2006 DOE Hydrogen Program

Hydrogen Generation from Biomass-Derived Carbohydrates via Aqueous-Phase Reforming Process

Dr. Randy D. Cortright

Virent Energy Systems, INC

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This presentation does not contain any proprietary or confidential information

Project ID #
PD 4

Overview

Timeline

- Start – Sept 2005
- Finish – Aug 2008 (Tentative)
- 10 % complete

Budget

- Total project funding
  - DOE share -1,942 K
  - Contractor share - 679 K
- Funding received in FY05
  - 100 K
- Funding received for FY06
  - 100 K
- Funding Reduction in FY06 resulted in limiting work to catalyst development

Barriers

- Feedstock Cost Reduction
  - 2005 Feedstock Cost Contribution $3.80/gge
  - 2010 Feedstock Cost Contribution $1.80/gge
- By 2010, reduce H_2 costs to $3.60/gge
  - Overall Efficiency 66%
- By 2015, reduce H_2 cost to $2.50/gge

Partners

- ADM
- University of Wisconsin

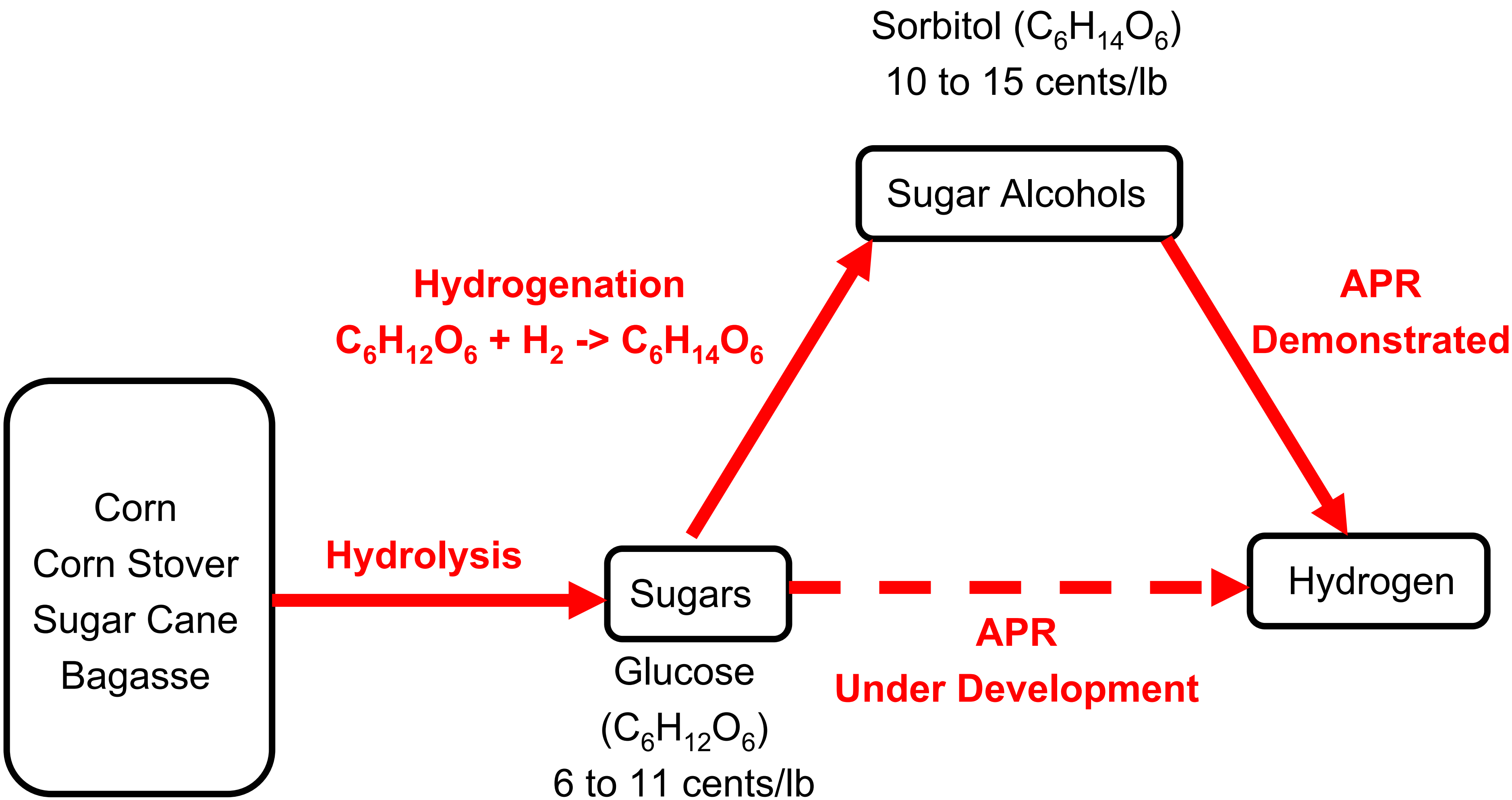
Objectives

Overall	• Design a generating system that uses low cost sugars or sugar alcohols that can meet the DOE H_2 cost target of $2.50/gge for 2015. • Fabricate and operate an integrated 50 kg of H_2/day generating system.
2006	• Limited scope of work for 2006 due to funding cutbacks. • Develop APR catalyst, reaction conditions, and reactor suitable for converting glucose to hydrogen.

