2005 DOE Hydrogen Program Review
Arlington, Virginia

# Hydrogen Generation from Biomass-Derived Carbohydrates via the Aqueous-Phase Reforming (APR) Process


Randy D. Cortright, Ph.D.
Virent Energy Systems, Inc.
3571 Anderson Street
Madison, WI 53704
www.virent.com


May 23, 2005

This Presentation does not contain any proprietary or confidential information

Project ID# PD7

# Overview

## Project Timeline

- Start Date - September 2005
- End Date - August 2008

## Barriers

- Barriers addressed
  - Cost Reduction of Distributed Hydrogen Generation from Renewable Liquids
  - By 2015, reduce cost to $2.50/gge

## Budget

- Total project funding $2.62 M
  - DOE share $1.94 M
  - Contractor share $0.68 M
- Funding for FY05 None to Date

## Partners

- Virent Energy Systems
  - Project Lead – Catalyst/Reactor
- Archer Daniel Midland
  - Feedstock/Demonstration Unit Location
- UOP LLC
  - Systems Engineering
- University of Wisconsin
  - Fundamental Studies

VIRENT ENERGY SYSTEMS

# First Year Objectives

- Identify candidate sugar streams (Glucose), document plant integration requirements and associated economic factors.
- Develop catalyst and reactor based on the Aqueous Phase Reforming (APR) process suitable for converting candidate sugar streams to hydrogen.
- Design a baseline hydrogen generation system utilizing the APR process.
- Calculate the thermal efficiency and economics of the baseline APR system.
- Assess the baseline APR system with respect to US Hydrogen program goals and make a go/no go decision to proceed with further development of a demonstration system.

VIRENT ENERGY SYSTEMS

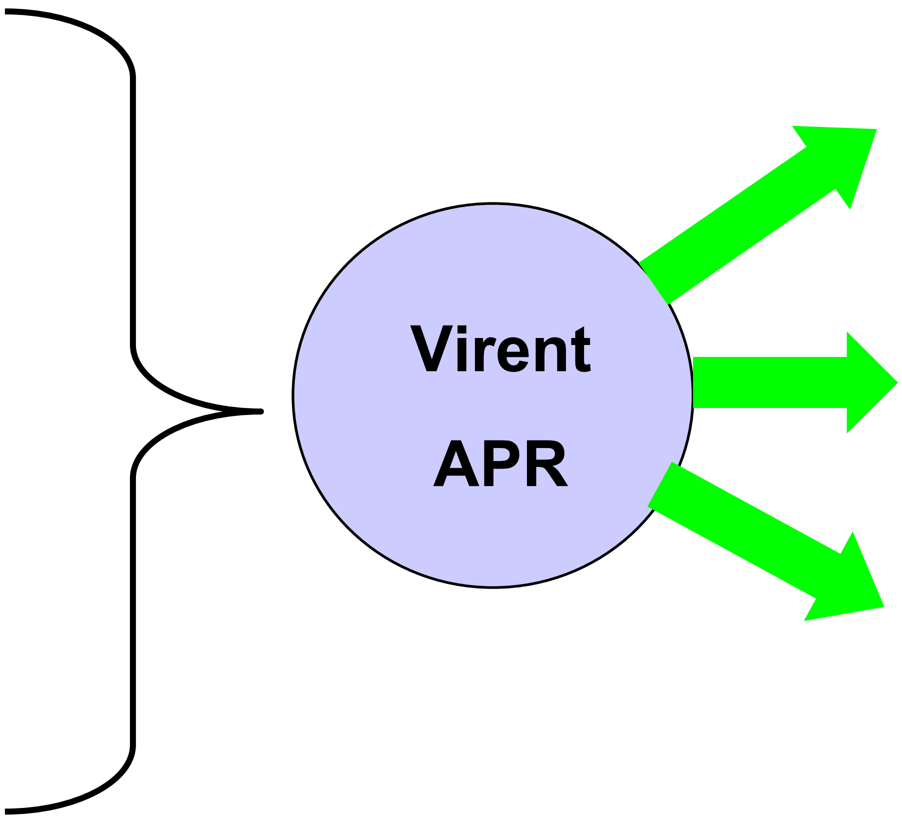
# Second and Third Year Objectives

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

VIRENT ENERGY SYSTEMS

# Approach
# Aqueous Phase Reforming (APR)

- **Ethylene Glycol (AntiFreeze)**
- **Glycerol** from Biodiesel
- **Sorbitol** from Glucose or Sucrose sugar
- **Glucose from Corn**
- **Sugars and Sugar Alcohols** from hemi-cellulose



