

# Hydrogen from Biomass Catalytic Reforming of Pyrolysis Vapors

2004 DOE Hydrogen, Fuel Cells &  
Infrastructure Technologies Program Review

R. Evans, L. Boyd, C. Elam, S. Czernik,  
R. French, C. Feik, S. Phillips, E. Chornet

National Renewable Energy Laboratory

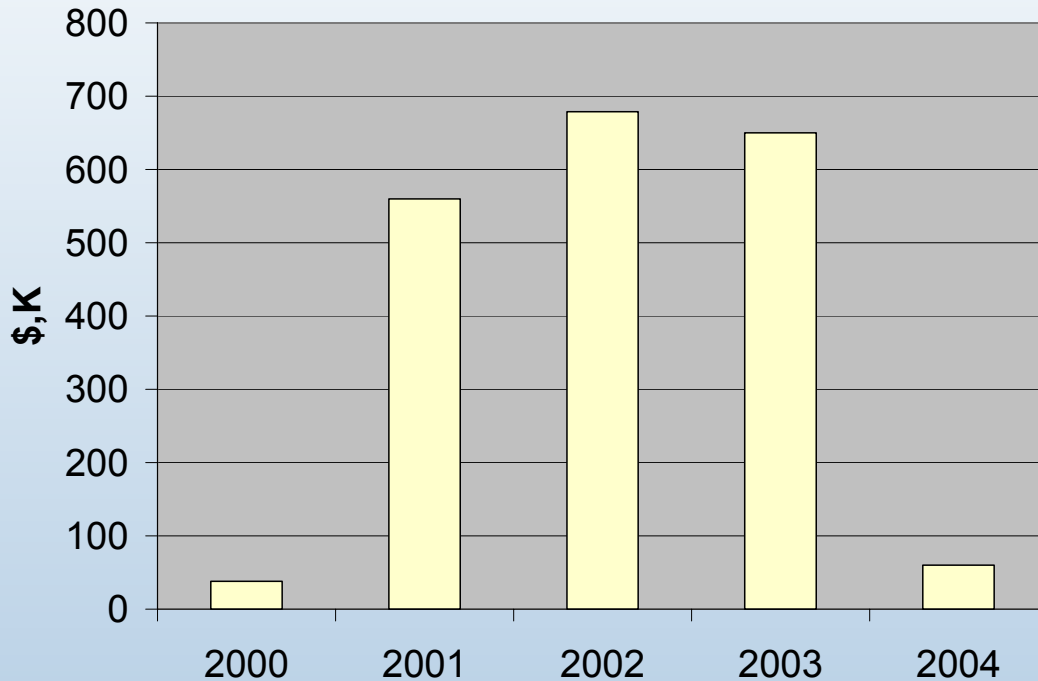
May 24-29, 2004

*This presentation does not contain any proprietary or confidential information.*

# Objectives

- Develop the engineering basis for scale up of the catalytic fluid bed reforming of biomass pyrolysis vapors and liquids
  - Conceptual design of the next scale:
    - 250 kg H<sub>2</sub>/day
  - Evaluation of Circulating Fluid Bed Systems
- Assist the Clark Atlanta team:
  - Recommend system improvements for the 1000 hour test
  - Continued development of co-product integration
  - Definition of deployment scenarios