Objectives (cont)

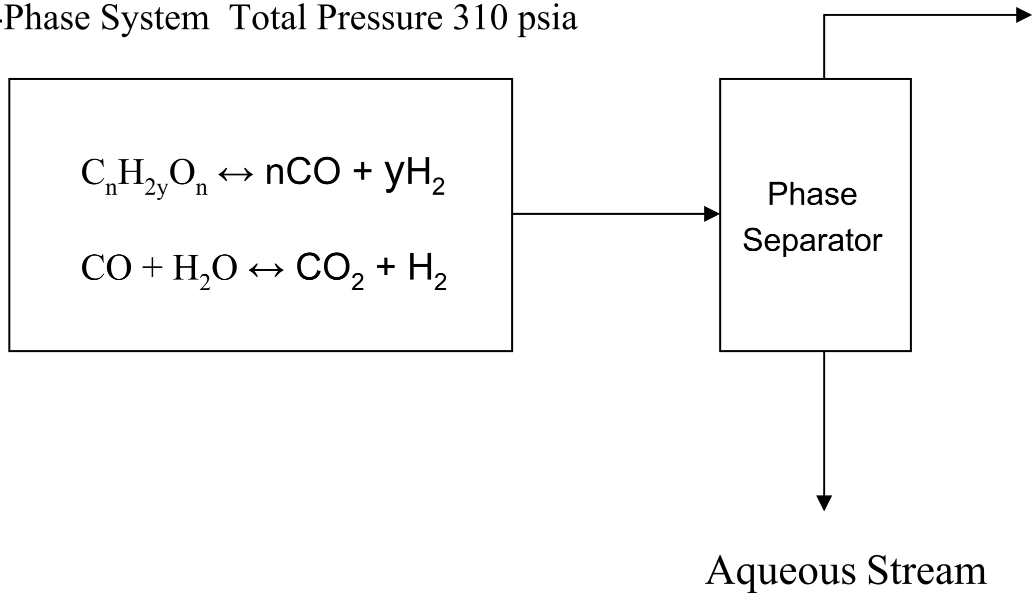
2007	• Development is funding dependent • Continued investigation of APR catalyst, reaction conditions, and reactor suitable for converting glucose to hydrogen • Calculate the thermal efficiency and economics of the APR system utilizing either glucose or sorbitol as a feedstock • Select preferred feedstock • Design of 50 kg H_2/day demonstration system
2008	• Fabrication of 50 kg H_2/day system • Startup and operation of 50 kg H2/day system • Analysis of 50 kg H2/day system

Approach


Sorbitol ($C_6H_{14}O_6$)
10 to 15 cents/lb
Sugar Alcohols
Hydrogenation
$C_6H_{12}O_6 + H_2 \rightarrow C_6H_{14}O_6$
APR
Demonstrated
Corn
Corn Stover
Sugar Cane
Bagasse
Hydrolysis
Sugars
Hydrogen
Glucose
($C_6H_{12}O_6$)
6 to 11 cents/lb
APR
Under Development

APR Processing of Sorbitol

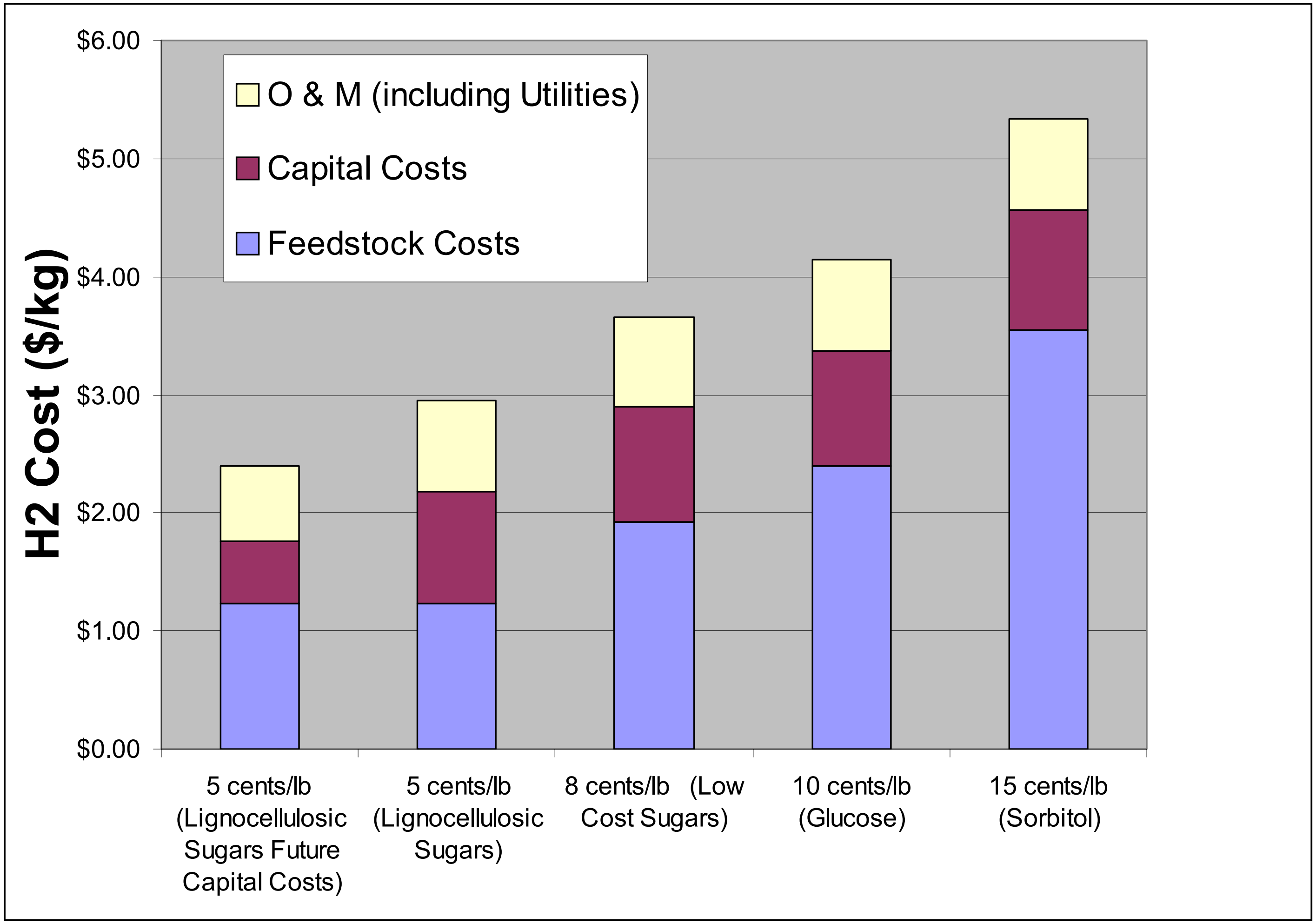
Low Temperature Reforming and Water-Gas Shift
215 ^{o}C over Platinum-Based Catalyst
Liquid-Phase System Total Pressure 310 psia