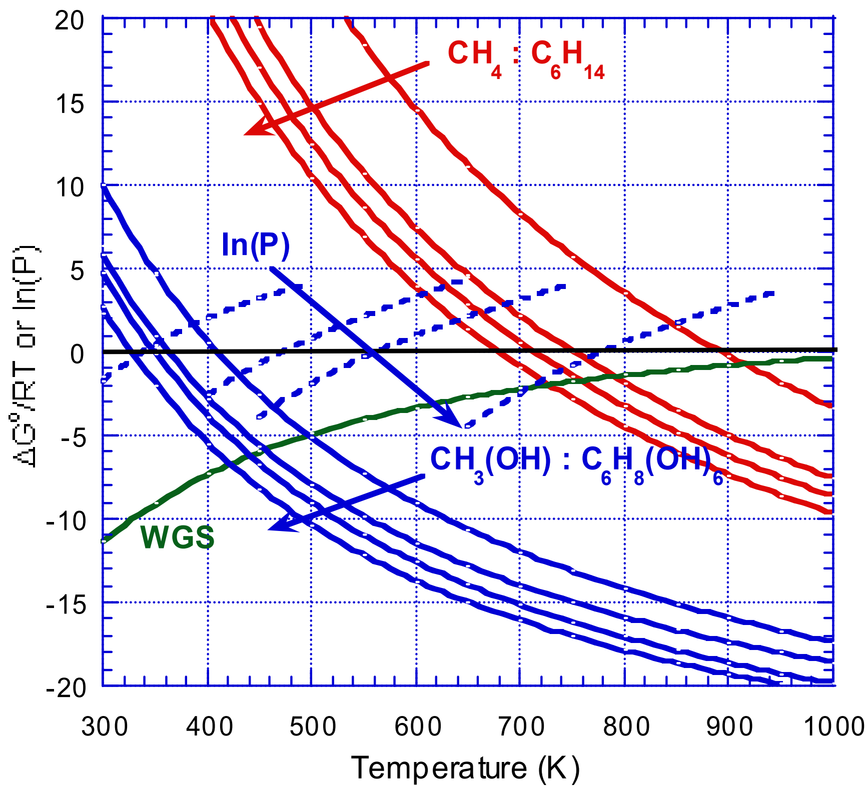

**Alkanes**

**$H_2$/Alkane Mix**

**Pure $H_2$**

VIRENT ENERGY SYSTEMS

# Reforming Thermodynamics




Reforming of Hydrocarbons

$C_nH_{2n+2} + nH_2O \leftrightarrow nCO + (2n+1)H_2$

Reforming of Oxygenated Compounds

$C_nH_{2y}O_n \leftrightarrow nCO + yH_2$

Water-Gas Shift

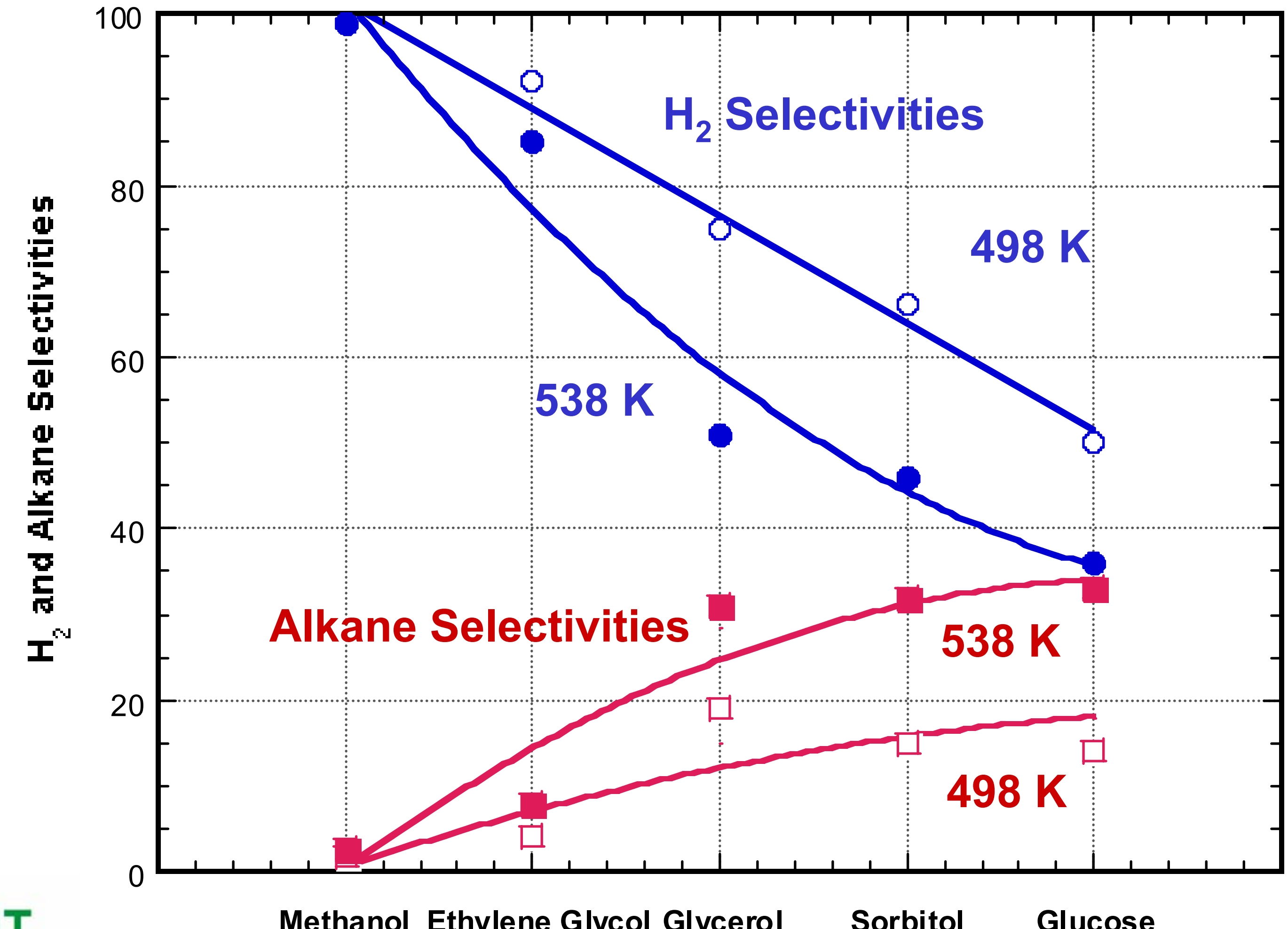
$CO + H_2O \leftrightarrow CO_2 + H_2$

⇒ Equilibrium is favorable for reforming of oxygenated compounds at low temperatures.

VIRENT ENERGY SYSTEMS

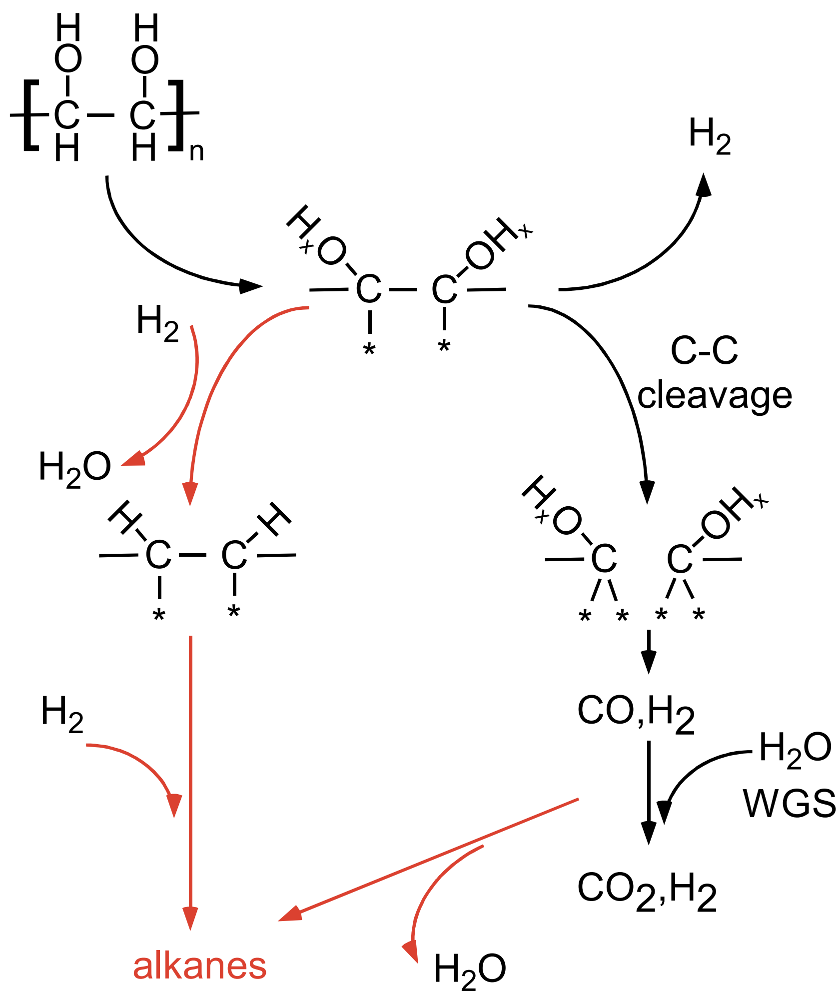
# Aqueous-phase Reforming of 1 wt% Methanol, Ethylene Glycol, Glycerol, Sorbitol & Glucose