# Budget History



**FY04 funding originally approved at \$725K but funded at \$60K**

# Technical Barriers and Targets Hydrogen Production

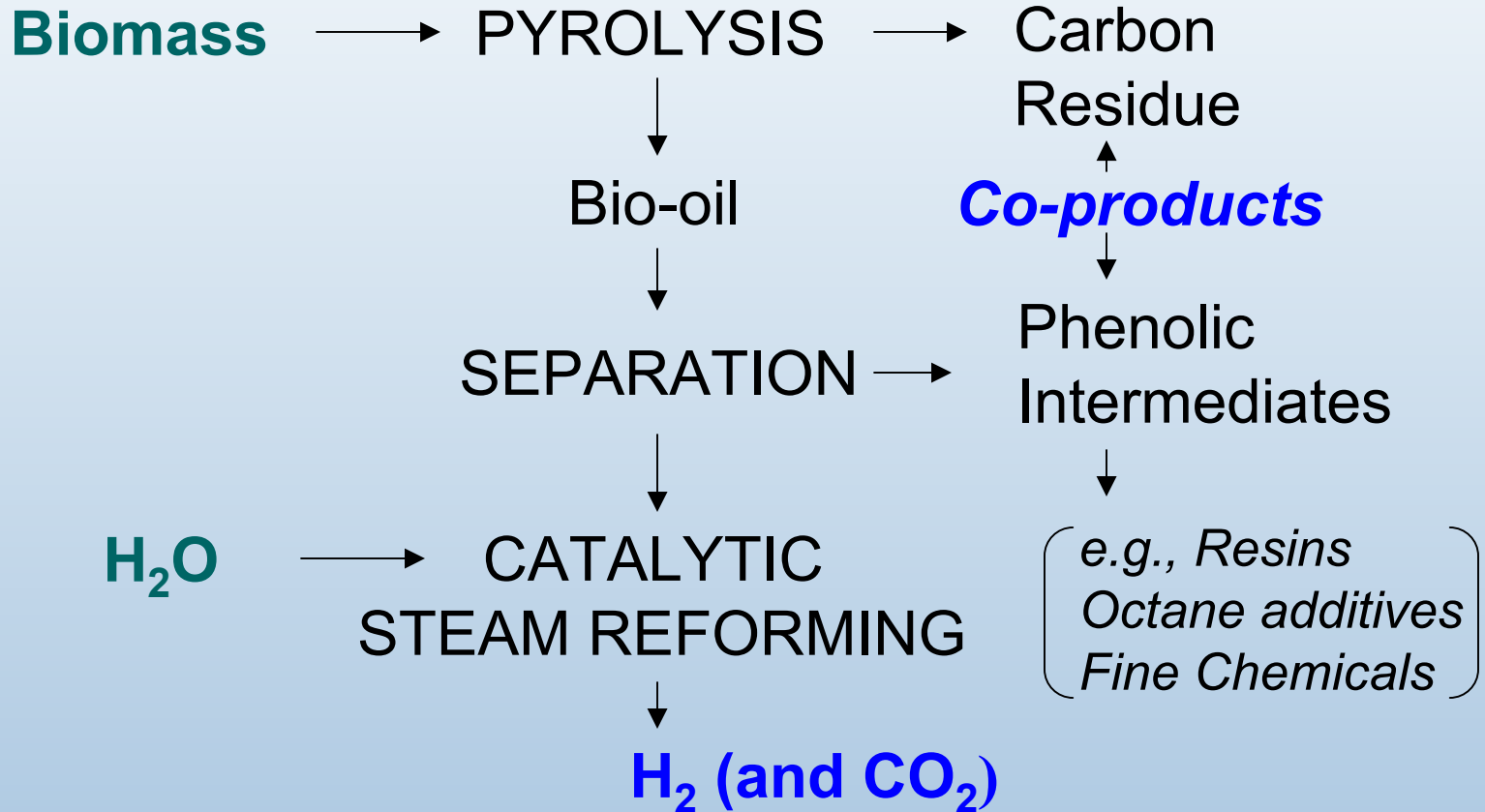
Barrier G: *Efficiency of Gasification, Pyrolysis and Reforming Technology:*

- Heat Integration
- Vapor Conditioning
- Catalyst Development and Regeneration
- Reactor Configuration
- Deployment: H<sub>2</sub> + Co-products

Target for Biomass Pyrolysis + Reforming:

- Demonstrate the production of hydrogen from biomass by pyrolysis –steam reforming for \$2.90/kg by 2010

