Biomass-Derived Hydrogen from a Thermally Ballasted Gasifier

DOE Hydrogen Program Contractors' Review Meeting
May 18-21, 2003

Robert C. Brown
Center for Sustainable Environmental Technologies
Iowa State University

Objective

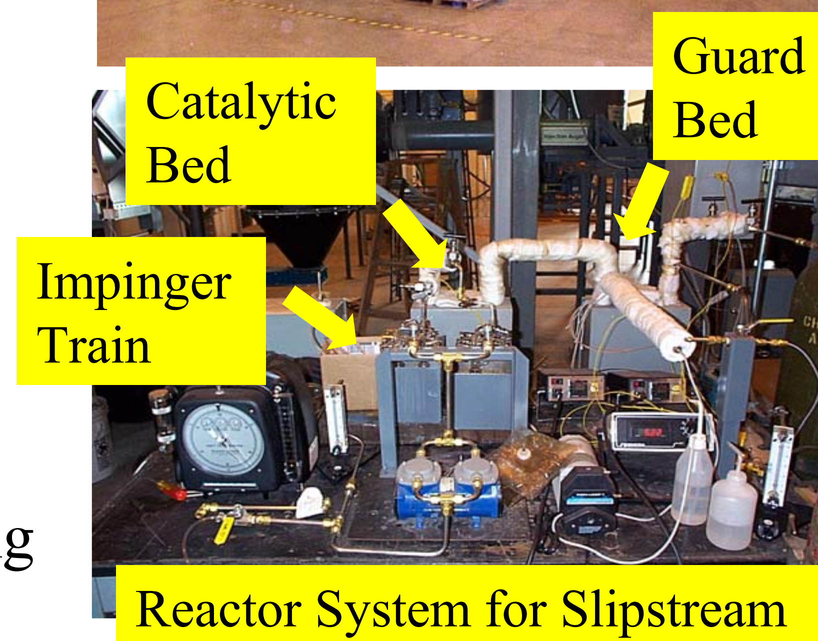
- Develop hydrogen production system based on thermal gasification of switchgrass

Relevance

- If successful, this project would provide a renewable source of hydrogen from biomass

Approach Outline

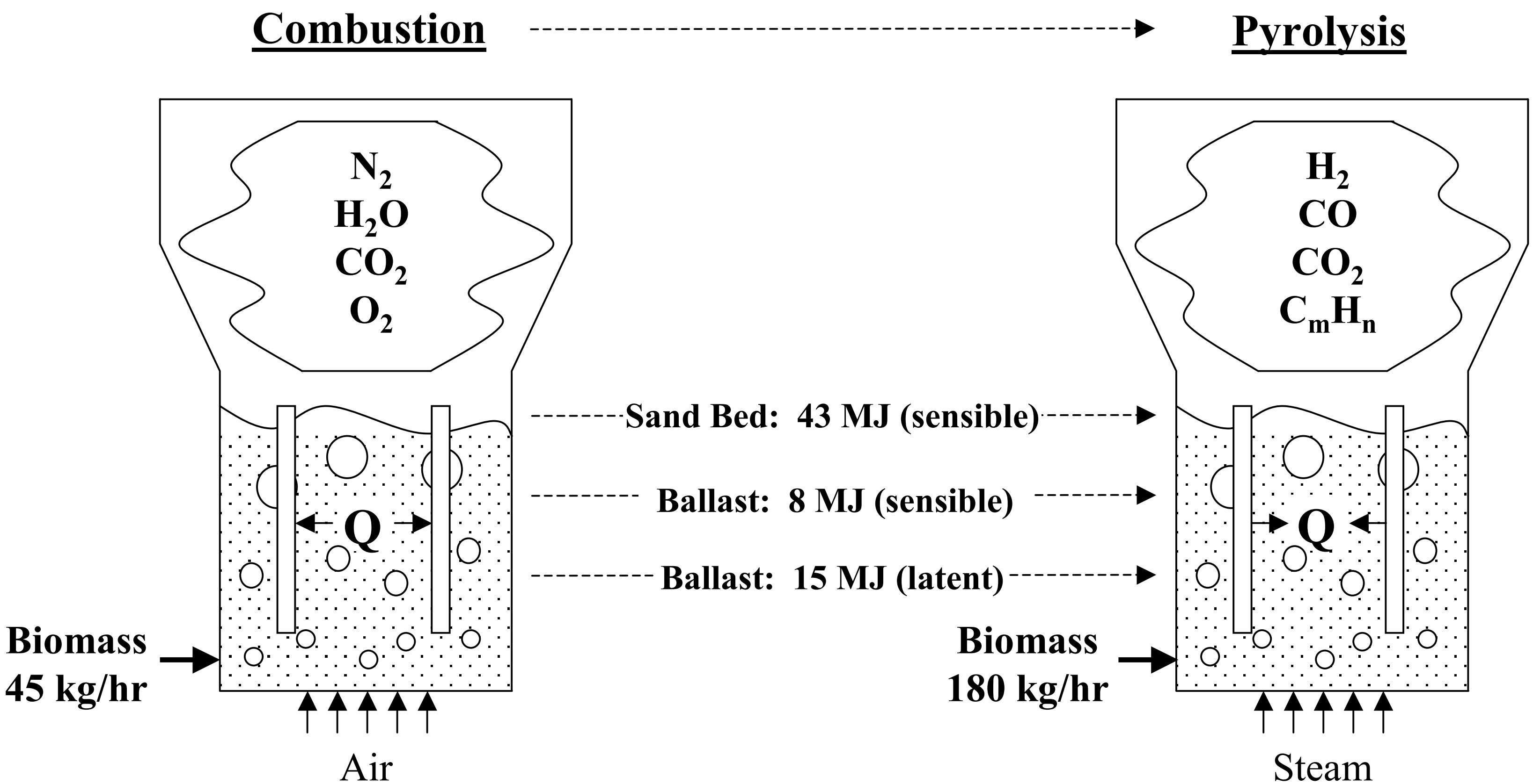
- Develop subsystems for the hydrogen production system:
  - Indirectly heated gasifier
  - Gas cleaning process
  - Gas conditioning system
  - Trace gas contaminant measurements
- Testing performed at two scales:
  - Pilot plants (5 tpd) for gasifier and gas cleaning system
  - Slip stream for gas conditioning system