193 psi H_2
115 psi CO_2
1.4 psi Hydrocarbons
0.2 psi H_2O
Less than <u>100 ppm</u> CO

- Utilizes a Single Reactor
- Generates High Pressure Hydrogen
- Low CO Concentrations

H2A Projected Cost of Hydrogen Generation using the APR Process



1500 kg H_2/day

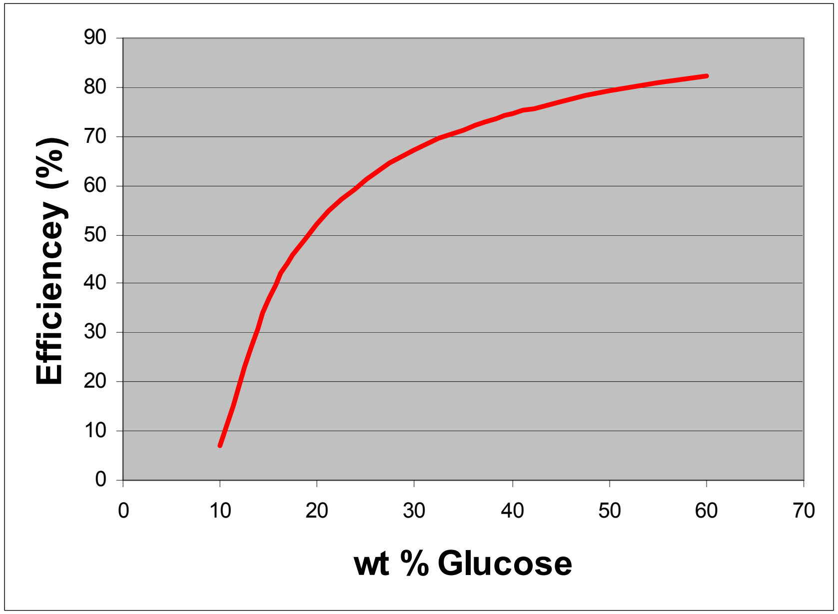
15000 kg Feedstock/day

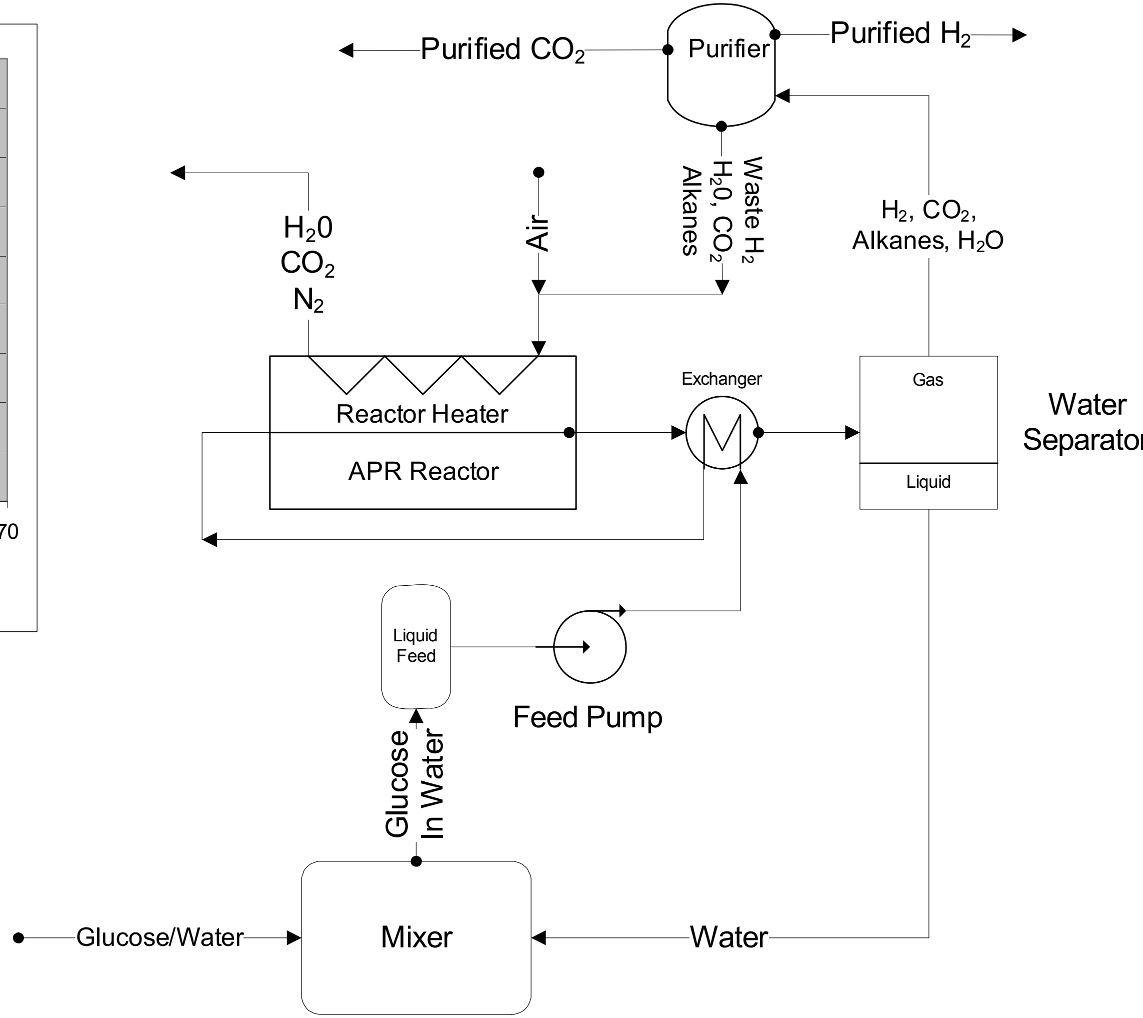
Capital Cost Includes
- APR
- PSA
- Compression
- Storage
- Dispensing