[Cortright, Davda, and Dumesic, **Nature**, Volume 418, page 964 (2002)]



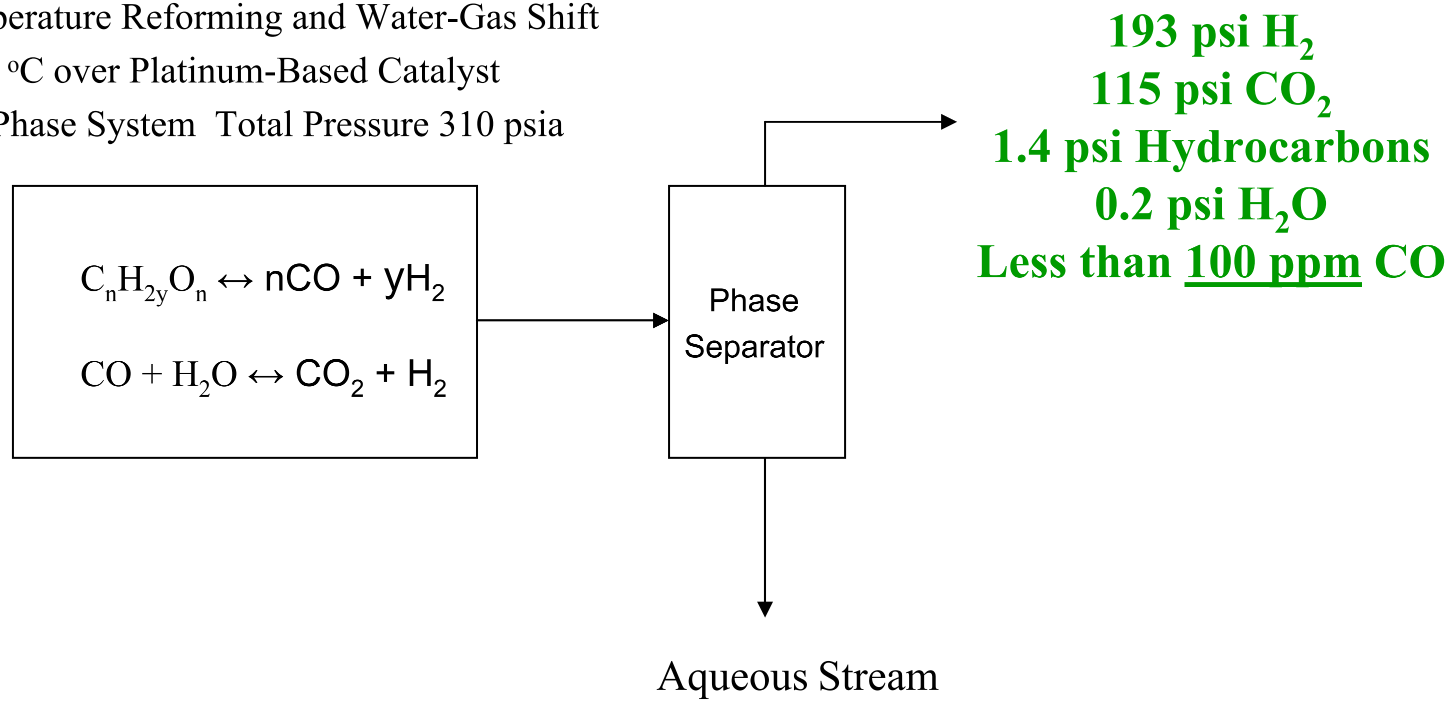

VIRENT ENERGY SYSTEMS

# Reaction Pathways



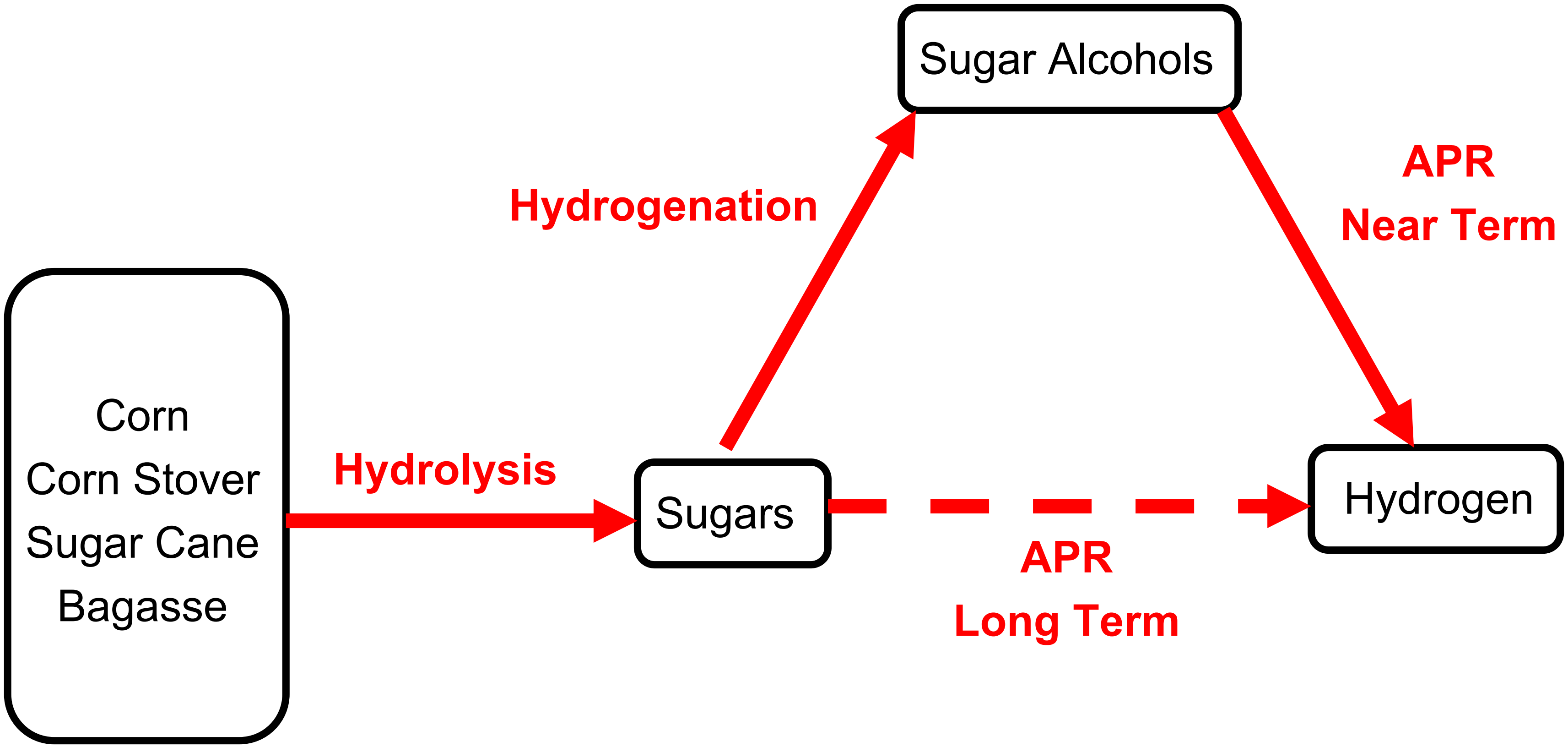
# APR Processing of Sorbitol

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

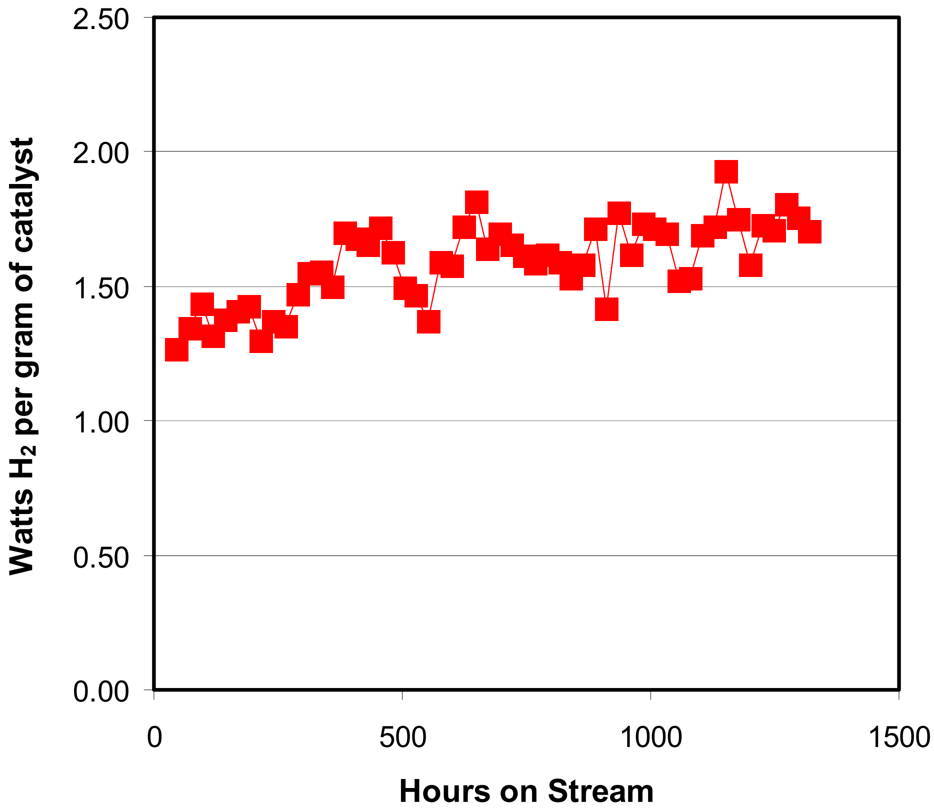



- Utilizes a Single Reactor
- Generation of High Pressure Hydrogen
- Low CO Concentrations