Approach: Indirectly heated gasifier

- Conventional fluidized bed gasification
  - Combustion and pyrolysis occur simultaneously in a single reactor
    - Exothermic combustion provides heat
    - Endothermic pyrolysis produces light gases and hydrocarbons
  - Products of combustion dilute product gas
- Indirectly heated gasification
  - Combustion and pyrolysis processes are separated (usually spatially)
  - No nitrogen dilution of product gas
  - Energy must be transported to the pyrolysis reactions

Approach: Indirectly heated gasifier



Combustion and Pyrolysis are Temporally Separated in the Ballasted Gasifier System

Approach: Indirectly heated gasifier

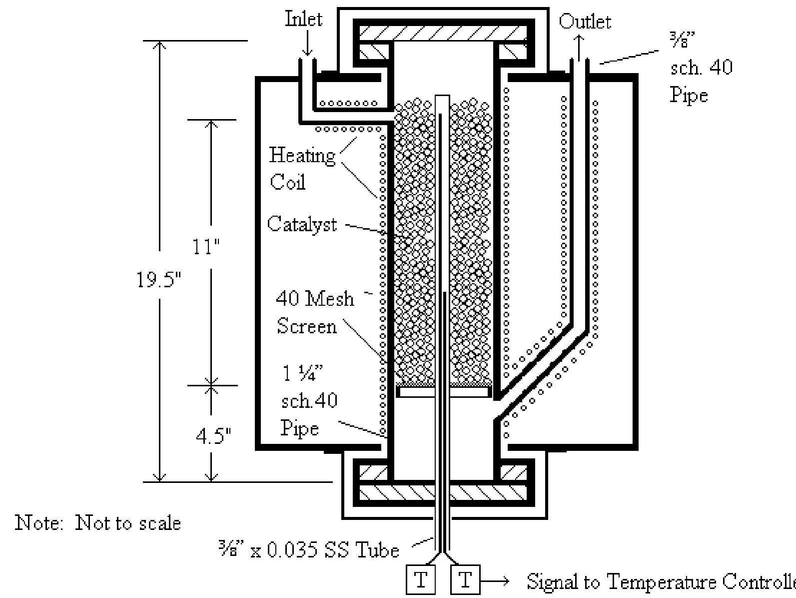
- Thermal ballast is high temperature phase-change material
  - Lithium fluoride sealed in stainless steel tubes which are immersed in fluidized bed
  - Thermal ballast consists of an array of 48 tubes
- Air fluidizes the bed during combustion
- Steam fluidizes the bed during pyrolysis
- Gasifier temperature varies between 922 K to 1172 K

Approach: Gas Conditioning

- Particulate removal
  - Required to prevent blinding of catalytic beds
  - Evaluating moving bed granular filter
- Trace contaminate removal using sorbent injection
  - H_2S and HCl removal to avoid poisoning of catalytic beds
  - Also removes some heavy tar
- Ammonia and tar removal
  - Steam reforming
- Water gas shift
  - Increases H_2 and removes CO

Approach: Gas Conditioning

- Guard bed for trace contaminant removal
  – Fixed bed of dolomite
- Steam reformer
  – Nickel catalysts
- High temperature water gas shift
  – Iron based catalyst
- Low temperature water-gas shift
  – Copper based catalyst

