Hydrogen from Biomass
Catalytic Reforming of Pyrolysis Vapors

2004 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

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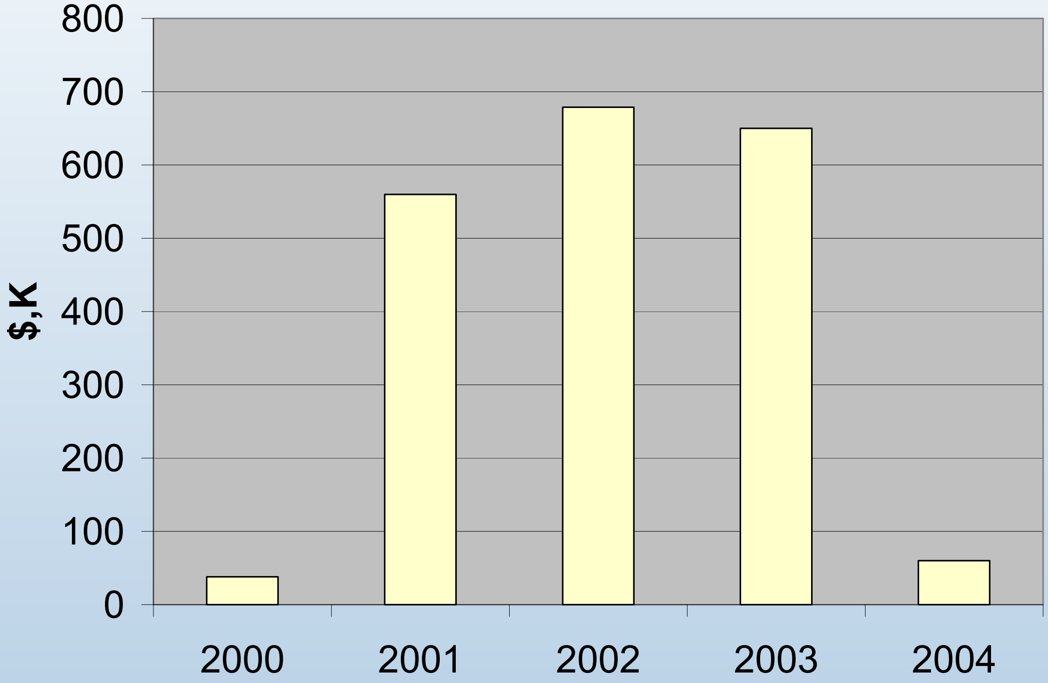
This presentation does not contain any proprietary or confidential information.

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 H2/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