# Hydrogen from Biomass-Derived Compounds



# Catalyst Lifetime Study



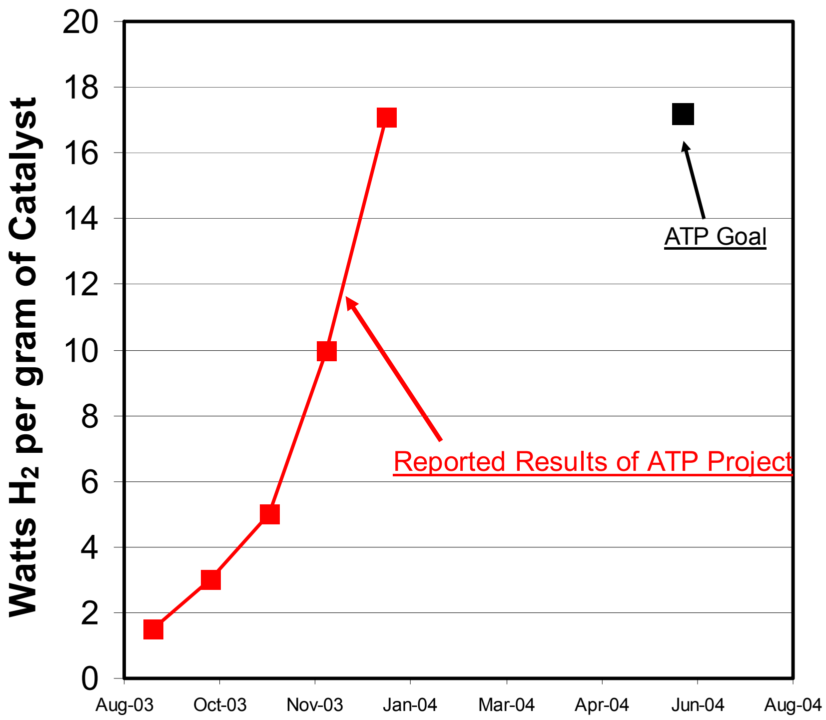

Results from NSF STTR Phase I Project

Platinum-Based Catalyst

10% Glycerol Feed

Two Month Run from September 2003 to November 2003

# Catalyst Activity Studies



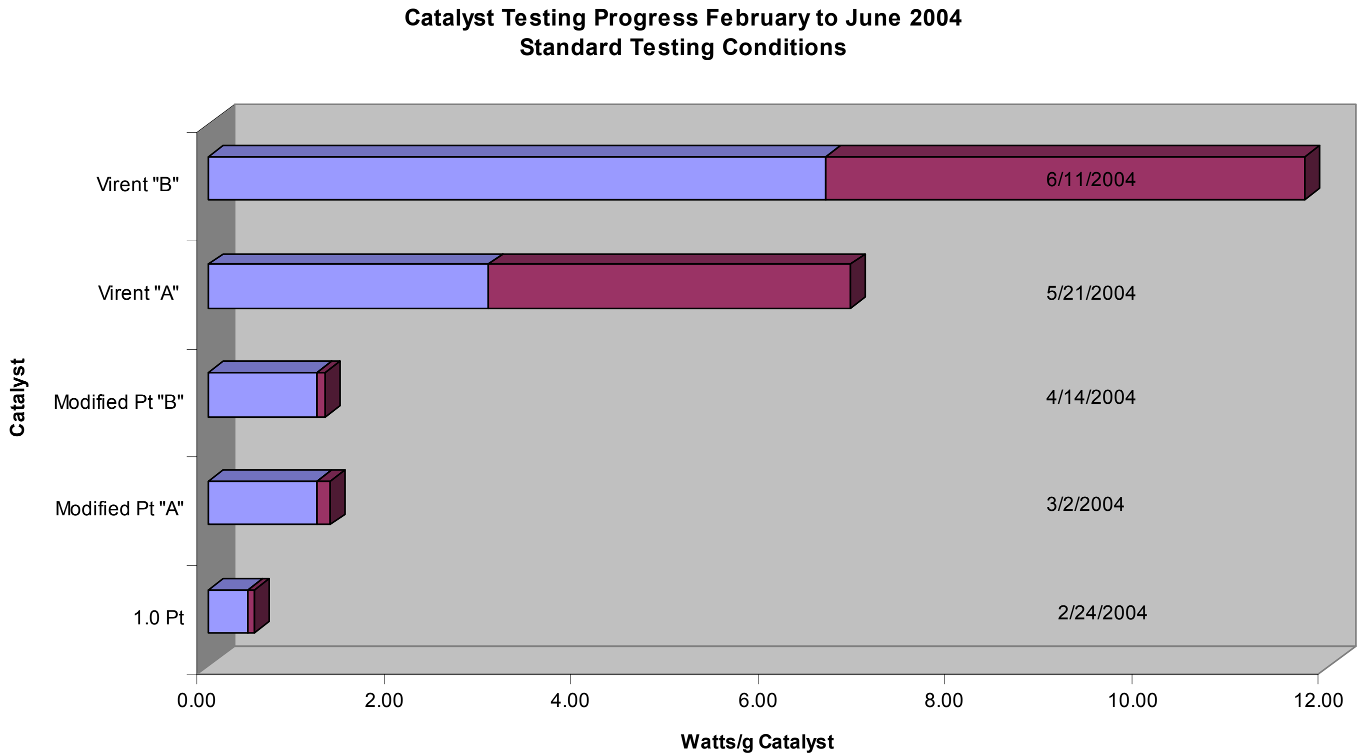

ATP Funded Project

Increased Activity due to Catalyst Composition, Reactor Design, and Reaction Conditions