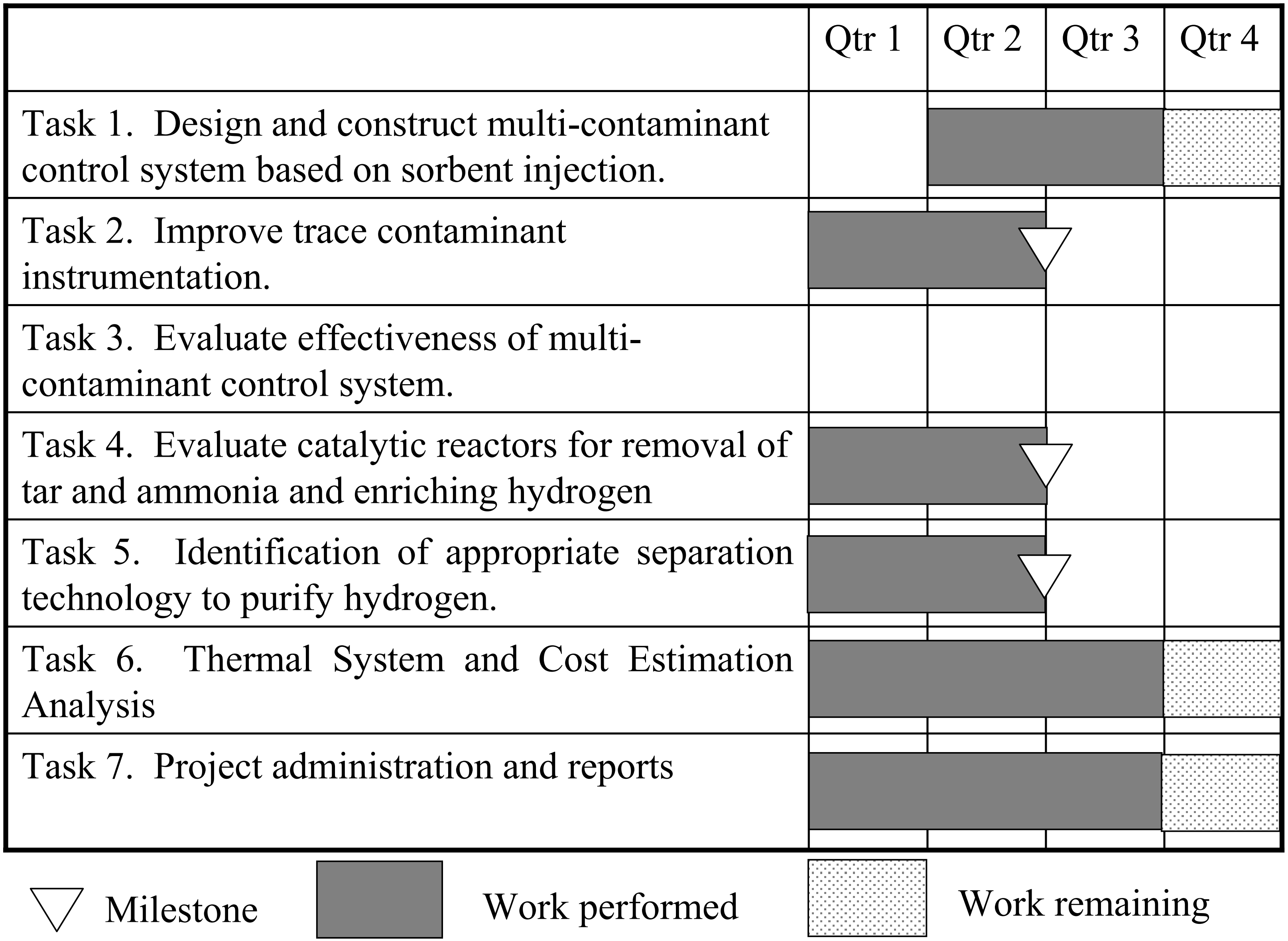


The four reactors are identical in construction

Approach: Gas Analysis

- Hot gas isokinetic sampling of *particulate matter*
- Impinger train using dichloromethane used for quantitative *tar* analysis
- Micro GC for periodic, *comprehensive gas* analysis
- Non-dispersive IR (CO, CO_2), thermal conductivity (H_2), and electrochemical (O_2) for *continuous gas* monitoring
- Quantitative methods developed for *trace contaminants*
  - NH_3 – collection in acid solution and analyzed at a commercial lab
  - H_2S – Draeger tubes and GC

