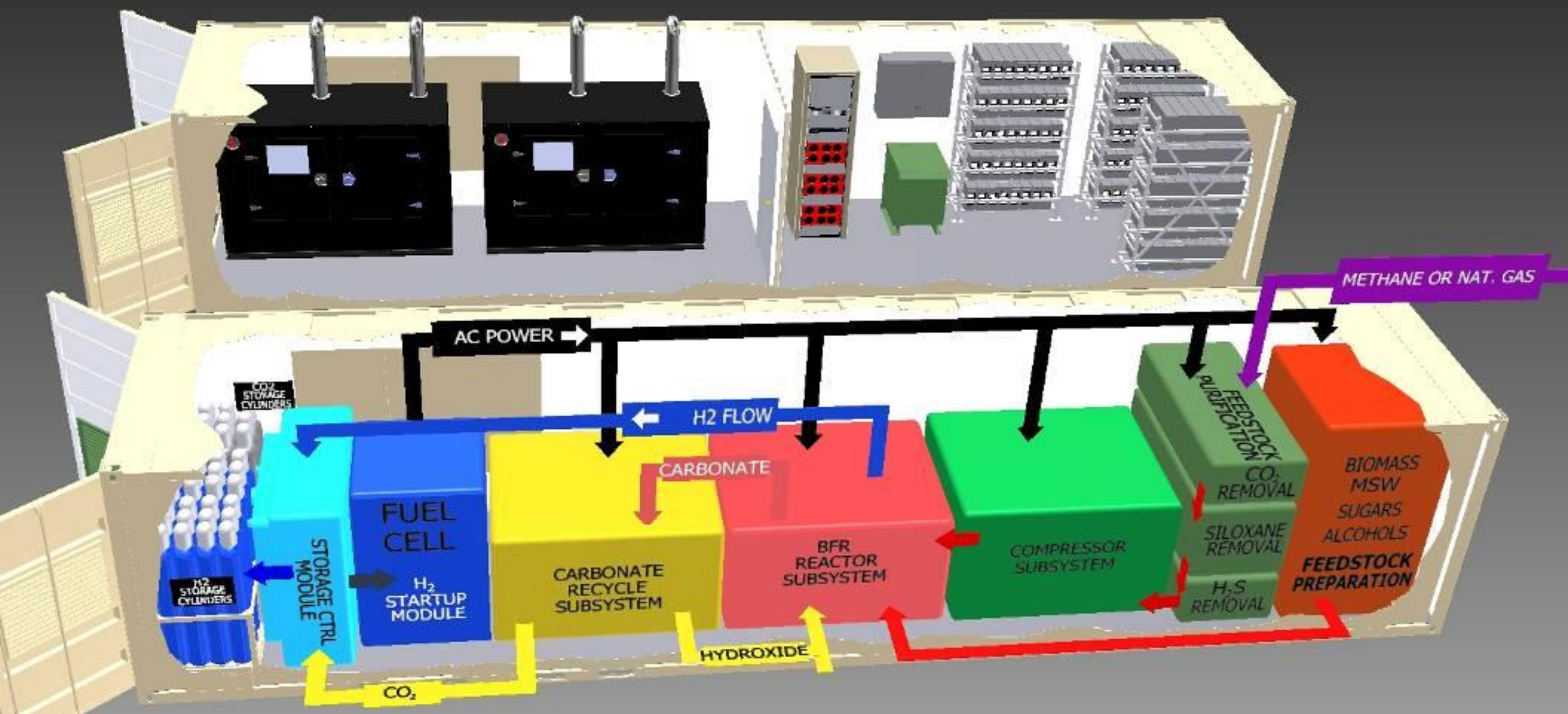
Hydrogen Fuel Reformation System

Applications and Configurations



Point of Use H2 Generation and AC Generation Application

Hydrogen Fuel Reformation System