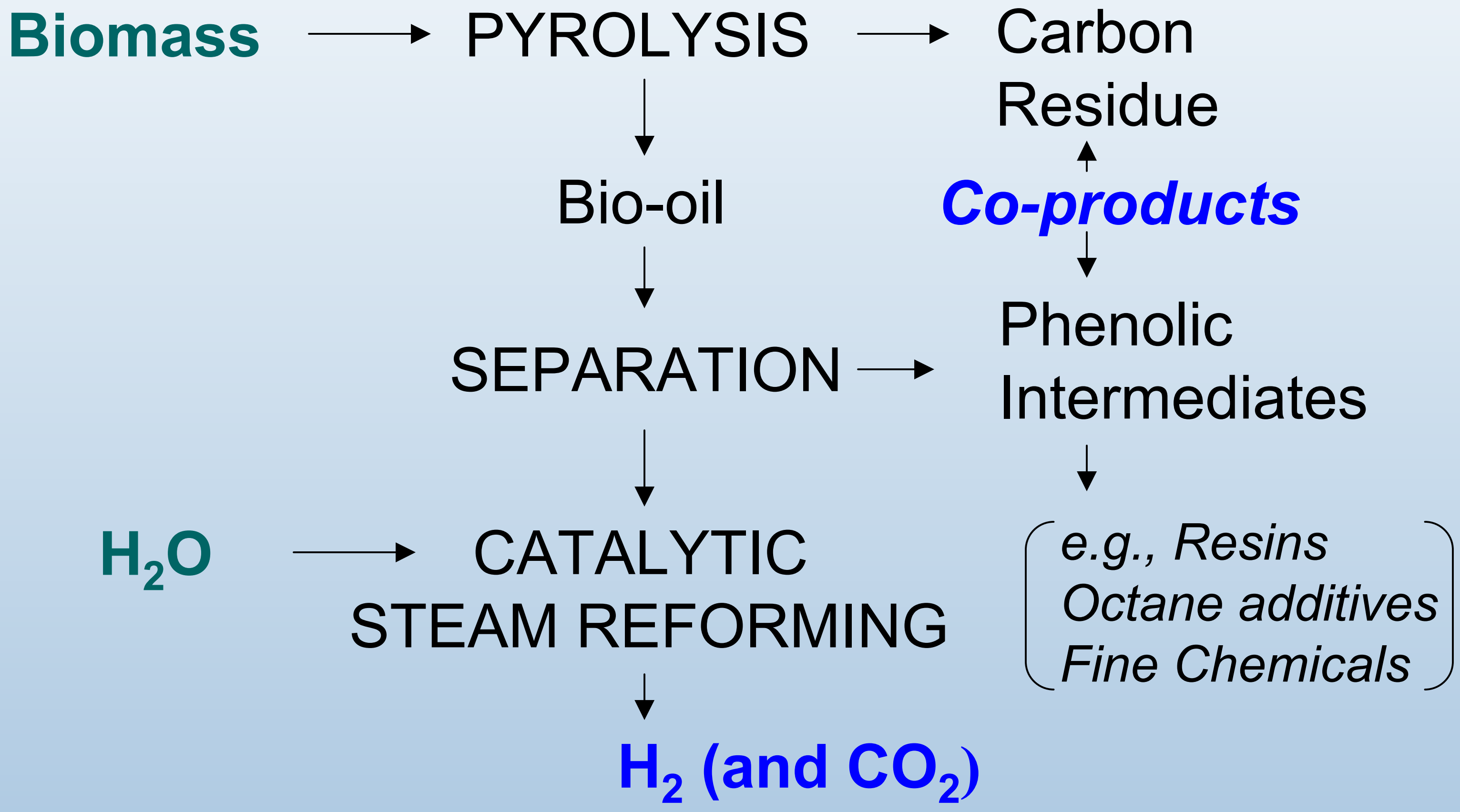
Barrier G: *Efficiency of Gasification, Pyrolysis and Reforming Technology:*

- Heat Integration
- Vapor Conditioning
- Catalyst Development and Regeneration
- Reactor Configuration
- Deployment: H2 + 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