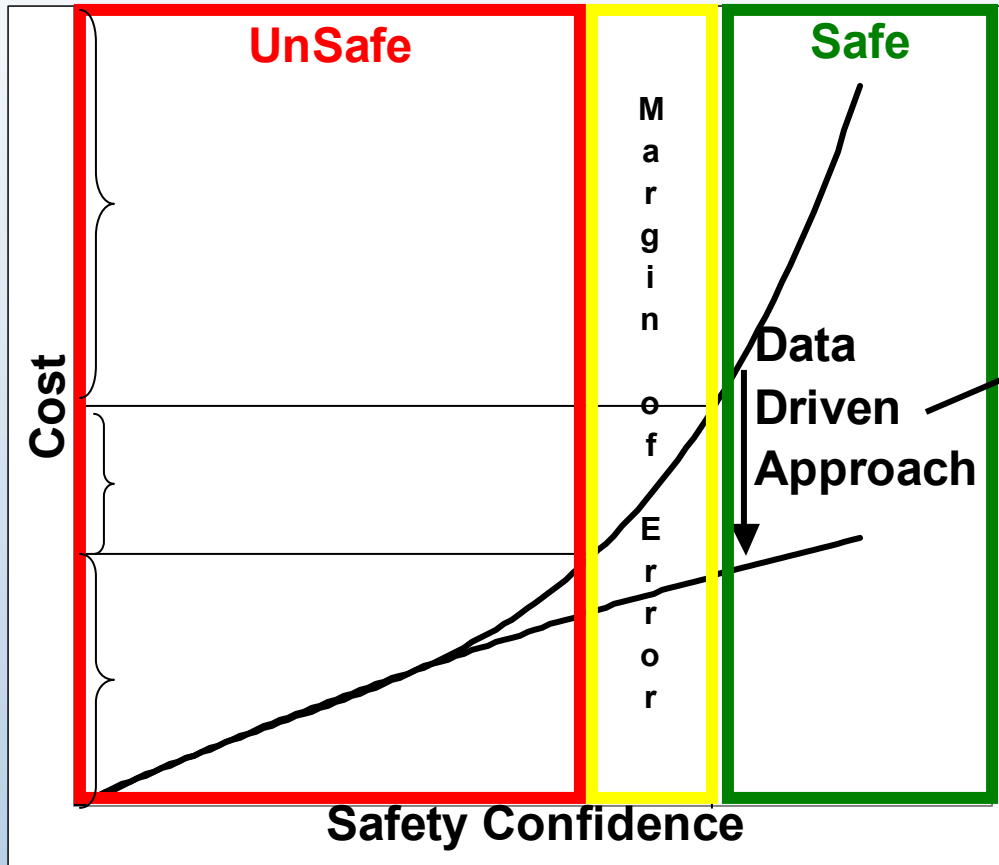
# Approach



# Safety

- NREL's Thermochemical Users Facility as a Biomass Hydrogen Resource
  - Process Control Development
  - Training
  - Initial Biomass to H<sub>2</sub> Performance Data
- Work with Scale-up Partners
  - Clark Atlanta Team
  - Establish Hydrogen Engineering at the University of Georgia Biomass Facility