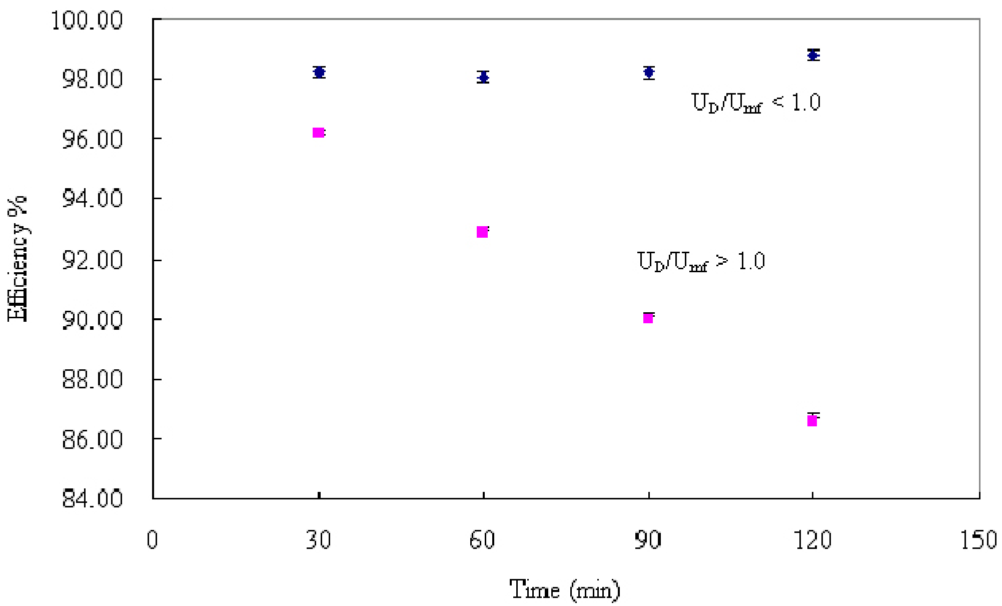
Project Timeline (FY 03)

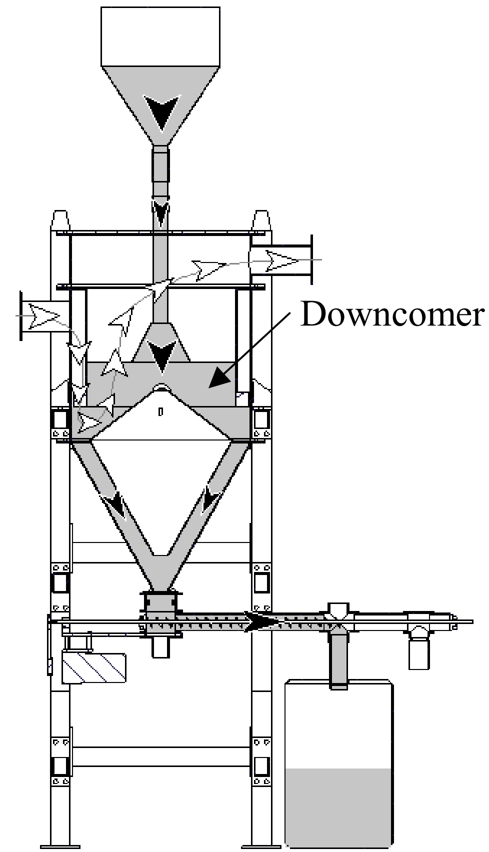


Accomplishments/Progress

Multi-contaminant Control

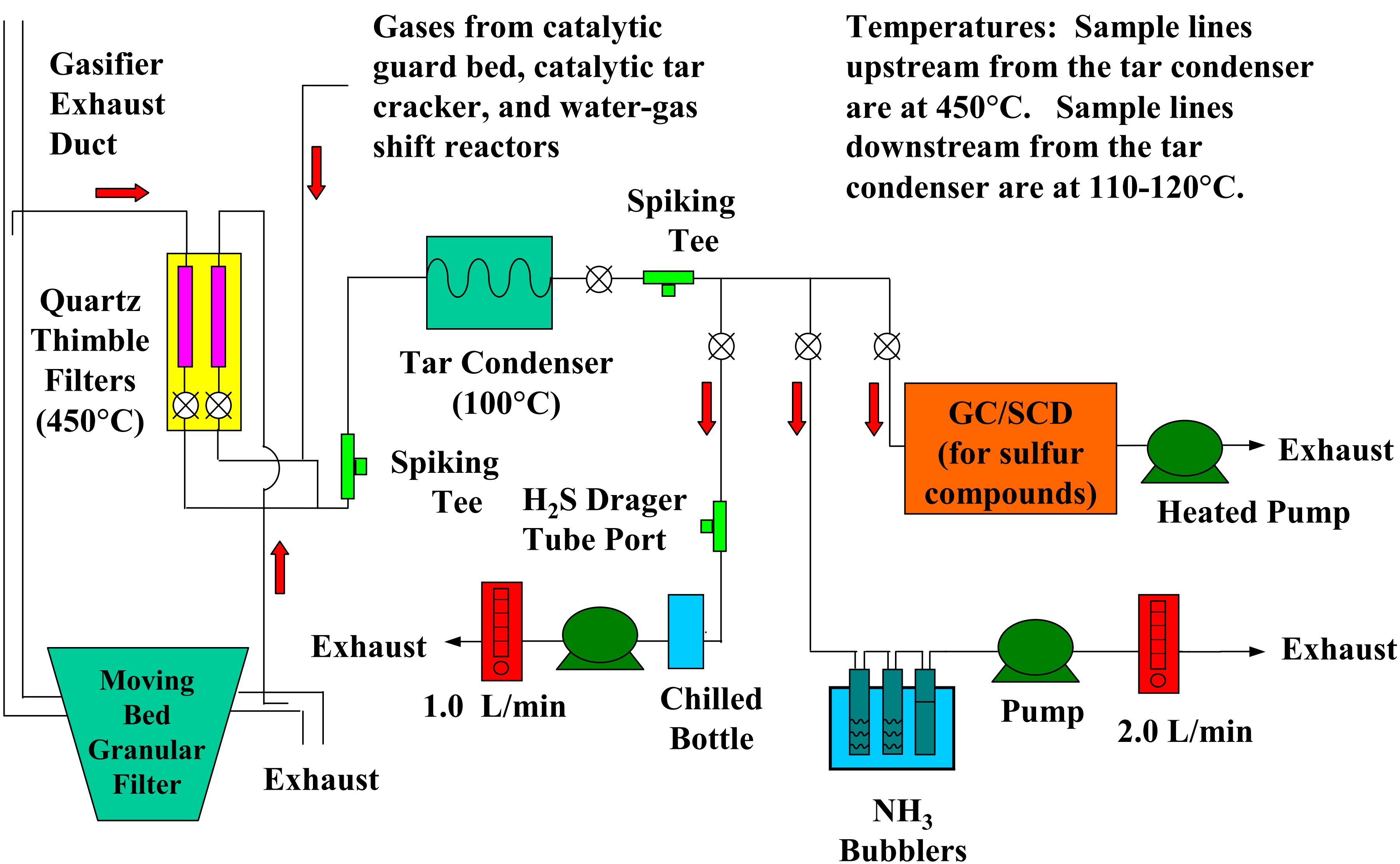
- Established ability of pilot-scale moving bed granular filter to remove fly ash
  - Efficiencies exceeding 90%
- Must keep velocity in downcomer (U_D) below the minimum fluidization velocity (U_{mf})of the granular media in the filter to keep efficiency high