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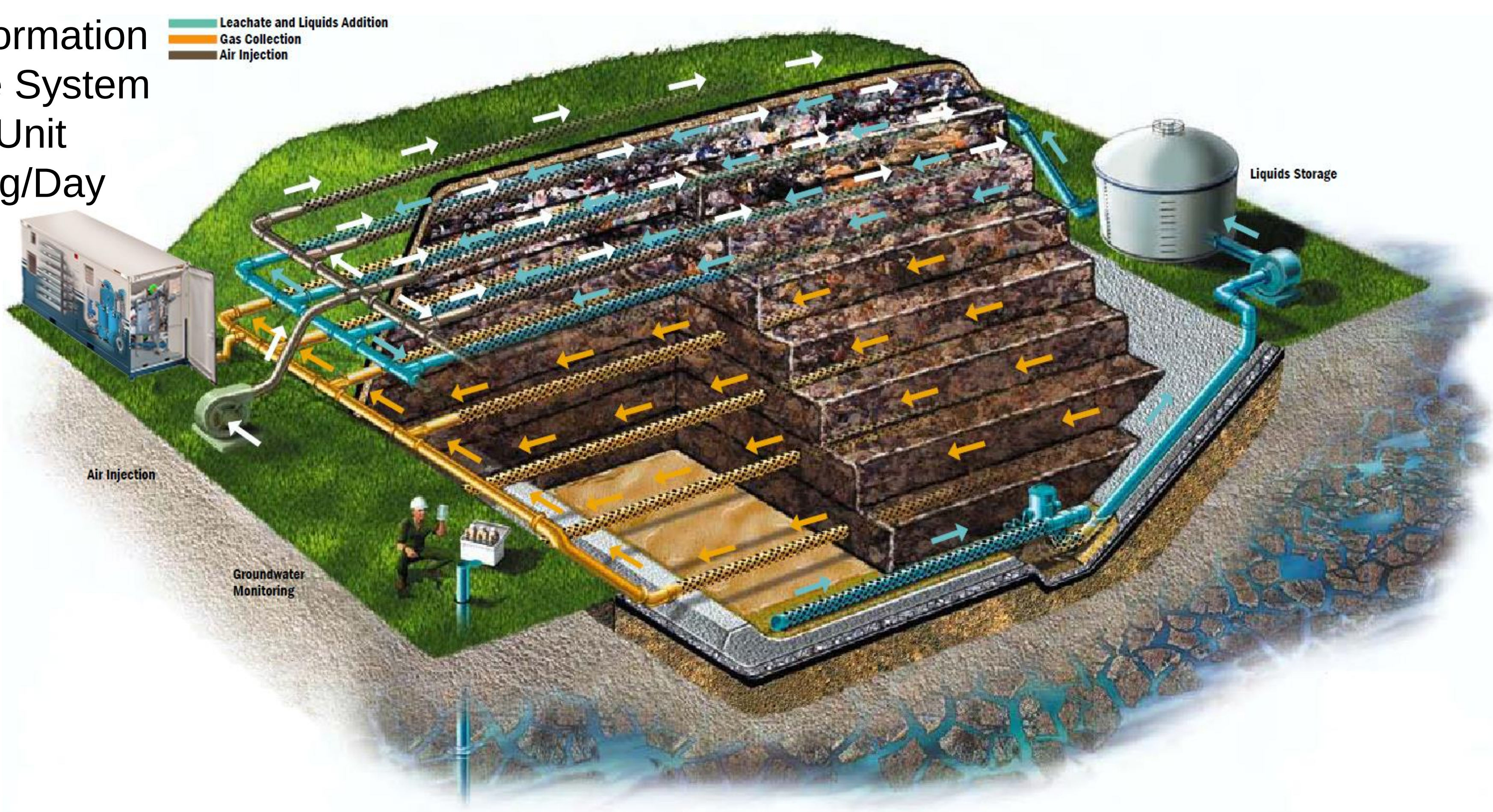
Applications and Configurations
Landfill Site H_2 Generation, Storage and Distribution