    - Develop Hydrogen engineering safety education capability
  - Participated in Multiple Production Solicitations
    - Safety Role

# Safety Approach



U of GA Facility:

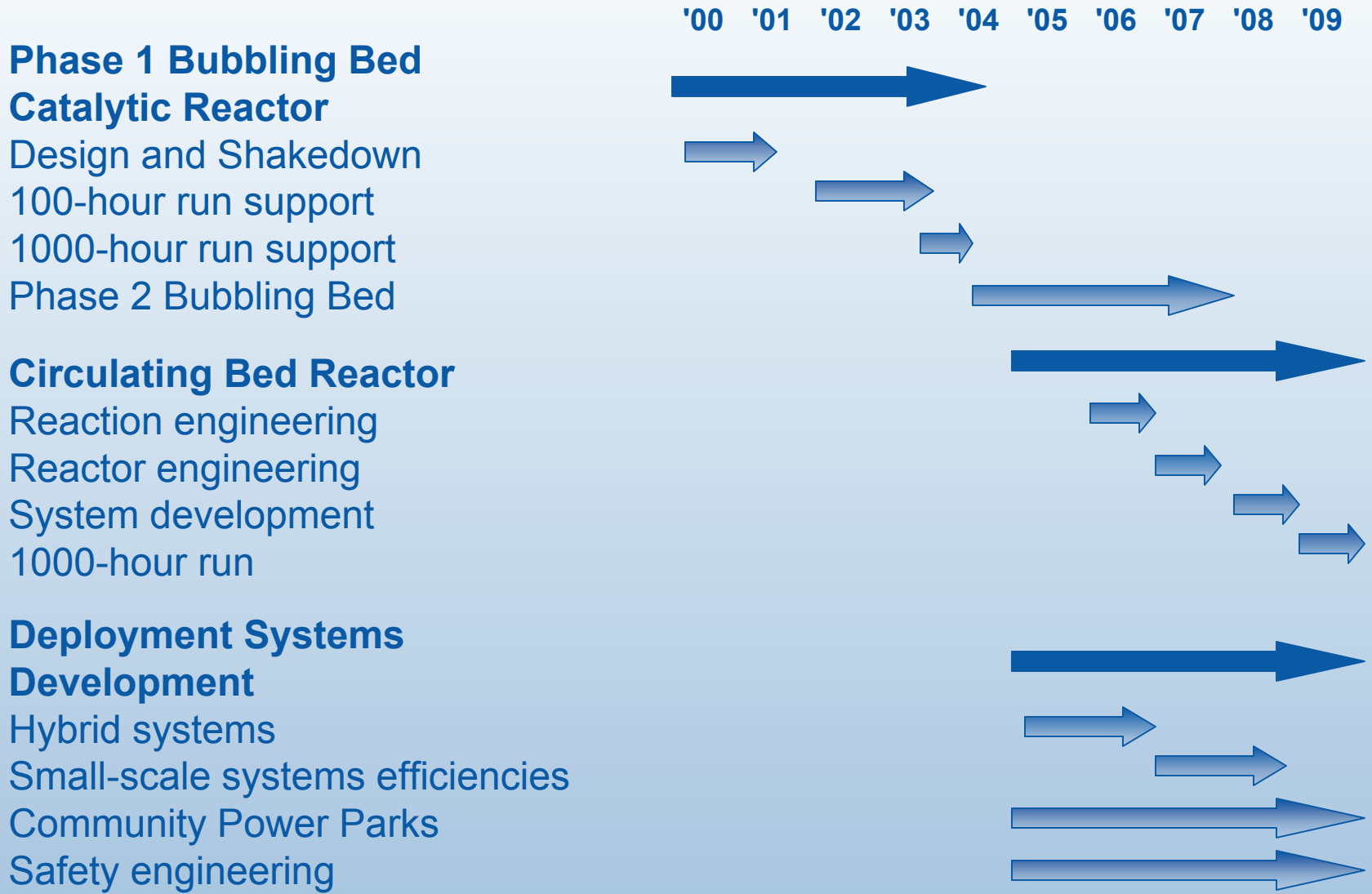
- Train the Trainers
- Process control for safety **AND** efficiency (lower cost)