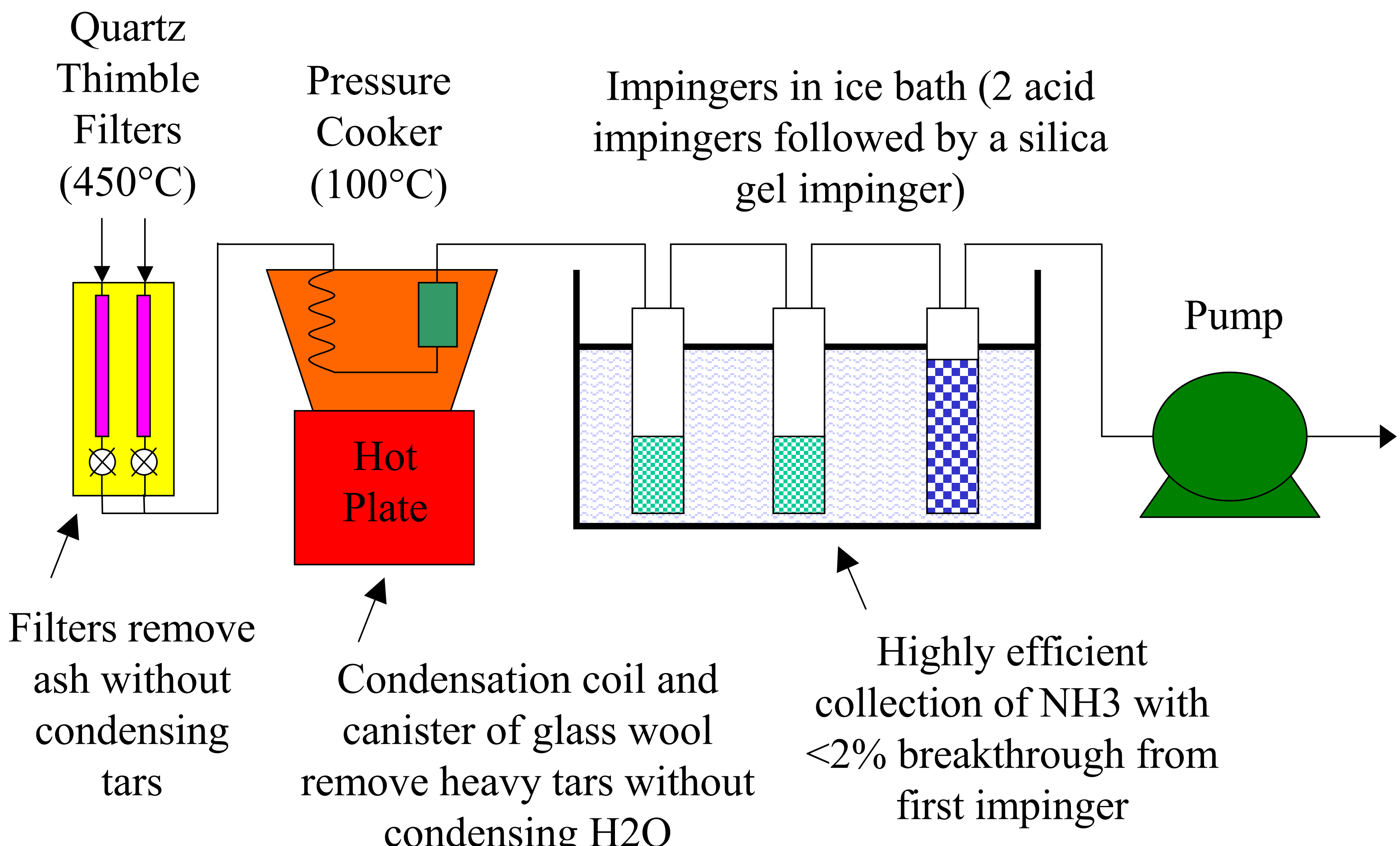
Accomplishments/Progress

Trace Contaminant Instrumentation



Accomplishments/Progress

Ammonia Sampling Procedure



Accomplishments/Progress

Gas Conditioning: Tar Cracking

Operating Conditions of Tar Cracking System

Parameter	ICI 46-1	Z409	RZ409
Calcined dolomite	120ml (132 g)	120ml (132 g)	120ml (132 g)
Ni-Based Catalyst	20 ml (22.3 g)	20 ml (23.2 g)	20 ml (23.1 g)
Inert material mixed with catalyst	20 ml (15.3 g)	20 ml (15.2 g)	20 ml (15.4 g)
Pretreatment of catalyst	No reduction	No reduction	Reduced by manufacturer
Guard bed temperature(T_{GB})	650°C	650°C	650°C
Steam reformer temperature (T_{CR})	740 - 820°C	740 - 820°C	740 - 820°C
Space Velocity (SV)	1500 – 6000 h^{-1}	1500 – 6000 h^{-1}	1500 – 6000 h^{-1}
Operating time	12 hrs	18 hrs	18 hrs

Accomplishments/Progress

Gas Conditioning: Tar Cracking

- Typical heavy tar levels in producer gas: 10 - 20 g/m^3
- All three metal catalysts proved effective
  - Greater than 99% destruction of heavy tar
  - Hydrogen increased by 6-11 vol-% (dry basis)
- Parametric effects:
  - Increasing space velocity had little effect
  - Increasing temperature boosted H2 and reduced light hydrocarbons
- Results consistent with tar destruction controlled by chemical kinetics
- Catalysts showed evidence of increasing pore size, which could lead to deactivation
- Evidence of coking and sulfur accumulation on metal catalysts

Accomplishments/Progress