Ethylene Glycol Feed

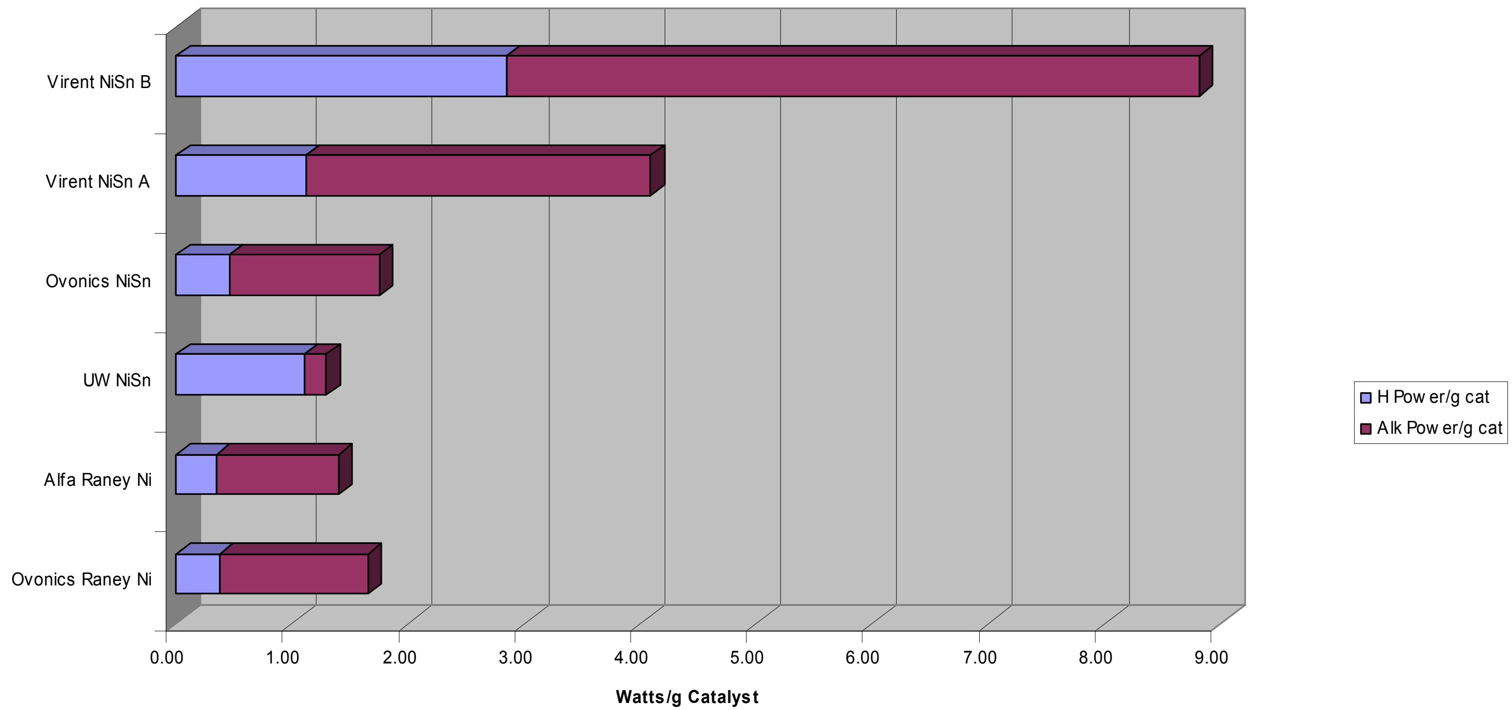
70 vol% $H_2$ in reactor Effluent

# Precious Metals Catalyst



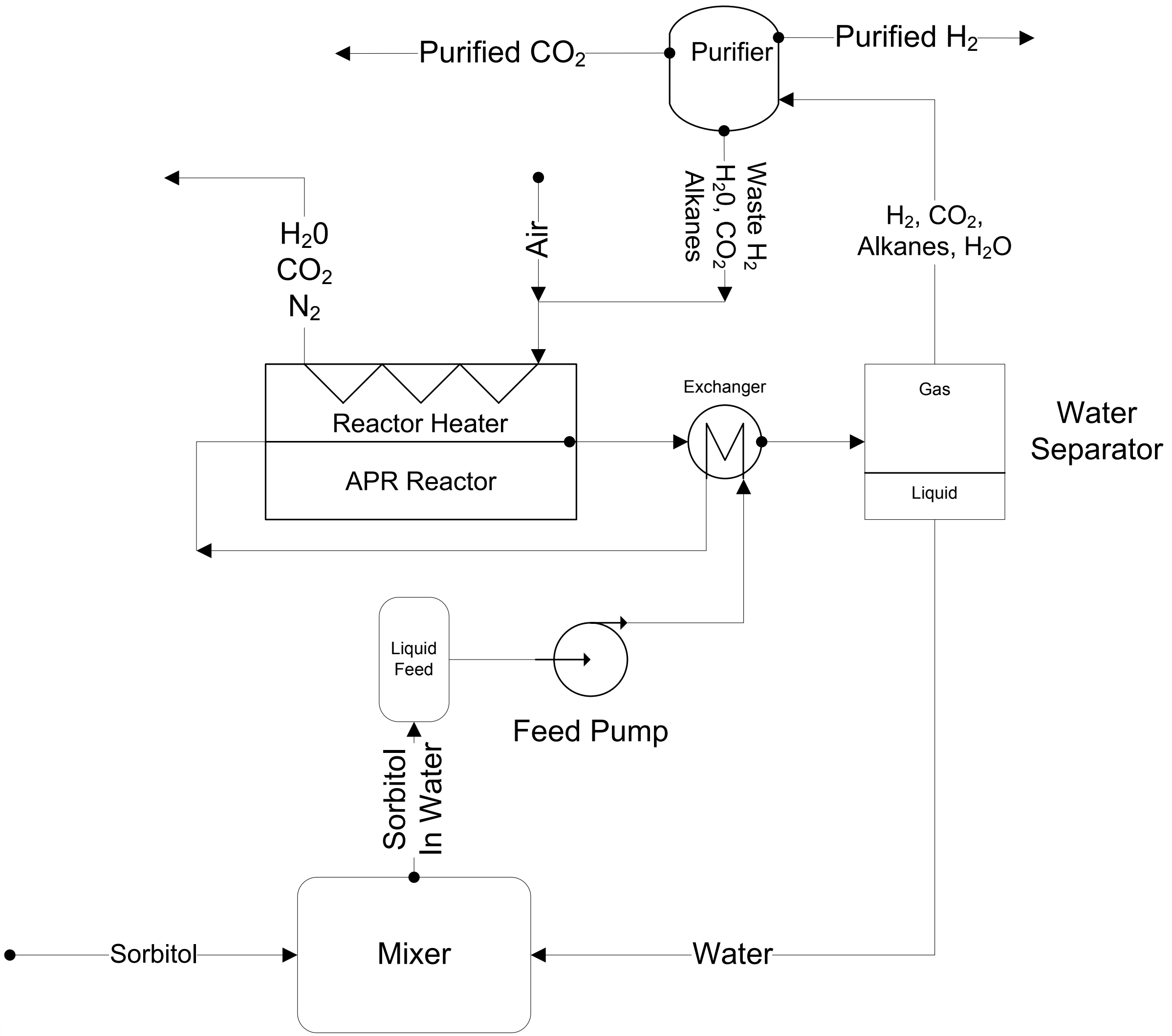

| | 1.0 Pt | Modified Pt "A" | Modified Pt "B" | Virent "A" | Virent "B" |
|---|---|---|---|---|---|
| Alkane | 0.07 | 0.13 | 0.09 | 3.87 | 5.12 |
| Hydrogen | 0.42 | 1.17 | 1.16 | 3.00 | 6.61 |