Must Develop:

- A Facility to study system safety boundaries
- A Statistical Basis for Safety Confidence

# Project Time Line

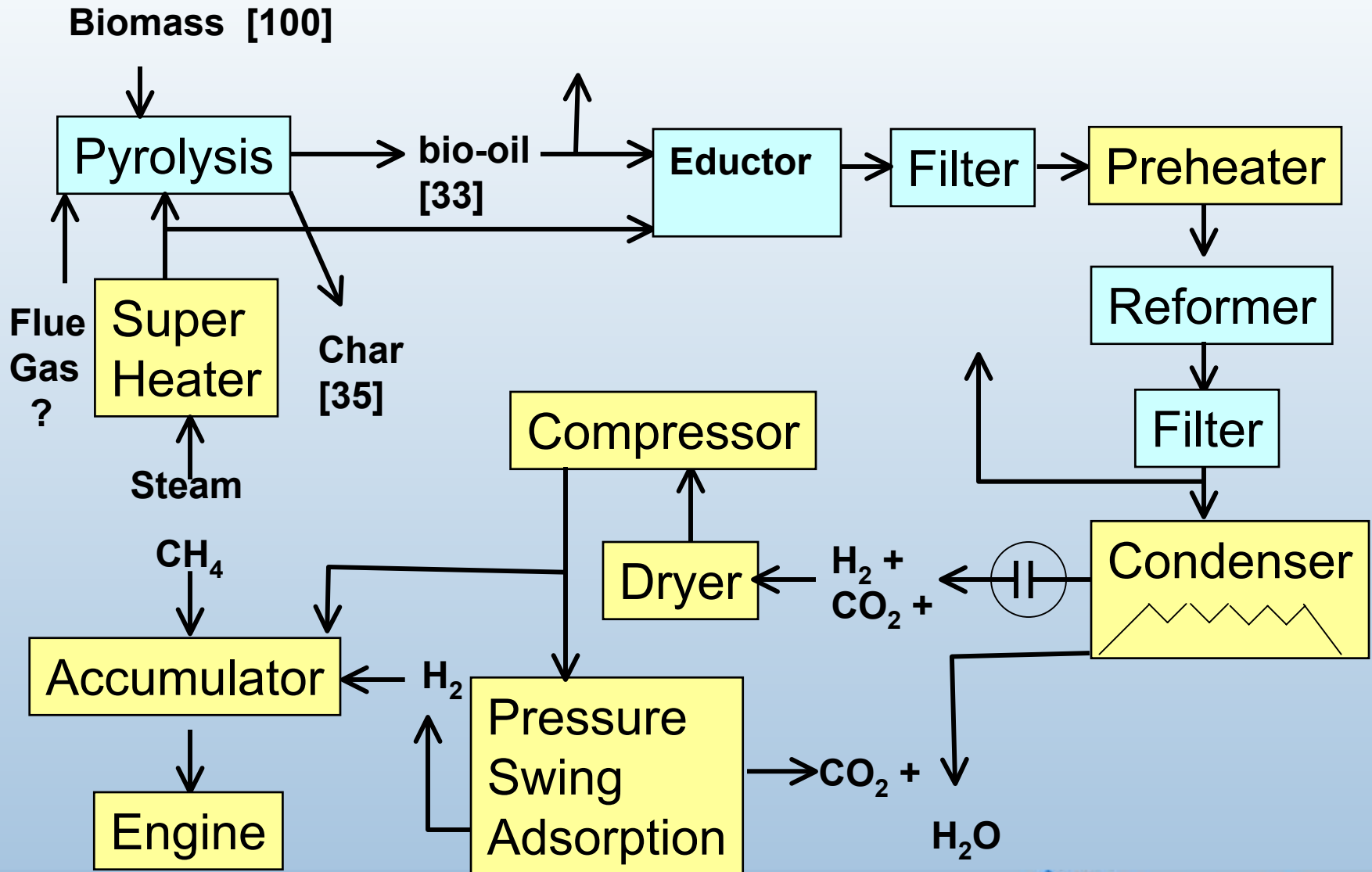




# Technical Accomplishments

- Scale up Conceptual Design Completed
- Design Challenges Addressed:
  - Reformer Preheater
  - Heat Recovery and Integration
  - Compression
  - Conditioning
  - Co-Product Optimization
  - Pyrolyzer Heat Optimization

# Integrated Pyrolysis/ Reformer System



O2 Sources	Air [%vol.]	VSA [%vol.]	Cryo.Liq. [%vol.]
O2:	20.95%	94.0%	100%
N2:	78.12%	1.83%	0%
Ar:	0.93%	4.17%	0%
fraction of O2 demand [%]:			
	100%	0%	0%

Super Heated STEAM	{by diff.}
Steam Load [%Pyro]:	0%
Steam Tin [°C]:	1000
Steam Tout [°C]:	500
Usable ?H [BTU/lbs]:	400
Required mass [kg/hr]:	0.0

*(uses HX efficiency stated for Burner)*

NG SOURCE

BM Feeder	Measured Elemental Composition [%w] dry basis
BM feed rate [kg/hr]:	350.0
moisture [%w]:	12.0%
PyroEnergy [kJ/kg]:	-1500.0
	Carbon: 45.97%
	Hydrogen: 6.33%
	Nitrogen: 2.03%
	Sulfur: 0.17%
	Chlorine: 0.17%
	Phosphorus: 0.0013%
	Ash: 3.00%
	total measured: 57.67%
	Oxygen (by diff.): 42.33%