Gas Conditioning: Steam Reforming & Water Gas Shift

Operating Conditions of Tar Cracking System

Items	GB	TR	HTS	LTS
Temp. of Central cat. Bed ºC	650	800	400	200
Temp. range of cat. Bed ºC	600-670	750-850	350-420	180-240
SV(h^{-1})		3000	1500	1200
Catalyst	Calcined dolomite	ICI 46-1	Fr-Cr based LB	Cu-Zn-Al based B202
Catalyst volume (ml)	200	60	120	150
Inert material (ml)	0/20	20/20	20/50	25/50
Gas Composition (%-vol)	Inlet gas	Outlet gas	Outlet gas	Outlet gas
H_2	8.5	19.44	23.7	27.1
CO	14.5	8.9	1.37	0.18
CO_2	18.1	20.1	26.8	27.2
CH_4	4.3	3.5	3.4	3.1
C_2H_4	1.5	0.27	0.31	0.13
Tar content (g/Nm^3)	19.5	-	-	-

*Volume of inert material above and below catalyst layer respectively

Accomplishments/Progress

Gas Conditioning: Steam Reforming & Water Gas Shift

Air-blown gasification of switchgrass (ballast system not operated)

Gas constituent	Raw gas	Steam reformer*	High temperature shift reactor*	Low temperature shift reactor*
H_2 (vol-%)	8.5	19.4	23.7	27.1
CO (vol-%)	14.5	8.9	1.4	0.18
CO_2 (vol-%)	18.1	20.1	26.8	27.2
CH_4 (vol-%)	4.3	3.5	3.4	3.1

*Concentration exiting the reactor

Accomplishments/Progress

Trace Gas Sampling

H_2S Measured from Gasification of Waste Seed Corn

- H_2S levels (Drager tubes) were consistently 190-220 ppm over a 5-hr period
- H_2S concentrations were 50-70% lower than what would be expected if ALL the sulfur remained in the gas phase
- Limestone added to the fluidized bed reactor to suppress agglomeration is the likely reason for sulfur retention