Technical Accomplishments/ Progress/Results

- Initiated project in September 2005
- ADM provided glucose samples for processing.
- Established catalyst and conditions for operations with high concentrations of glucose.

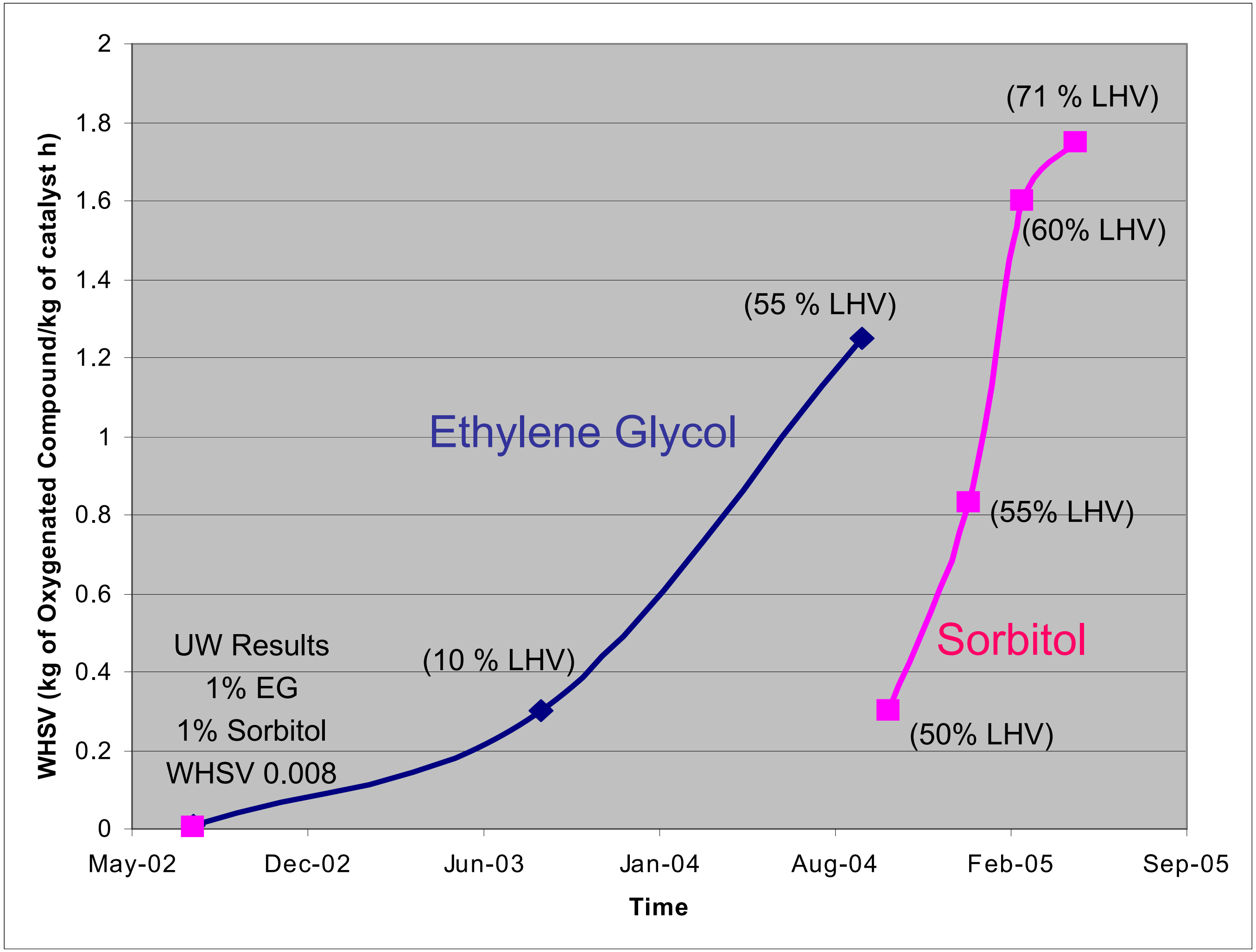
Effects of Feed Concentration





- System Efficiency
  - Combustion of Hydrogen for Process Energy Required
  - Higher Feedstock Concentrations Reduce Heating Requirements