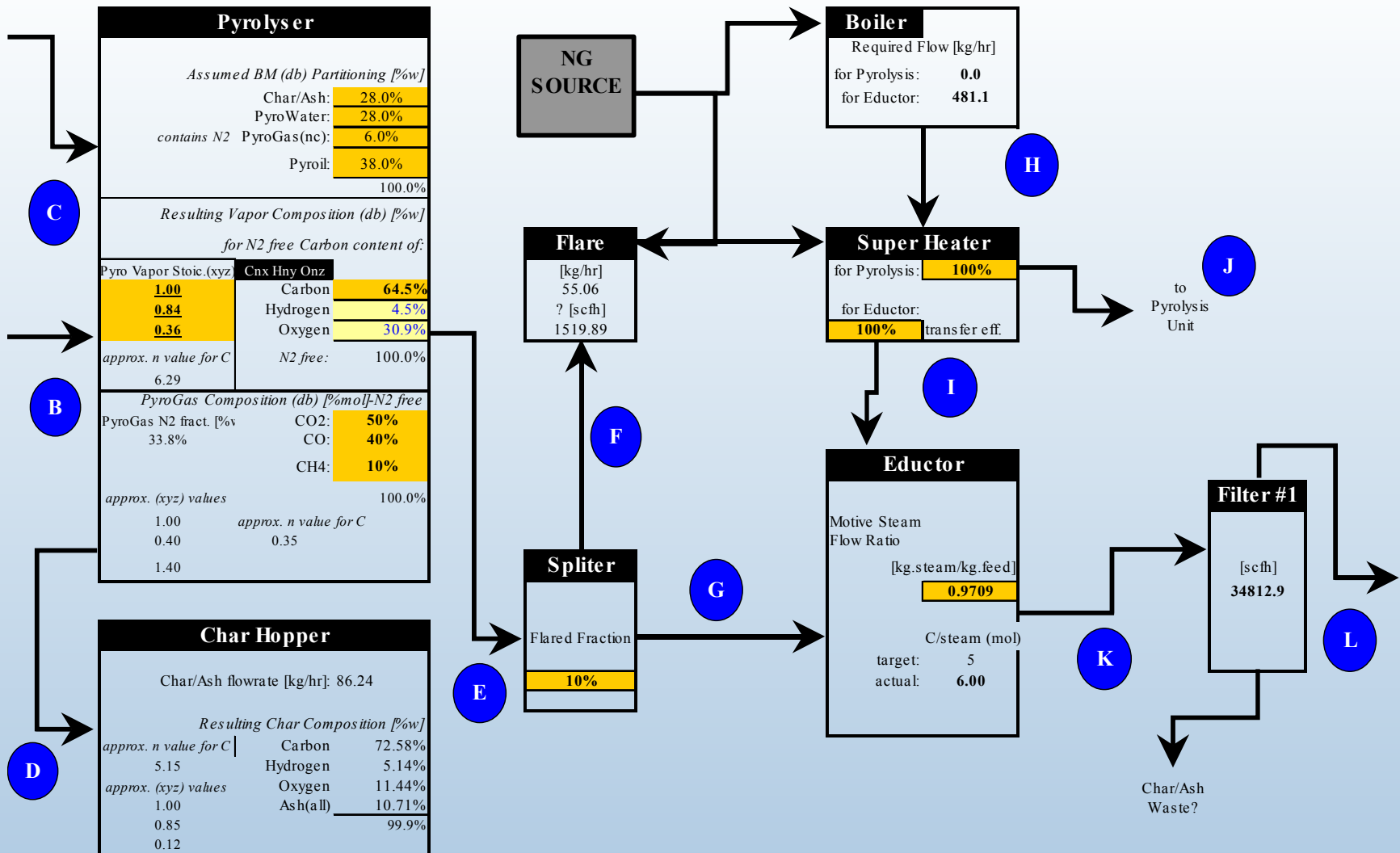
Burner		
Pyro load [kJ/hr]:	-525000	
[kW]:	-145.8	
[BTU/hr]:	-497711	
Burner Load [%Pyro]:	100%	"PyroEnergy" Equiv.
HeatExchange Efficiency:	57%	-2632 [kJ/kg]
	(stoic.=2.0)	
Burn Ratio Setting [O2/NG]:	2.0	
corrected combustion load [kW]:	-255.8	-873177 [BTU/hr]
minimum NG to burn [scfh]:	776.2	15.73 [kg/hr]
imposed NG feed [scfh]:	776.2	15.73 [kg/hr]
imposed O2 required [scfh]:	1552.3	62.76 [kg/hr]