Biomass → PYROLYSIS → Carbon Residue

Bio-oil

Co-products

SEPARATION → Phenolic Intermediates

e.g., Resins
Octane additives
Fine Chemicals

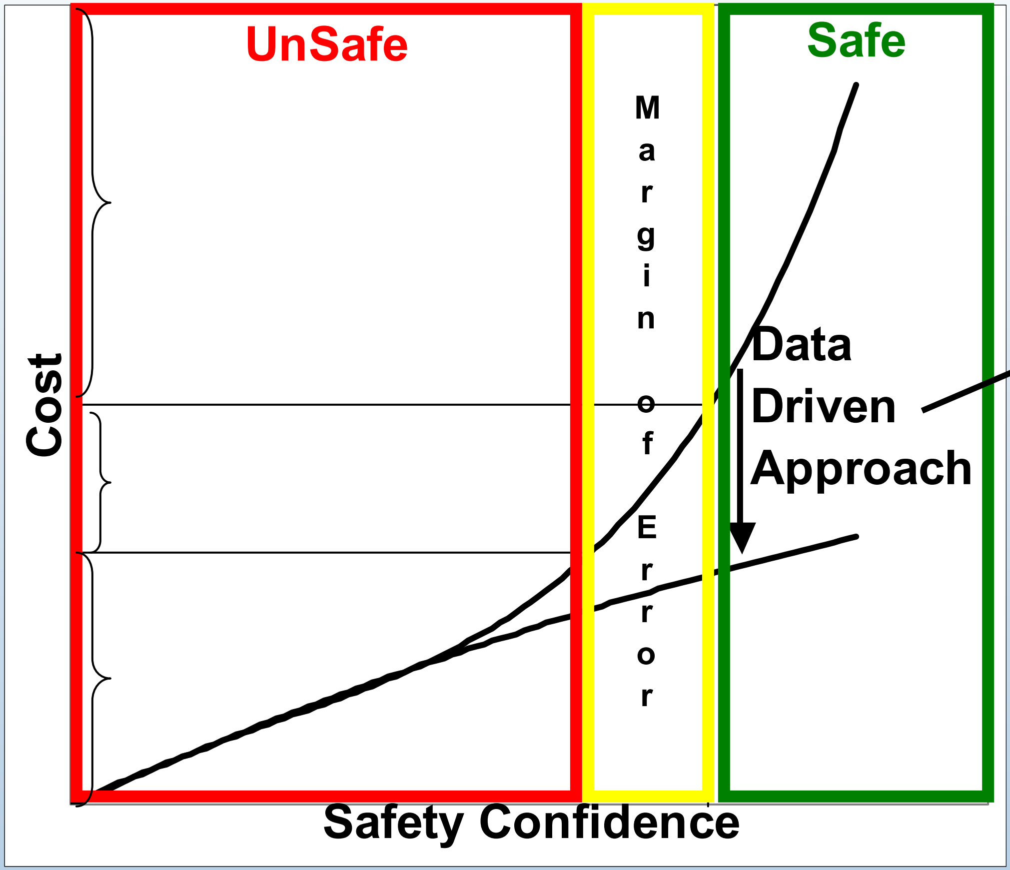
H_2O → CATALYTIC STEAM REFORMING

H_2 (and CO_2)

Safety

- NREL's Thermochemical Users Facility as a Biomass Hydrogen Resource
  - Process Control Development
  - Training
  - Initial Biomass to H2 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



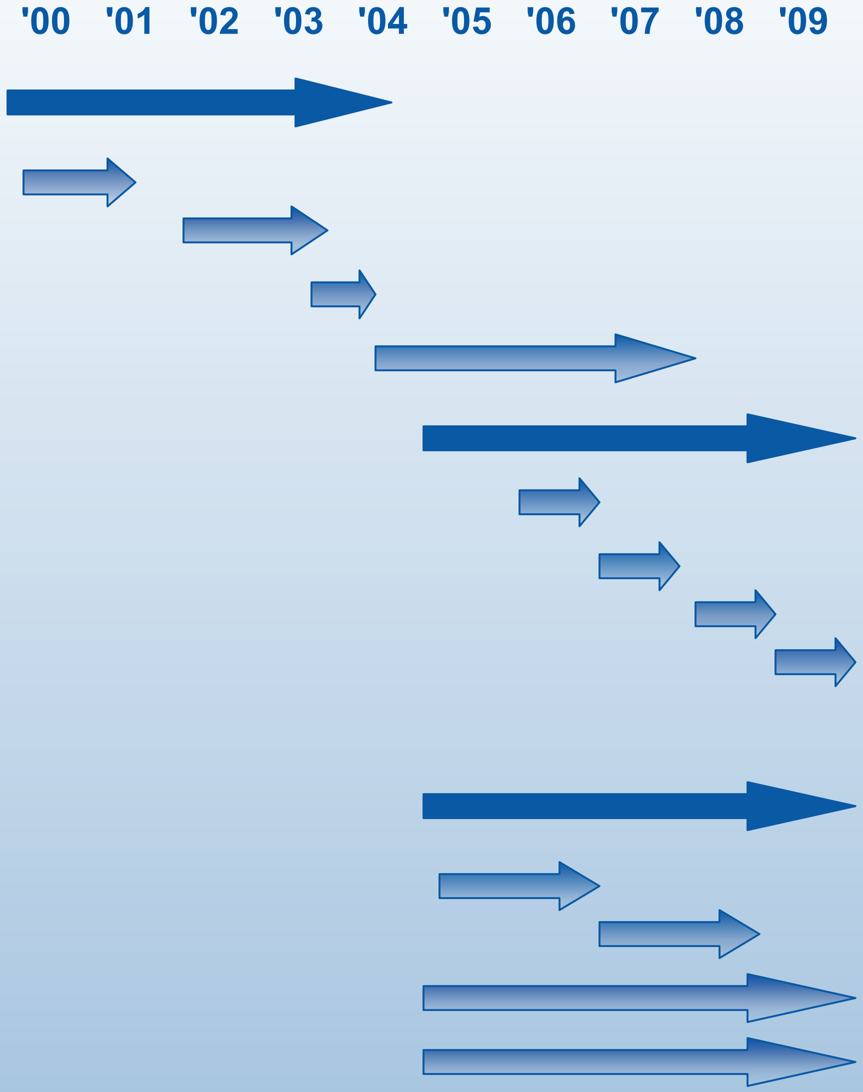
U of GA Facility:

- 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



Phase 1 Bubbling Bed Catalytic Reactor
Design and Shakedown
100-hour run support
1000-hour run support
Phase 2 Bubbling Bed