APR Improvements



(Thermal Efficiency)
Based on LHV

Theoretical
85 % LHV

Reforming of Glucose

Date		Apr-04	Sep-05	Jan-06
Feedstock	30% Sorbitol	3% Glucose	30% Glucose	30% Glucose
WHSV	2.0 /h	0.897 /h	0.996 /h	2.1 /h
Reactor				
Temperature	240 ^oC	230 ^oC	240 ^oC	240 ^oC
Pressure	500 psig	430 psig	500 psig	600 psig
Conversion	100%	73%	100%	100%
Conversion to Gas	75%	14%	58%	36%
H2 Selectivity	72%	33%	23%	58%
Watt H2/gram	4.2	0.12	0.39	0.91
Watt Alkane/Gram	2.1	0.03	1.26	0.73

WHSV – gram of oxygenated compound per gram of catalyst per h

Related Technical Accomplishments

- Design, fabrication and operation of an integrated APR alpha unit for Madison Gas and Electric

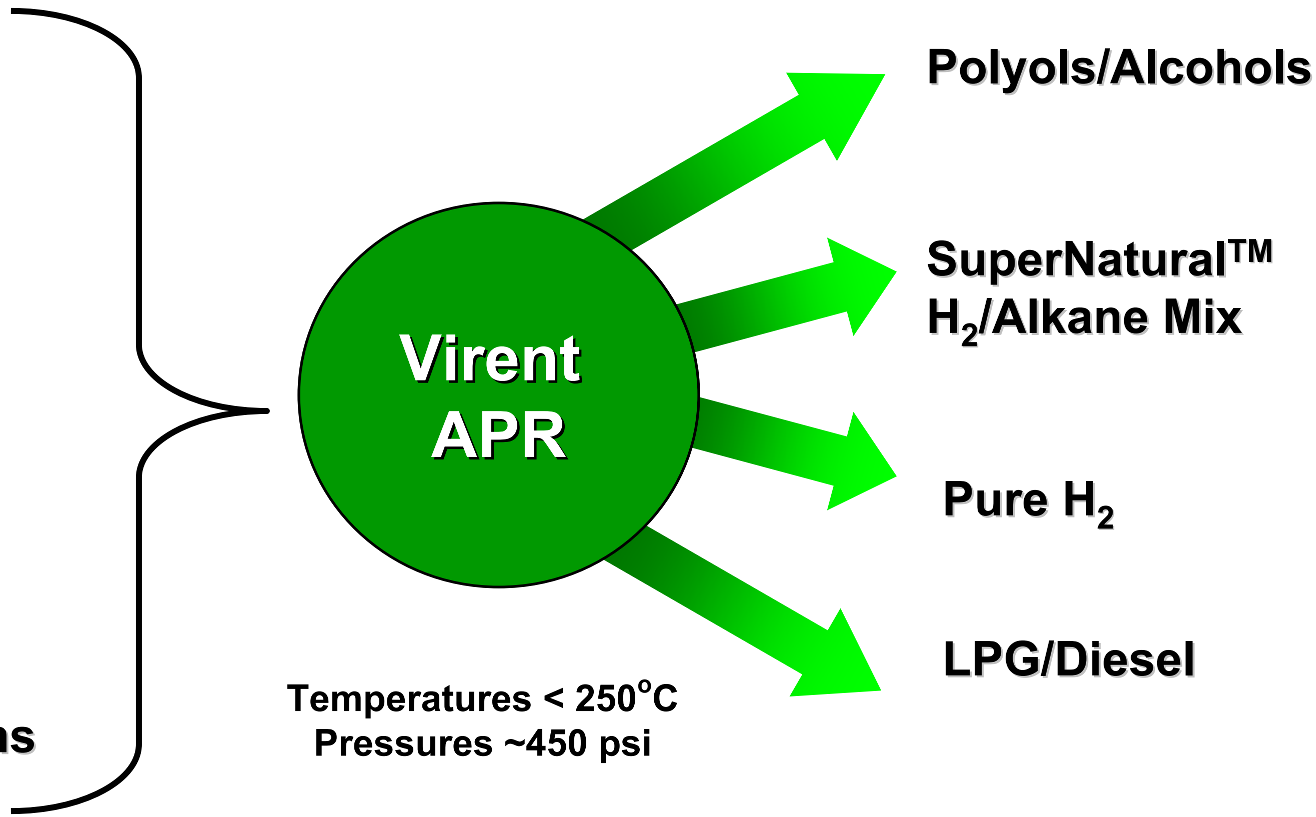
- High Conversion of Biodiesel-Derived Glycerol