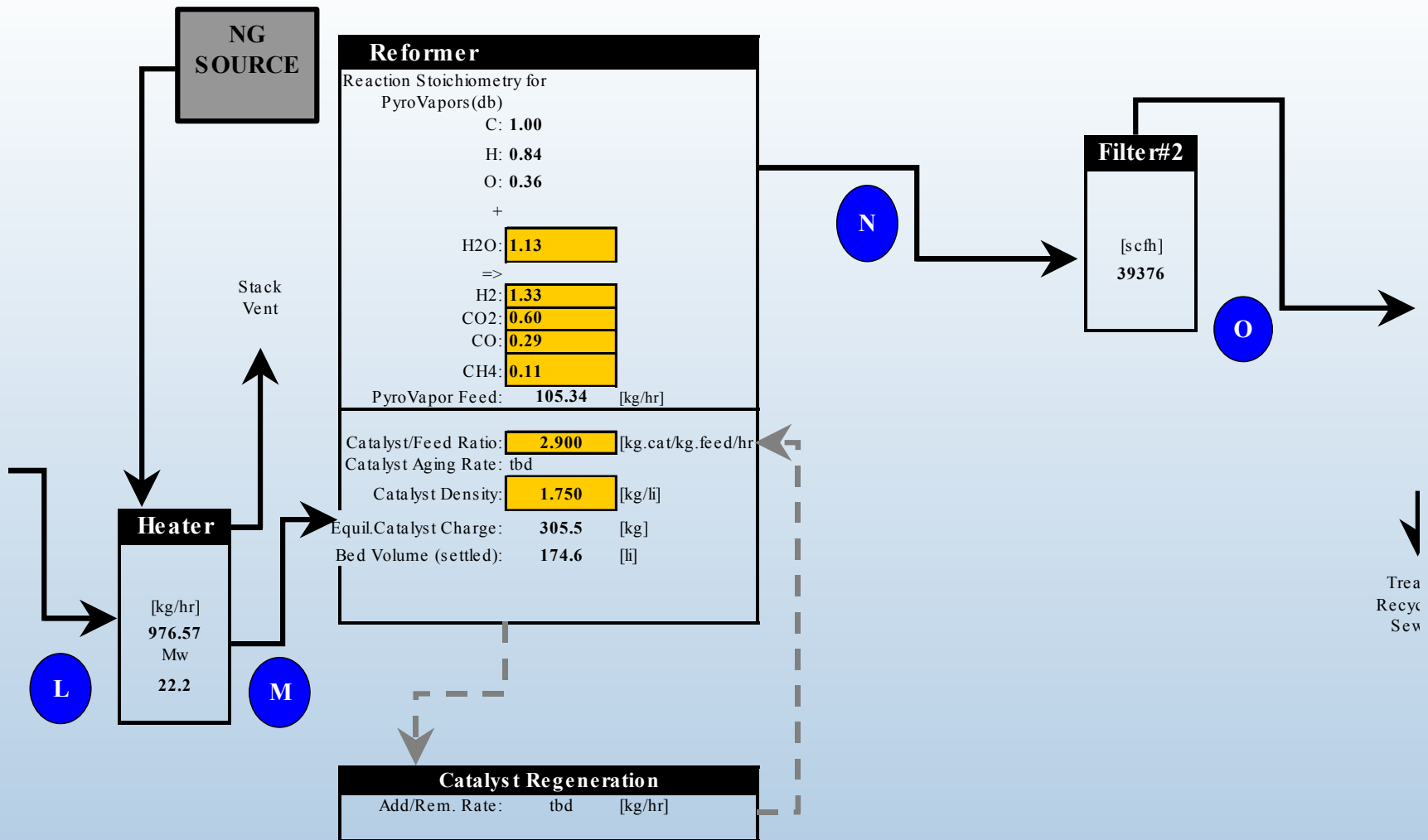
A

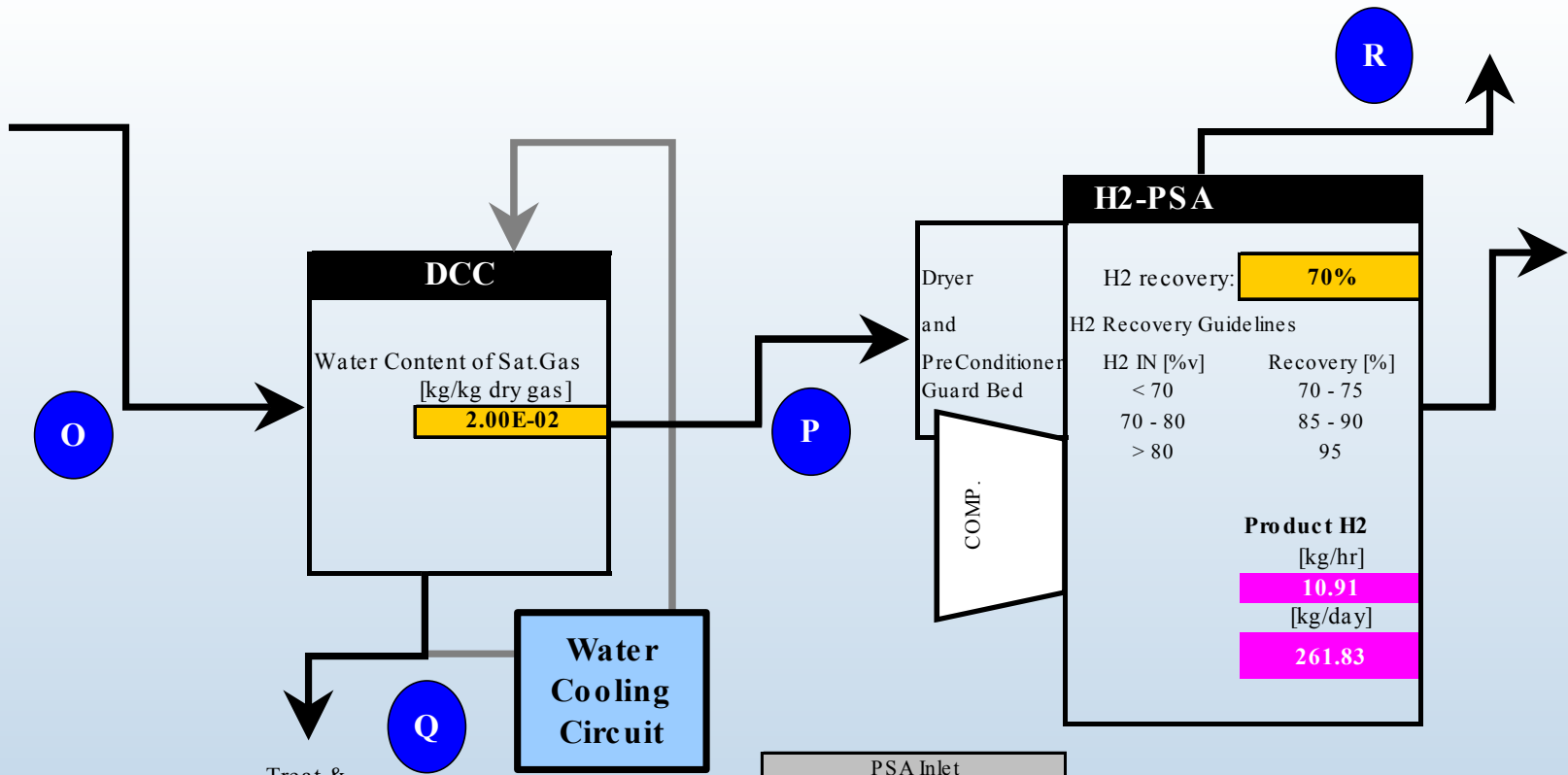
C

B

D







Treat &  
Recycle &  
Sewer

PSA Inlet	
	mol.fraction
CH4	0.029
H2	<b>0.352</b>
O2	0.000
N2	0.309
Ar	0.004
CO	0.077
CO2	0.206
H2O	0.024

0.104

# Reformer Design

Main contributor to reformer size is the flow rate of gases used to heat the pyrolysis reactor. **Five scenarios used to calculate reformer size:**

Heat Source	Oxidizer	Eductor	Reformer inlet Flow (kg/hr)	H2O/C	Bed Diameter (inches)
Steam	No	Yes	2224	20	62
Steam	No	No	1129	10	44
NG	Air	Yes	977	6	38
NG	O2	Yes	615	4.2	30
Both	O2	No	680	5	32

# System Heat Management

- Preheater
  - Can only provide a fraction of FBR Heat
- Reformer
  - Use Internal Heat Tubes at this Scale
- Exit Gas Heat Exchanger
  - Cascading uses: preheater, superheat steam, generate saturated steam, and preheat combustion gas
- PSA Off Gas Utilization
  - Fuel in FBR Internal Heat Tubes
  - Pyrolysis Heating
- O<sub>2</sub> vs. Air in Pyrolyzer, Preheater and FBR
  - Impact on Reactor Size



# Catalyst Management Plan

- Low Deactivation Rate  $\sim 1\%/hour$ 
  - Allows simplified regeneration loop
- Perform batch wise
  - Periodic or Incremental Removal and Additions
  - Same vessel for Oxidation, Reduction, & Feeding
- Integrate with new catalyst addition
  - Equilibrium Catalyst: 90% of full activity

# Interactions and Collaborations

- Georgia Team:
  - Clark Atlanta University
    - Technical Assistance in Catalytic Reforming
  - Eprida/Scientific Carbons Inc.
    - Development of pyrolysis co-product options
  - University of Georgia