Bio-reformation
Module System
Single Unit
2000 Kg/Day



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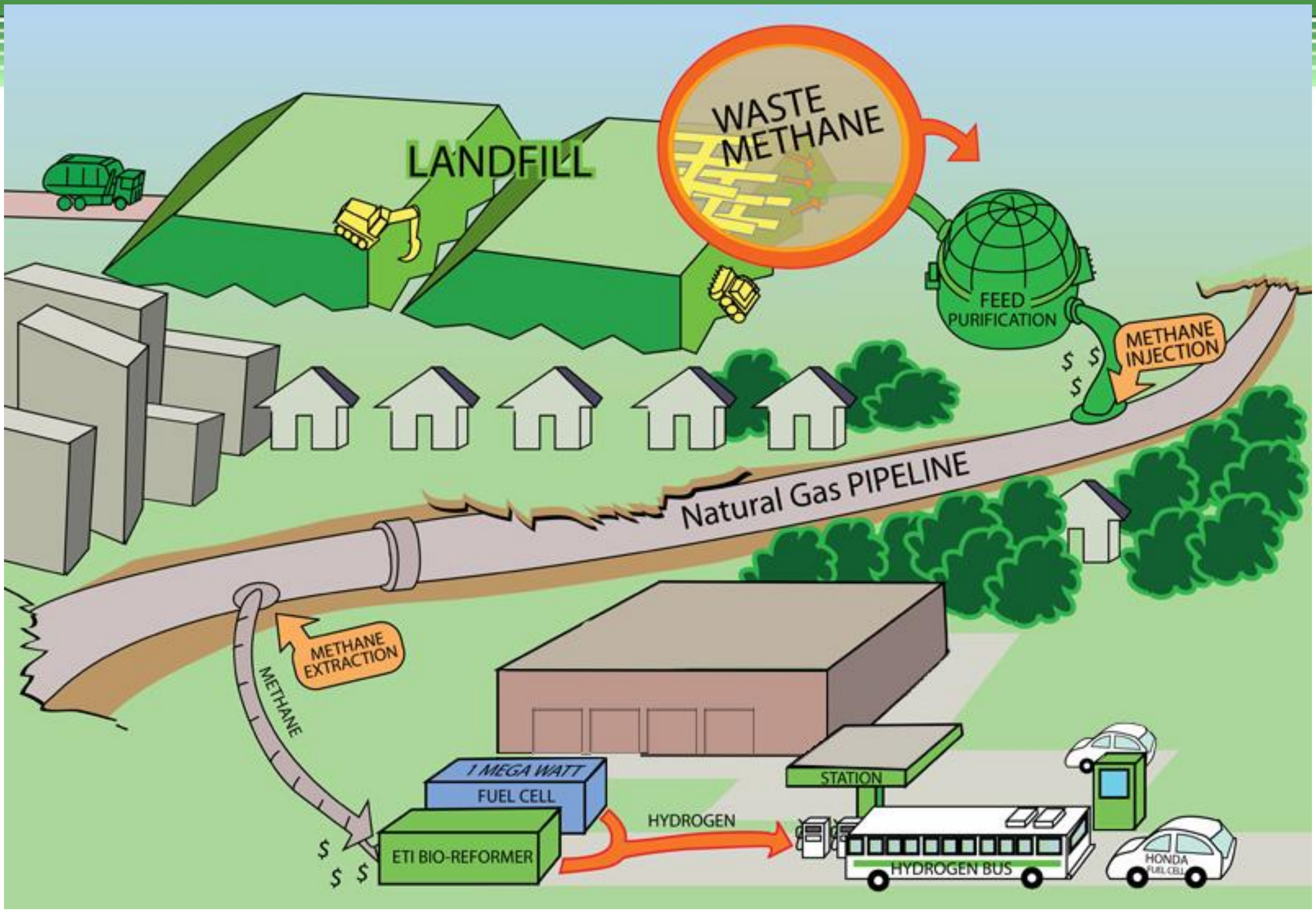
Waste to Fuel Reformation Process Concept



Hydrogen Fuel Reformation System

DOE/FTA Fuel Cell Bus Projects

Both DOE and the Federal Transit Administration (FTA) fund NREL's hydrogen and fuel cell evaluations. A joint plan describes these evaluations, and the table below summarizes both current and planned DOE- and FTA-funded projects.