- Design of Effective Reactor System

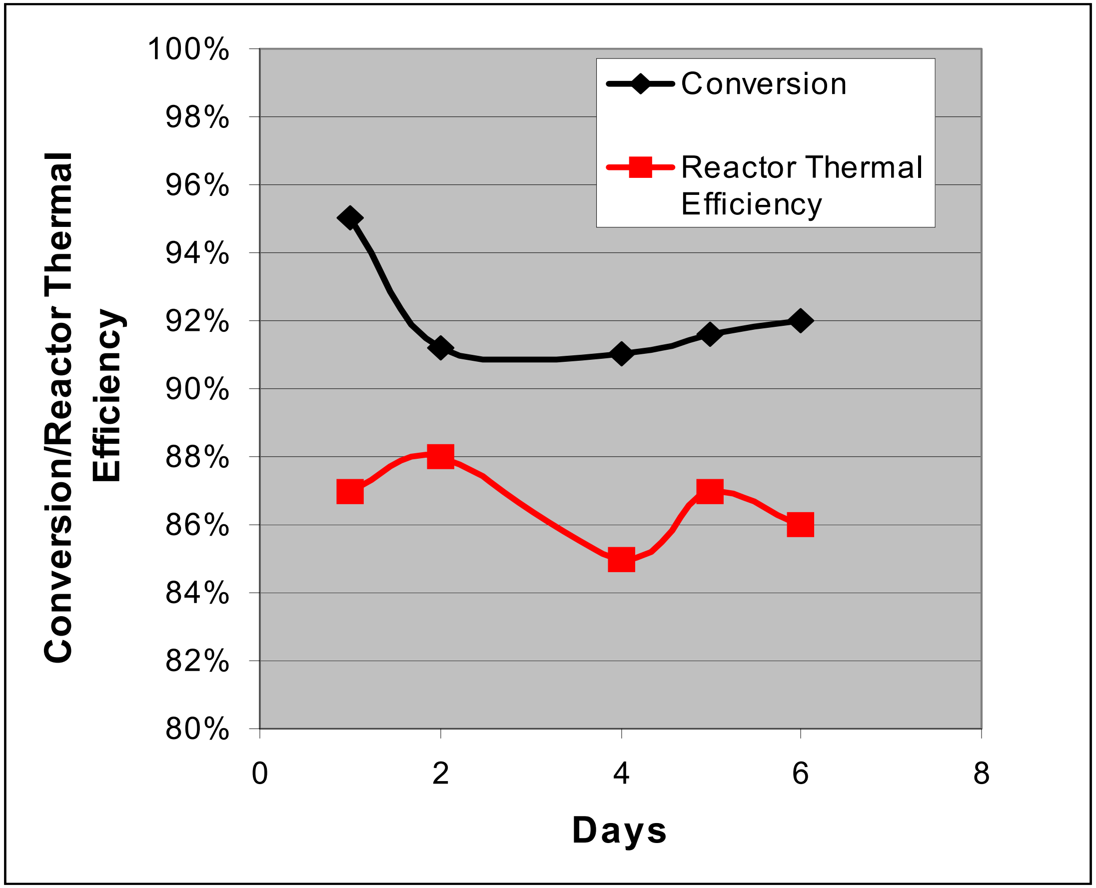
- Integration of an APR Reactor System with ICEGenset

Approach
Aqueous Phase Reforming (APR)

- Glycerol
- Sorbitol
- Glucose
- Sucrose
- Five Carbon Sugars
- Alcohols
- Mixed Streams