# Investigation of Nickel-Based Catalyst

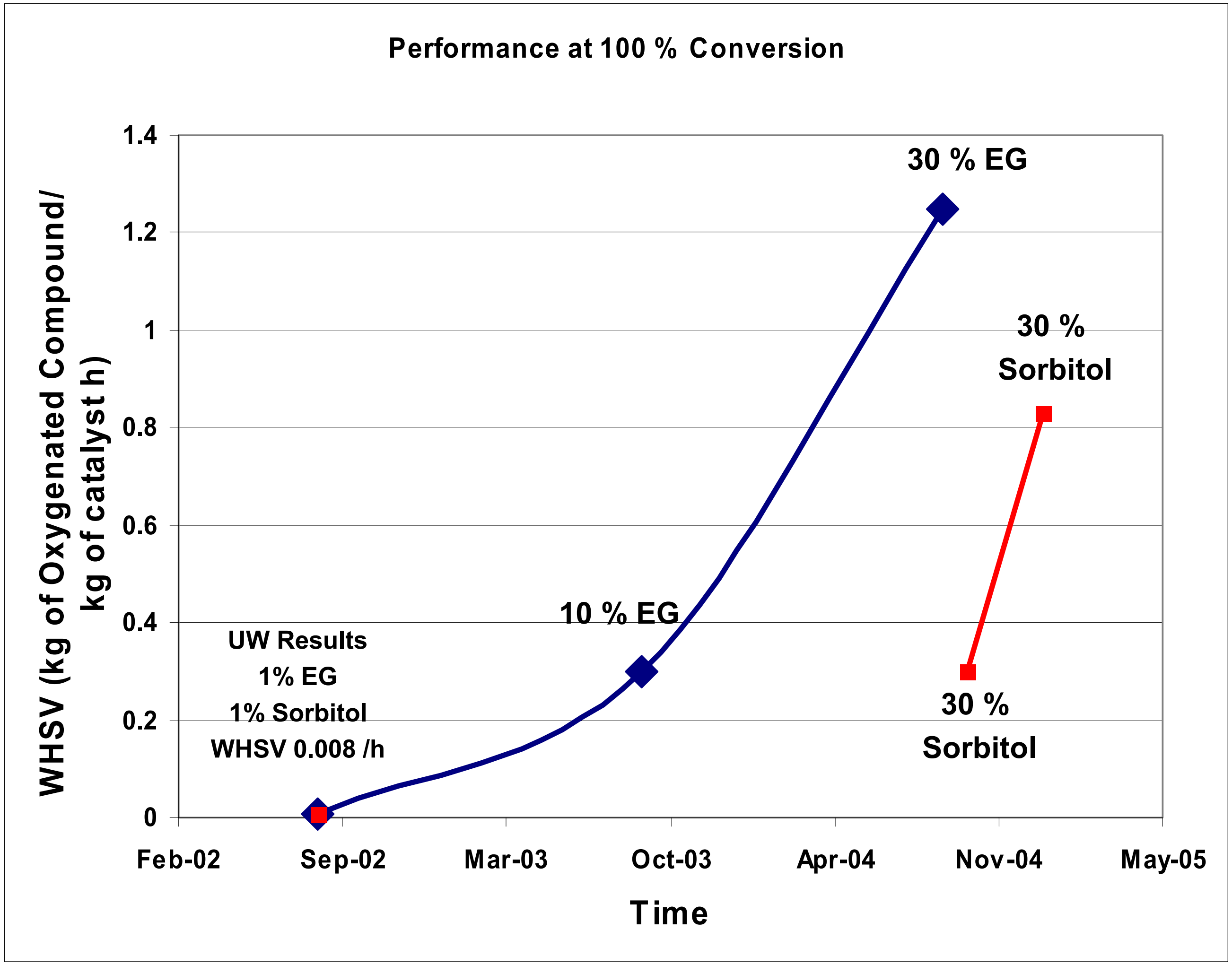



| | Ovonics Raney Ni | Alfa Raney Ni | UW NiSn | Ovonics NiSn | Virent NiSn A | Virent NiSn B |
|---|---|---|---|---|---|---|
| Alk Pow er/g cat | 1.28 | 1.06 | 0.19 | 1.29 | 2.97 | 5.97 |
| H Pow er/g cat | 0.37 | 0.34 | 1.10 | 0.46 | 1.12 | 2.84 |