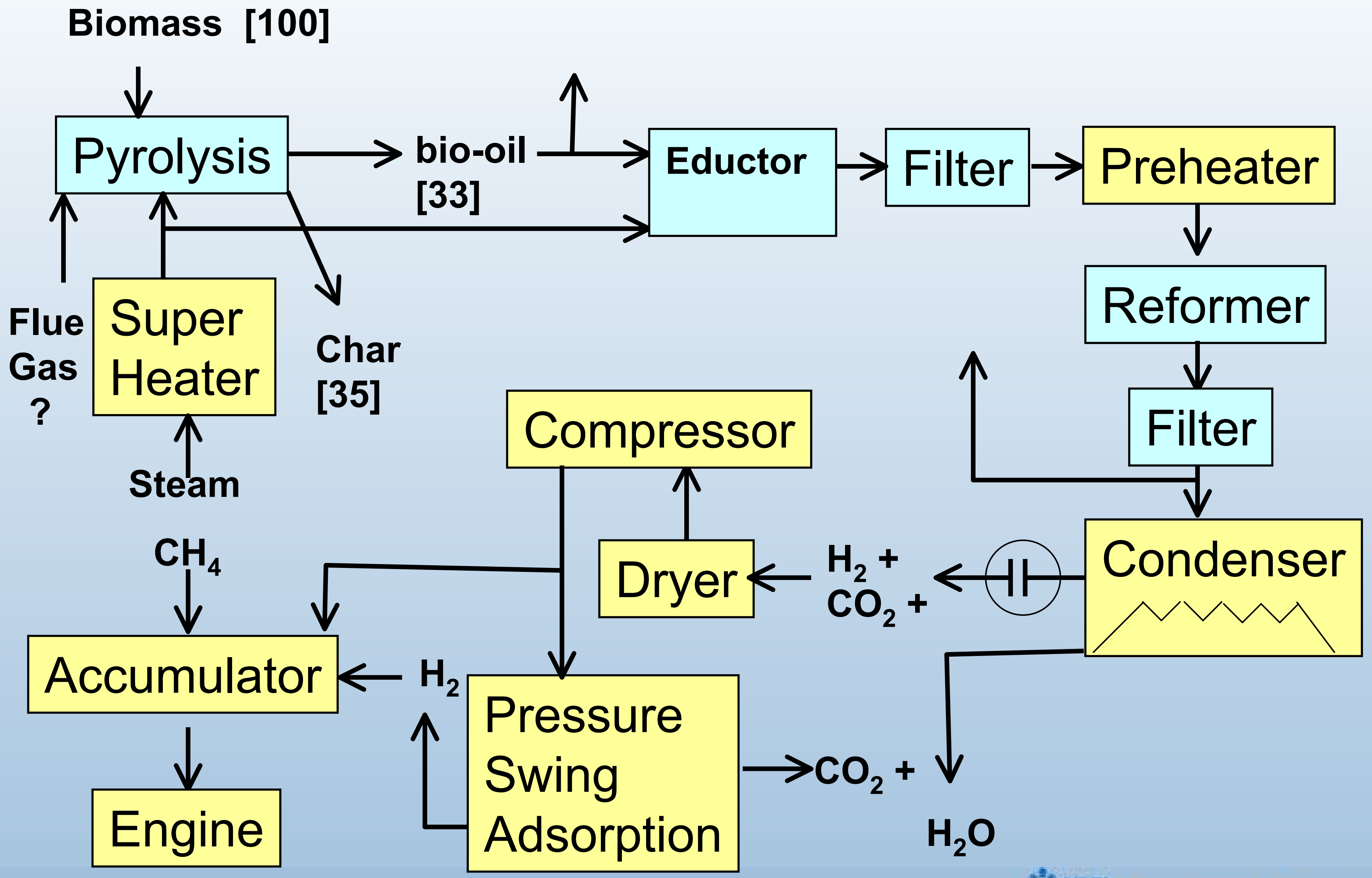
Circulating Bed Reactor
Reaction engineering
Reactor engineering
System development
1000-hour run

Deployment Systems Development
Hybrid systems
Small-scale systems efficiencies
Community Power Parks
Safety engineering

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



Biomass [100]

Pyrolysis

bio-oil [33]

Eductor

Filter

Preheater

Reformer

Filter

Condenser

Flue Gas ?