APR Reactor Performance



Single Pass Conversion

1.8 WHSV

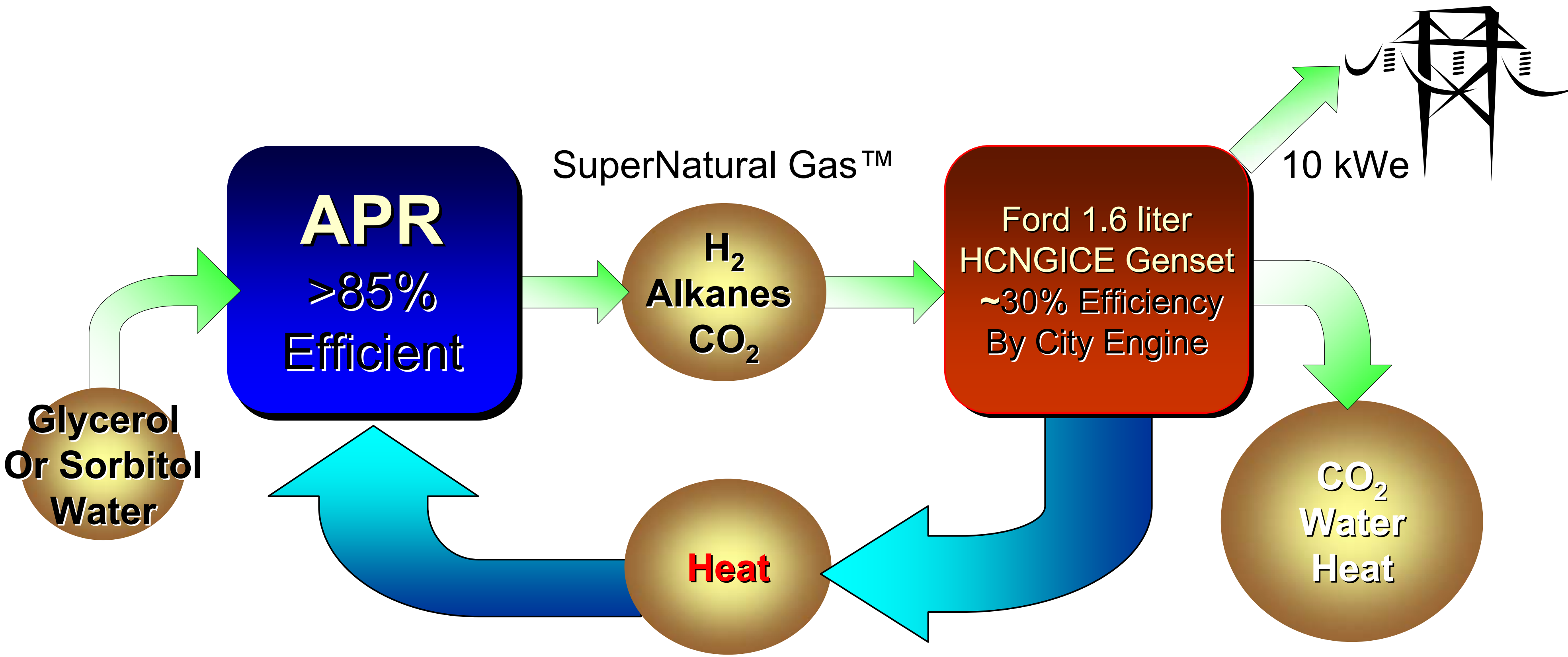
based on Glycerol

Reactor Thermal Efficiency

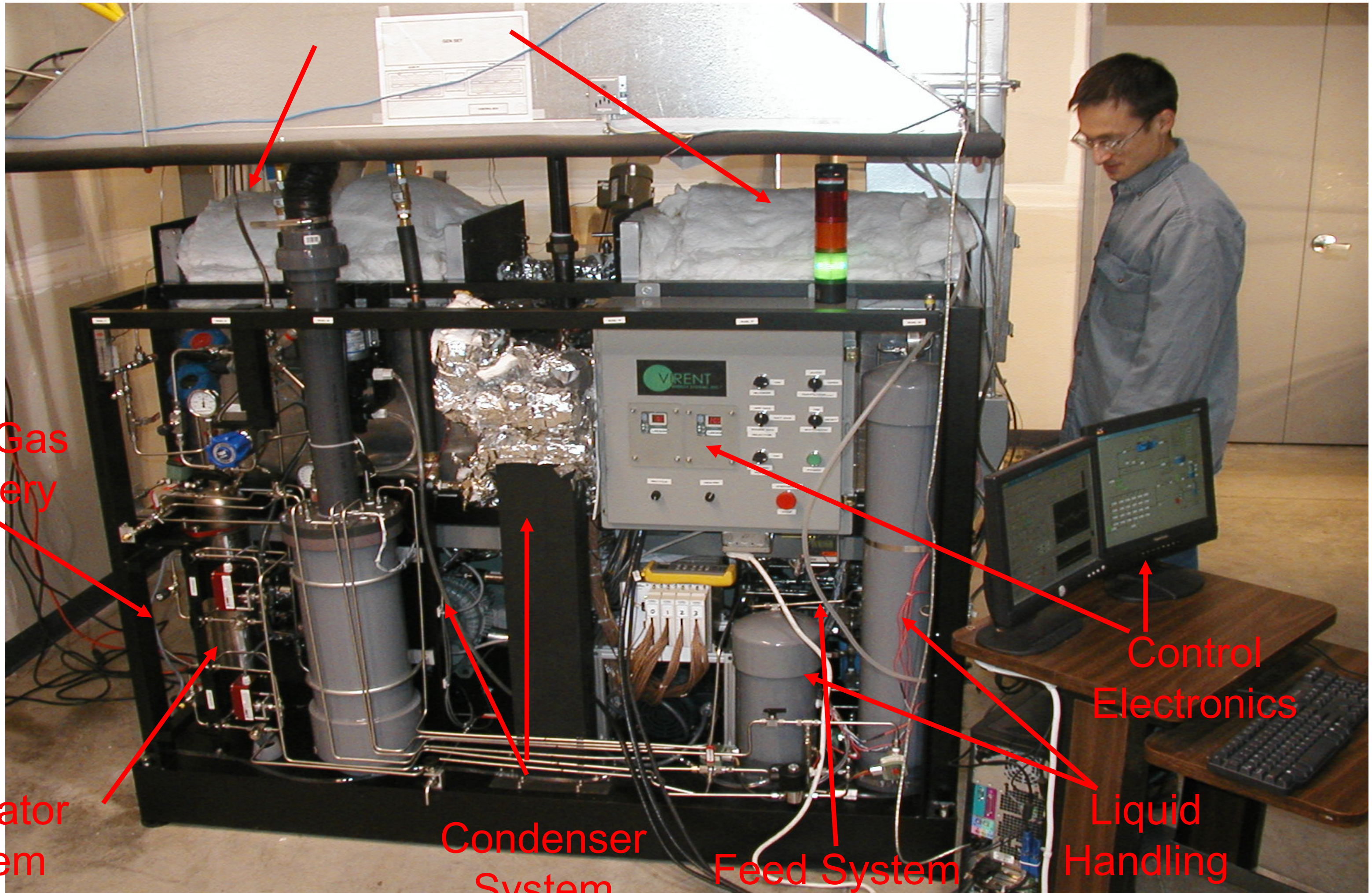
$$100 \times \left(1.0 - \frac{\text{Process Energy}}{\text{Generated Energy}}\right)$$

Process Thermal Efficiency
78.5 % of LHV of Feed

APR: ICE Integration
Madison Gas & Electric Project



Green Energy Machine (GEM)



SuperNatural™ Gas Properties

Composition (by volume)