Fuel Cell Electric Bus Evaluations for DOE and FTA

Demonstration	State	City	# Buses	2014		2015				2016				2017			
				3	4	1	2	3	4	1	2	3	4	1	2	3	4
ZEBA Demonstration *	CA	Oakland	12	AC Transit	AC Transit	AC Transit	AC Transit	AC Transit	AC Transit	AC Transit	AC Transit	AC Transit	AC Transit	AC Transit			
American Fuel Cell Bus (AFCB) *	CA	Thousand Palms	1	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine		
	NY	Ithaca	1						TCAT	TCAT	TCAT	TCAT	TCAT	TCAT			
	OH	Canton, Cleveland	2							SARTA/GCRTA	SARTA/GCRTA	SARTA/GCRTA	SARTA/GCRTA	SARTA/GCRTA	SARTA/GCRTA		
	CA	Irvine	1			UCI	UCI	UCI	UCI	UCI	UCI	UCI					
AFCB (TIGGER)	MI	Flint	1				Flint MTA	Flint MTA	Flint MTA	Flint MTA	Flint MTA	Flint MTA	Flint MTA				
	CA	Thousand Palms	2	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine
Birmingham FCEB *	AL	Birmingham	1	BJCTA	BJCTA	BJCTA	BJCTA	BJCTA									
Massachusetts AFCB *	MA	Boston	1			MBTA	MBTA	MBTA	MBTA	MBTA	MBTA	MBTA					
Advanced Composite FCEB *	TX	Austin	1			Capital Metro	Capital Metro	Capital Metro	Capital Metro								
	DC	Washington								DCDOT	DCDOT	DCDOT	DCDOT				
Next-gen Compound Bus *	CA	San Francisco	1						SFMTA	SFMTA							
Battery Dominant AFCB *	CA	Thousand Palms	1							SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine	SunLine

* National Fuel Cell Bus Program project

Color coded by Design Strategy:
- Green: Fuel cell dominant hybrid electric (AC Transit, SunLine, TCAT, SARTA/GCRTA, UCI, Flint MTA, MBTA)
- Blue: Battery dominant hybrid electric (BJCTA, Capital Metro, DCDOT, SunLine battery dominant)
- Red: Diesel hybrid with fuel cell primarily for accessories (SFMTA)

Hydrogen Vehicle Introductions

- Toyota (US Introduction in 2015)
- Honda (US Production in 2016)
- Hyundai (US Introduction 2014)
- Other companies, like General Motors, Ford, and Audi are working on similar cars.

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Remote Site H2 Generation, Storage and Distribution

Distribution of H2 Storage Module to Mobile Refueling Vehicle & Permanent Station

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Mobile H2 Distribution for Vehicle and Bulk Station Refueling

By-Product (carbonate) Recycling

What do we do with solid carbonate?

- ƒDisposal of carbonate to sequester CO_2

- Use the carbonate to generate pure CO_2 for various industrial applications (soda, liquid fuel synthesis, etc..)

- Sell Na_2CO_3 or $CaCO_3$ for various industrial applications (i.e. glass)

- Recycling back to hydroxide

Recycling of Na_2CO_3

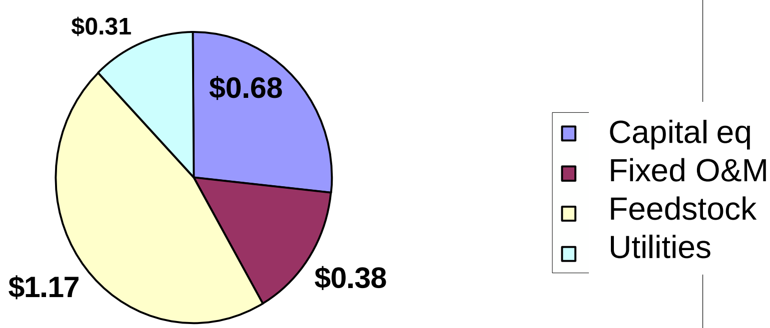
- $Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH$
- $CaCO_3 \xrightarrow{heat} CaO + CO_2$
- $CaO + H_2O \rightarrow Ca(OH)_2$