# Hydrogen from Sorbitol

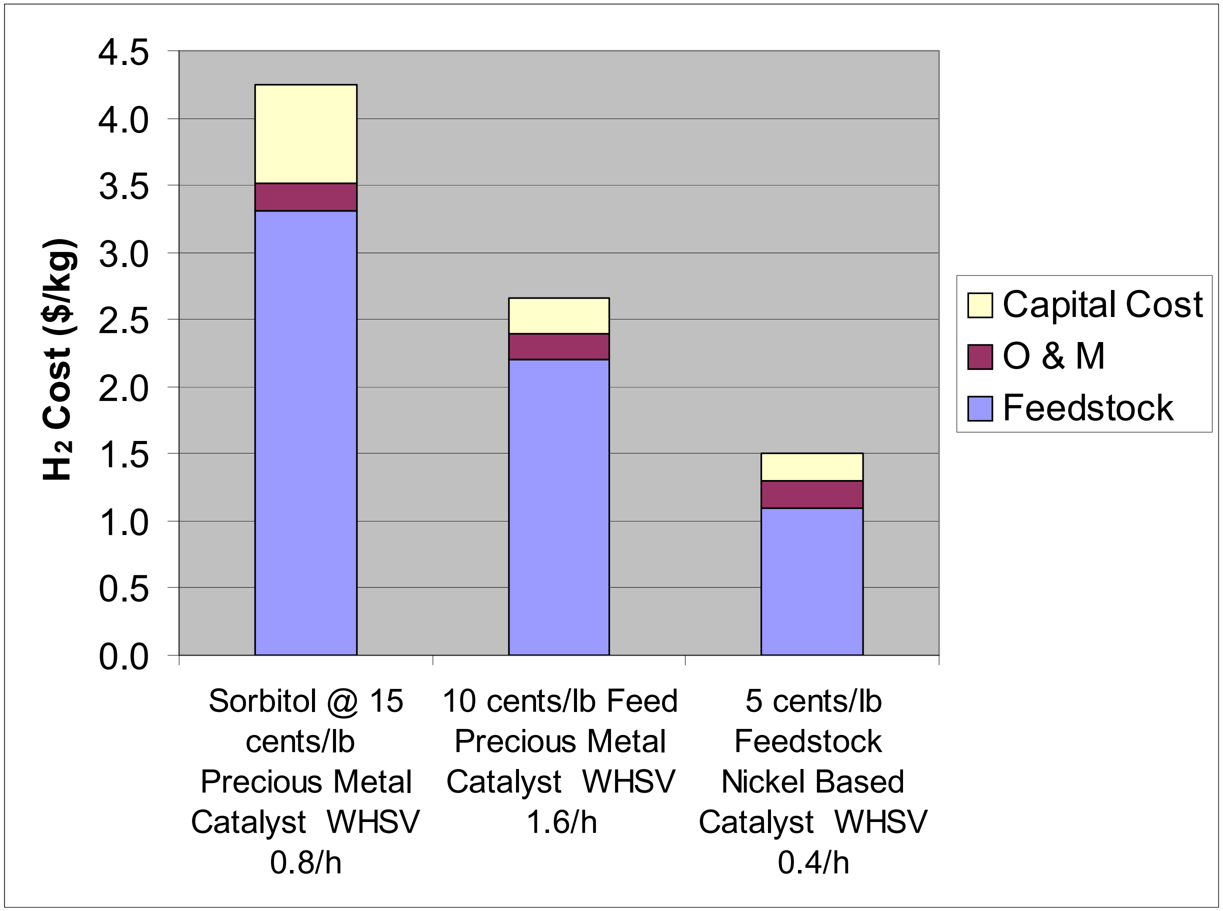


# APR Catalytic Reactor Improvements




VIRENT ENERGY SYSTEMS

# Projected Cost of Hydrogen Generation using the APR Process




Filling Station Application

500 kg $H_2$/day

5000 kg Sorbitol/day

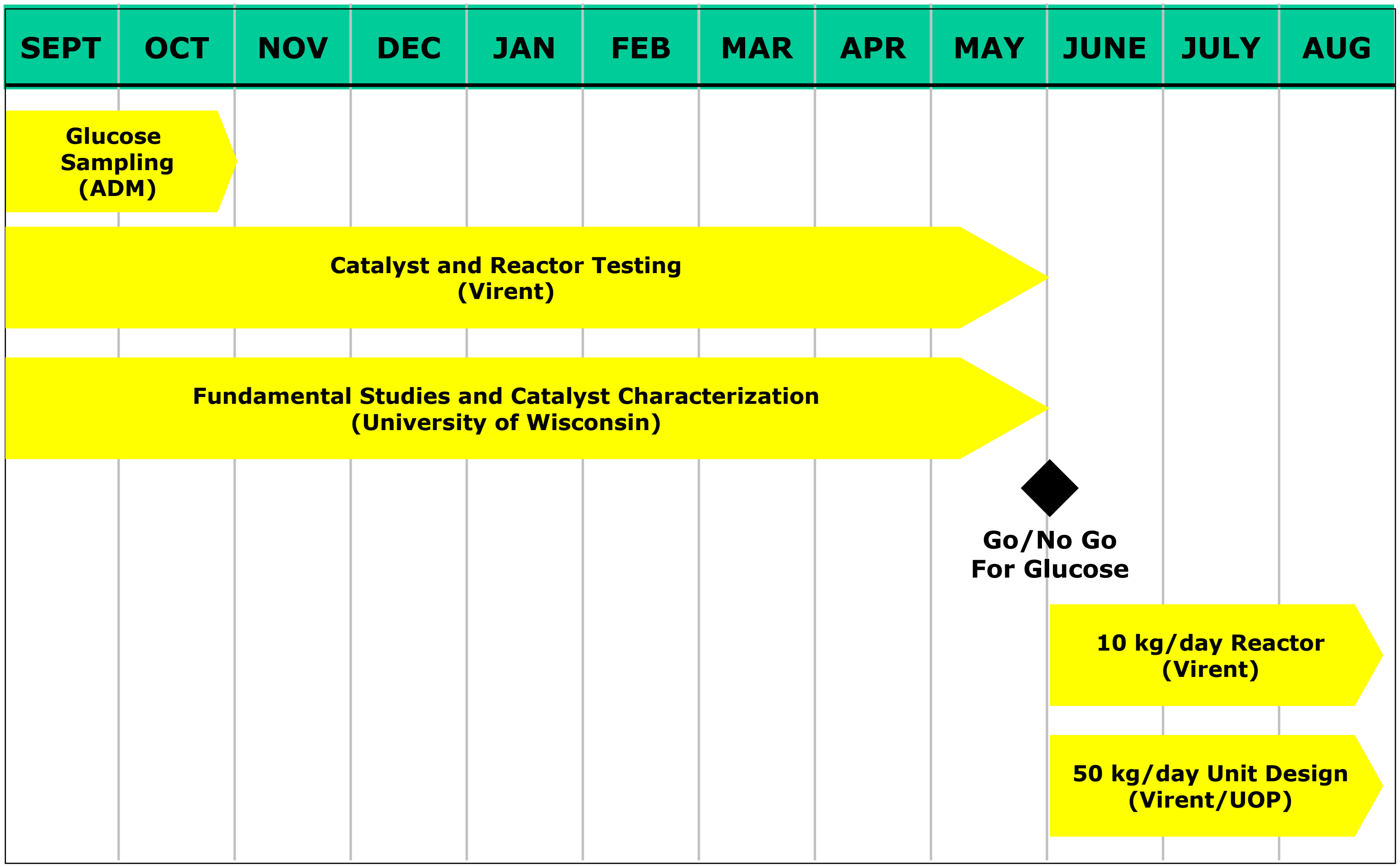
Catalyst Included in Capital Cost

10% ROI

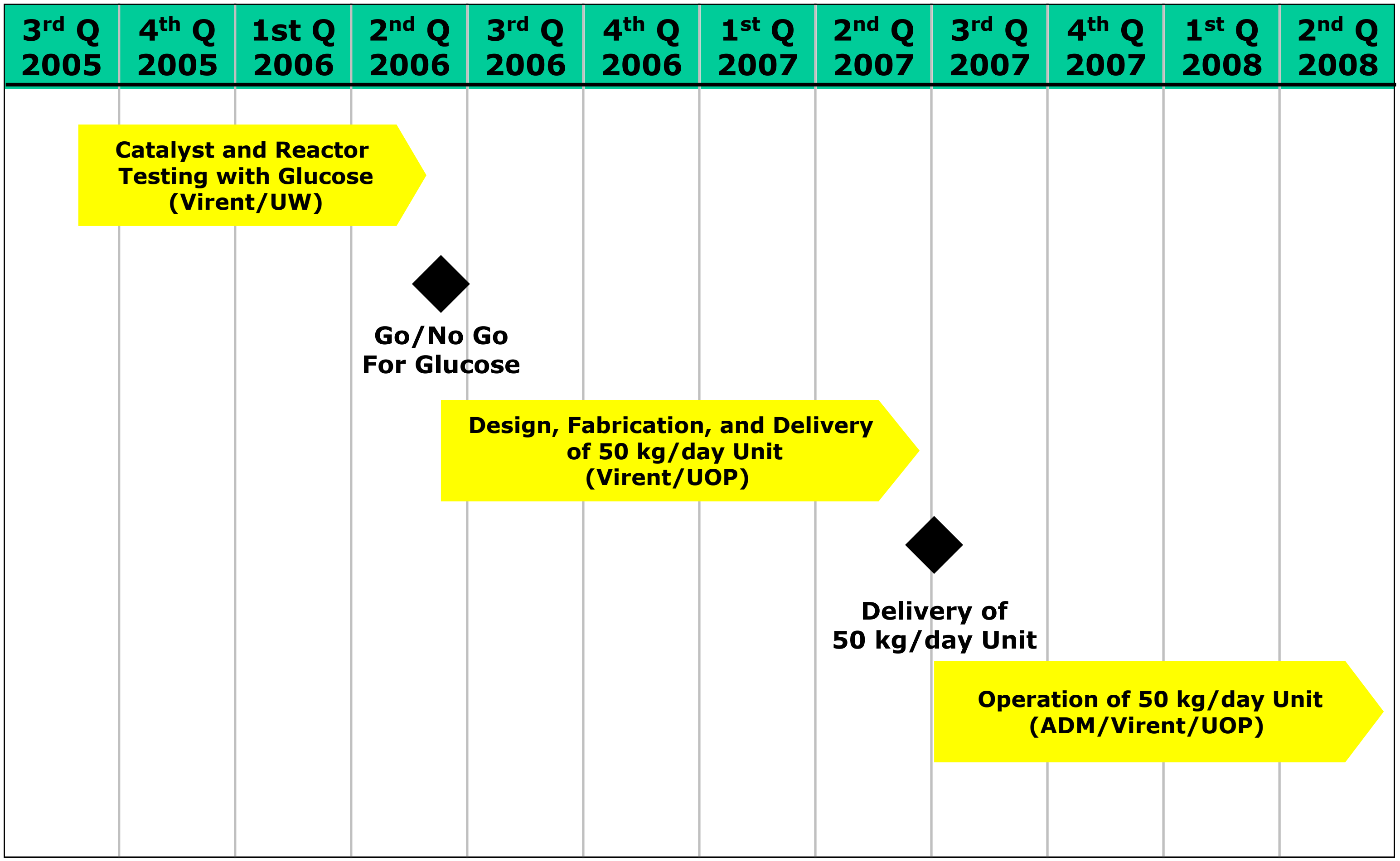
15 Year Depreciation

1 kg H2 is approximately 1 gge

# Future Work - First Year Timeline



# Future Work - Overall Project Timeline



# Facilities

- 6500 square feet facility in Madison, Wisconsin
- 14 Technical Personnel
- 9 test stands available
- Catalyst Preparation Equipment
- 3 GC, 1 TOC, 1 GCMS, and analytical backup from ADM
- Fully-equipped machine shop
  - Experienced machinist for prototype production

VIRENT ENERGY SYSTEMS

# Virent Laboratory Hydrogen Safety System

- Hydrogen Exhaust System
  - Two inch SS tube running North to South in lab.
    - Blower is rated at 17000 L/min.
  - All Test Stand Vent into this system.
- Lab Hydrogen Monitor
- Master Permit Relay
  - Permits test stands to operate **unless** Hydrogen Exhaust System or Lab Hydrogen Monitor **are in alarm state.**

# Supplemental Information

- Next Slides Contain Requested Supplemental Information

# Publications and Presentations

- None to Date

# Hydrogen Safety

The most significant hydrogen hazard associated with this project would be would be accumulation of a significant amount of hydrogen in the laboratory, for example near the ceiling. The impact to personnel, and/or destruction or loss of equipment or facilities could be devastating if that accumulation reached or exceeded the lower explosion limit (LEL) of 4% and subsequently did explode.

VIRENT ENERGY SYSTEMS

# Hydrogen Safety

- Our approach to deal with this hazard is:
  - Limited Hydrogen Inventory
  - Hydrogen Exhaust System
  - Laboratory Ventilation
  - Hydrogen Monitor
  - Safety Interlocks

VIRENT ENERGY SYSTEMS