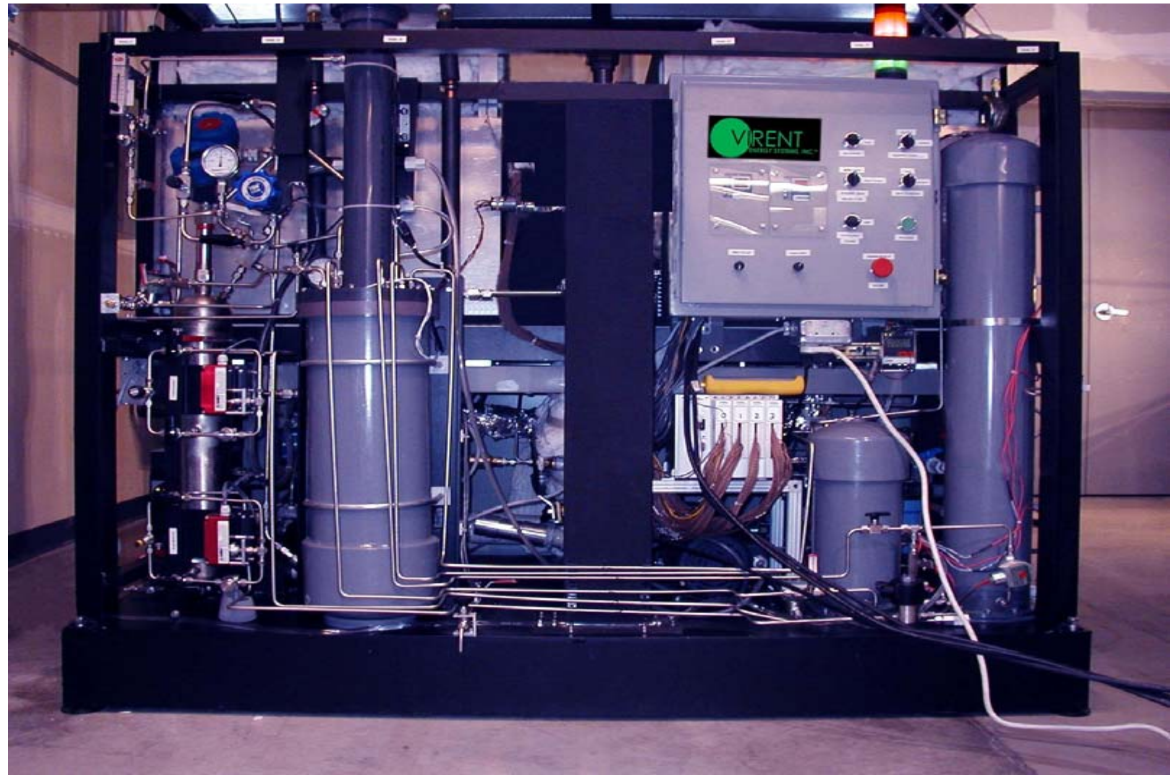
Hydrogen:	~35%
Methane:	~ 8%
Ethane:	~12%
Propane:	~ 5%
CO_2:	~40%

Heating Value: 510-600 BTU/ft^3

Pressure (exit of APR): 400-600 psig

10kWe GEM System

- Efficient, scalable, liquid phase reactor design.
- Generates > 6 NM^3/h of Supernatural Gas
- Less than 260°C operating temperature.
- “Unteathered” Operation
- Runs on glycerol or sorbitol.



Future Work

- <u>Worked Planned for 2007 (with restoration of funding)</u>

  – Develop APR catalyst and reactor that converts glucose to hydrogen.

  – Calculate the thermal efficiency and economics of the baseline APR system utilizing glucose as the feedstock.

  – Evaluate the baseline APR system against US Hydrogen program goals and determine whether to proceed with either glucose or sorbitol for further development the demonstration system.

Future Work beyond 2007

- Develop the detail design of the demonstration APR hydrogen generation system (50 kg/day).
- Fabrication of the integrated hydrogen generation system.
- Install and operate the APR hydrogen generation system at a sugar facility owned by ADM.
- Evaluate APR hydrogen generation system performance against US Hydrogen program goals.

Summary

- Initiated Project in September 2005 with limited funding.
- Initial work with higher concentrations of glucose shows promise.
- Virent has already built and operate a 6 NM^3/h Alpha Unit utilizing glycerol as a feedstock.
- Will continue work with glucose as funding is available.

Back-up Slides

- The following slides are included for evaluation purposes.

Responses to Previous Year Reviewers' Comments

Comment
Ultimately how much hydrogen could be expected from agriculture biomass in the U.S., without impacting food and industrial uses?

Response
An April 2005 report from DOE/USDA entitled "Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply" shows study results that indicate over 1 billion tons of biomass could be produced in the US above what is need for food and industrial use. Sugars extracted from this biomass could be converted using the APR process to generate over 45 billion kg of H2.

Responses to Previous Year Reviewers’ Comments

Comment

What about less clean feeds such as hydrolyzed lignocellulosics?

Response

Virent is currently investigating how to handle “dirty” feeds such as waste glycerol from biodiesel production.

In the future, it will be possible to handle hydrolyzed lignocellulosic feeds with either proper hydrolysis technology or implementation of low cost clean of the resulting sugar streams.

Critical Assumptions and Issues

- Conversion of high concentrations of sugars
  - As discussed previously, it is necessary to run at higher concentration of sugars to better thermal efficiency of the APR process.
- Development of lower cost catalyst
  - In this program, Virent will investigate catalyst formulation that will reduce the cost of the necessary catalyst.

Critical Assumptions and Issues

- Catalyst lifetime issues
  - Virent will conduct lifetime studies of the catalyst, identify deactivation modes, and either identify catalyst formulations that are resistant to deactivation or determine in-situ regeneration procedures
- Feedstock Purity Issues
  - Initially Virent will utilize clean glucose or sorbitol samples provide by ADM.
  - In the future, less pure feedstocks will be investigated.