Recausticizing - a common commercial process in the paper mill industry

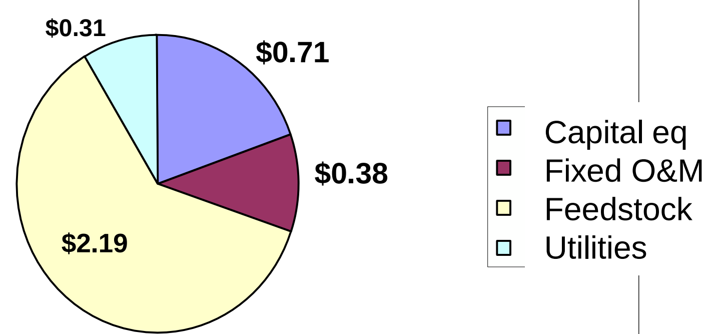
Hydrogen Fuel Reformation System

Reformation at 1,500 kg Hydrogen Per Day
Cost Structure

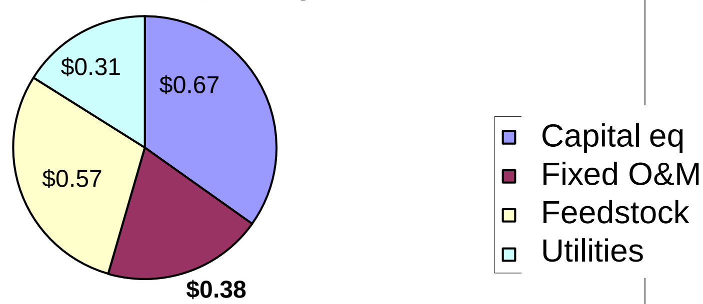
Methane Feedstock ($2.54/kg)



Ethanol Feedstock ($3.59/kg)



Biomass Feedstock ($1.93/kg)



Economics of Base-Facilitated Reformation

- Used the DOE H2A economic analysis tool
  - Net present value with Internal Rate of Return (IRR): 10%
  - 20 years depreciation on facility equipment
  - 10 years depreciation on reactor
  - Cost of feedstock and electricity taken from Energy Information Administration (EIA) Annual Energy Outlook report

Hydrogen Fuel Reformation System

Substantiation of Technology and Business Case Performed by Independent Third Parties

- Basic H_2 Reformation Science R & D performed by
  Energy Conversion Devices (ECD) / Ovonics, Rochester Hills, MI

- Department of Energy (DOE) SBIR Phase 1 and 2 managed by
  Directed Technologies and Strategic Analysis, Inc., Arlington, VA

- Business Model Marketing Analysis performed by
  SRA International, Inc., Fairfax, VA

- Emerging Hydrogen Market Forecast performed by
  Navigant Research, Washington, DC

- Business Case Studies and Financial Analysis performed by
  University of Michigan Global MBA MAP Team, Ann Arbor, MI

Summary

- The Base-Facilitated Reforming (BFR) process has been demonstrated on wide variety of fuels.
- The reforming temperatures using the BFR process are significantly lower than the electrolysis or steam reformation process of the fuels.
- The BFR process exhibits good H_2 generation rates at the low temperatures of operation.
- The BFR process is a simple one step process. Pure H_2 and no CO and CO_2 produced. WGS reaction and PSA are therefore avoided and the process is environmentally clean.
- The BFR process is economically feasible and competes well with other technologies.

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Hydrogen Fuel Reformation System

Summary

ƒ

- High conversion of raw biomass feedstock's and high yield (close to 100%) of H_2 was obtained using BFR.

ƒ • The process operates at low temperatures without producing CO and CO_2 gases and it is economically feasible.

ƒ • Commercialization of 100 kg, 500 kg, 1500 kg and 2000 kg of H_2 per day is underway.

- For example, an 1800 kg per day module can support a 1 Mw fuel cell at full load continuously.

- Besides being scalable, the module can work in parallel.

Contact Information

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