Accomplishments/Progress

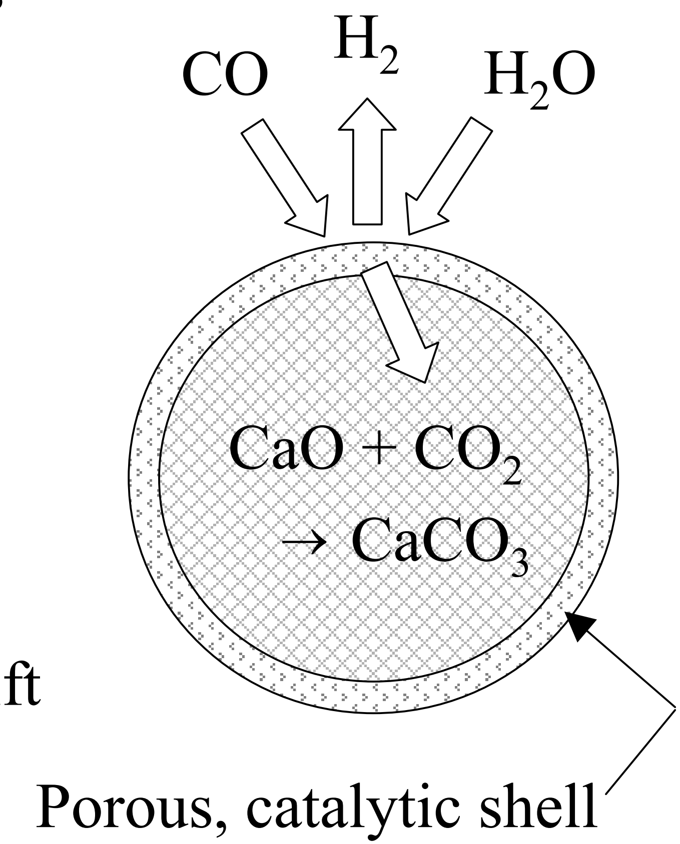
Trace Gas Sampling

<u>NH_3 Measured from Gasification of Waste Seed Corn</u>

- NH_3 levels were about 5000 ppm; results from duplicate sample runs were within 3% of one another
- Injection of NH_3 into producer gas yielded gas stream measurements within 5% of expected values

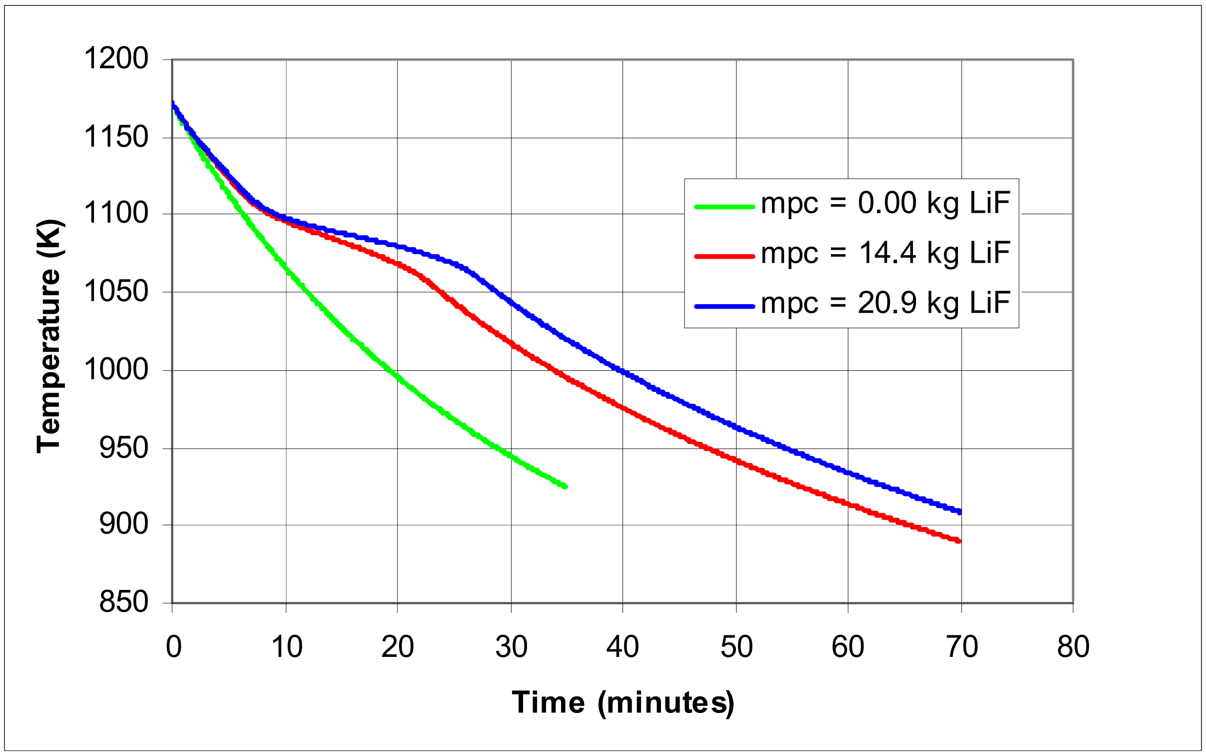
Accomplishments/Progress
Separation Technology