    - Safety and Demonstration Plans
  - Georgia Institute of Technology
    - Provide Technical Information for Engineering Assessment
  - Enviro-Tech Enterprises Inc
    - Defining deployment opportunities in Fresno CA, Detroit MI, and North Carolina

# Response to Reviewers Comments

- ***Reviewer does not believe technical feasibility of integrated process has been demonstrated.***
  - The next scale of operation is necessary to address issues related to thermal efficiencies and operational logistics such as catalyst regeneration
- ***Not responsive to 2005 goals.***
  - Only change in target from 2003 status in 2005 is a reforming cost reduction of \$.10, which can be demonstrated by reduction in catalyst attrition rate during the 1000 hour run
- ***“Is thermal instability of pyrolysis oil a potentially fatal flaw?”***
  - The approach to providing reformer heat is critical. The 200 hr bench scale tests have been encouraging using the aqueous fraction. Pipes and distribution plate will be less susceptible to plugging in larger systems.

# Future Work

- Hybrid Systems Development
  - Distributed Community Resource + NG
    - Opportunities for heat integration
  - Safety Engineering
    - Control systems
- Circulating Bed Reactor Development
  - Coordination of Catalysis and Process Research
  - Reaction Engineering
  - Reactor Engineering
- Solicitation Partnerships
  - Scale up System Development

# Circulating Fluid Bed

- Smaller Catalyst Particles → Harder
- Fluid Dynamics → Higher Gas Flows
- Direct Heating → Partial Oxidation
- Optimized Catalytic Coke Gasification