- Identification of a combined water-gas shift/CO_2 removal system
- Builds upon engineered materials developed at ISU
  - Core-in-shell concept developed for gas sorption
  - Nickel catalyst in shell to promote steam reforming of methane
- This new task will explore copper and iron catalysts in shell for water-gas shift reactions



Accomplishments/Progress

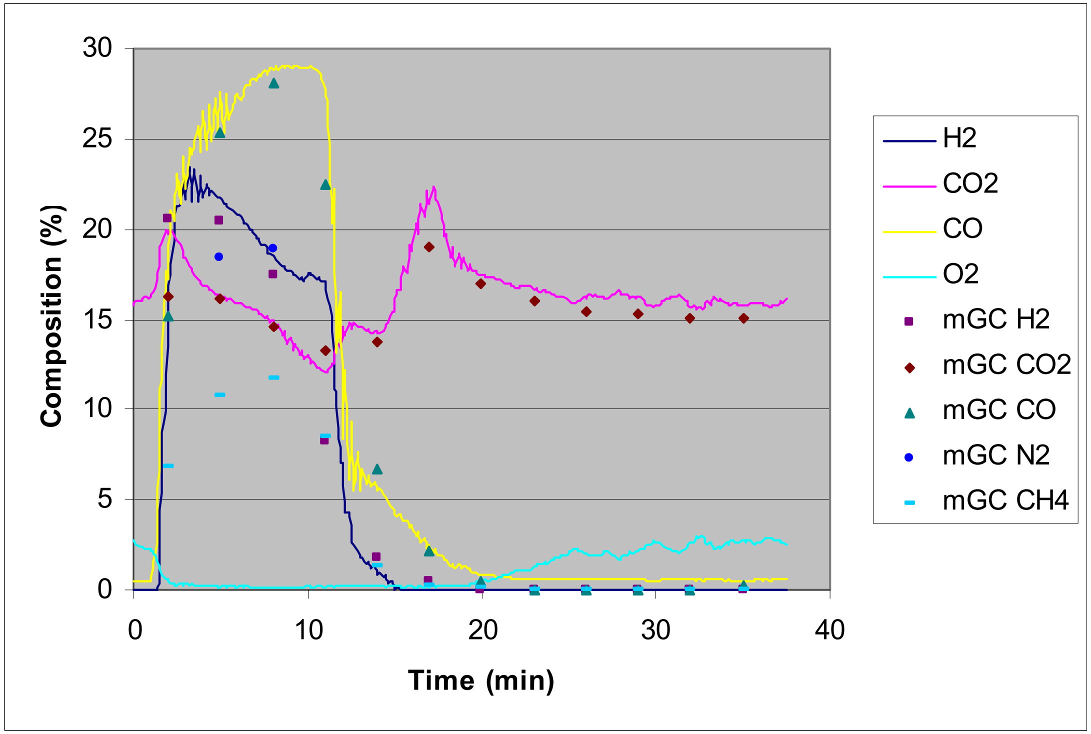
Thermal System Analysis



- Computer simulation of ballasted reactor during cooling with steam
- Phase change material plays significant role in increasing time to cool the reactor

Accomplishments/Progress

Thermal System Analysis



- Experimental data for pyrolysis phase of cycle
  - H_2 and CO_2 decrease, CO increases
  - Micro-GC data consistent with the CEM data

Interactions & Collaborations

- Energy Products of Idaho
  - Licensing technology on moving bed granular filter for control of particulate matter
- Community Power Corporation
  - Investigating use of moving bed granular filter for multi-contaminant control
- University of Victoria, University of British Columbia & National Renewable Energy Center
  - Coauthored paper on hydrogen from biomass (under review by the Int. J. Hydrogen Energy)
- Zhengzhou University, China
  - Visiting scientist working on gas conditioning catalysts

Future Plans

- Testing of multi-contaminant control system (limestone injection upstream of moving bed granular filter)
- Evaluating combined water-gas shift/CO_2 sorption concept
- Operate ballast system with gas conditioning system

Responses to FY 02 Panelist

Reviewer Comment	Investigator's Response
Gasification of switchgrass is not economical…	The ultimate advantage of hydrogen energy is replacement of polluting fossil fuels. Thus, biomass is the ultimate fuel even if not cost-effective by current economic measures.
Project is heavy on analytical methods and light on technical results…	The first year of the project was devoted to building equipment and establishing analytical methods. Significant data was collected on all phases of the project during the second year.

Acknowledgements

- Collaborators in this study include Jerod Smeenk, Andy Suby, Glenn Norton, Ruiqin Zhang, Ming Xu, Nate Brown, and Colin Brue
- This work was performed at the Iowa Energy Center's BECON facility
- This work was funded by the U.S. Department of Energy's Hydrogen Energy Program with cost-sharing from the Iowa Energy Center and Iowa State University