Super Heater

Steam

Char [35]

Compressor

Dryer

H_2 + CO_2 +

CH_4

Accumulator

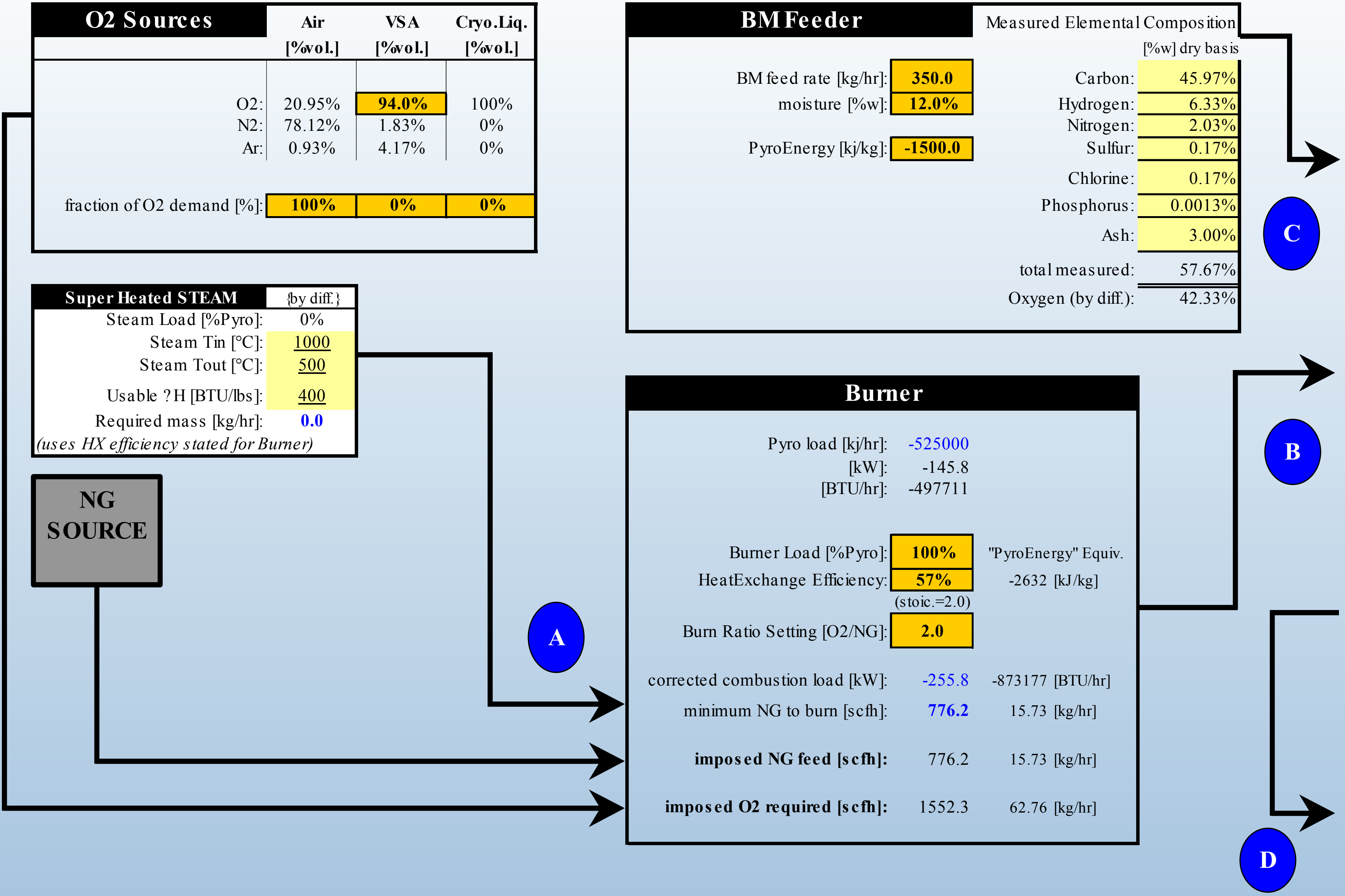
H_2

Pressure Swing Adsorption

CO_2 +

H_2O

Engine



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**

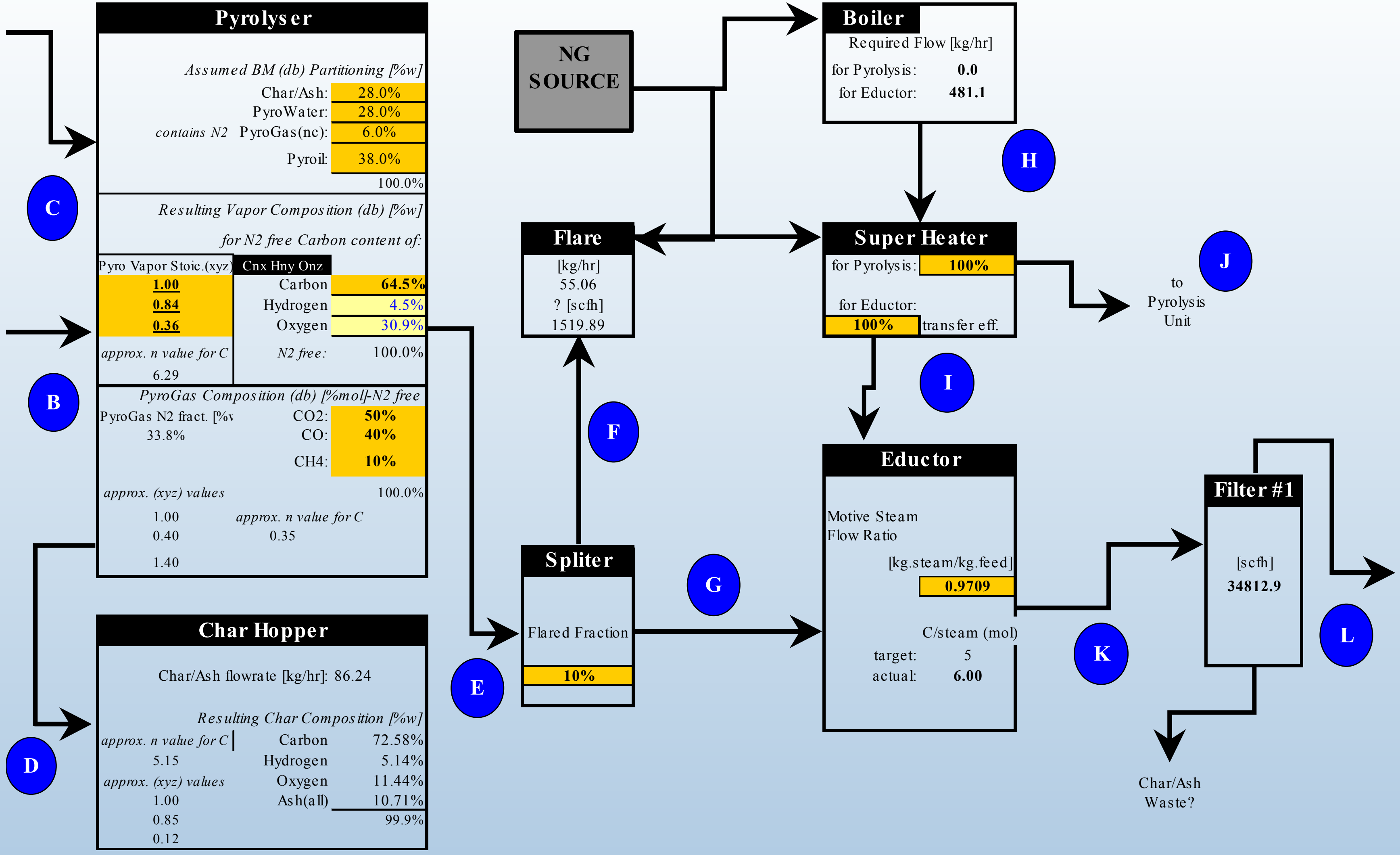
(uses HX efficiency stated for Burner)

NG SOURCE

BM Feeder	
BM feed rate [kg/hr]:	**350.0**
moisture [%w]:	**12.0%**
PyroEnergy [kj/kg]:	**-1500.0**

Measured Elemental Composition [%w] dry basis	
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]



Pyrolyser

Assumed BM (db) Partitioning [%w]

Char/Ash: 28.0%
PyroWater: 28.0%
contains N2 PyroGas(nc): 6.0%
Pyroil: 38.0%
100.0%

Resulting Vapor Composition (db) [%w]
for N2 free Carbon content of:

Pyro Vapor Stoic.(xyz)	Cnx Hny Onz	
1.00	Carbon	**64.5%**
0.84	Hydrogen	4.5%
0.36	Oxygen	30.9%
approx. n value for C	*N2 free:*	100.0%
6.29		

PyroGas Composition (db) [%mol]-N2 free

PyroGas N2 fract. [%v
33.8%
CO2: **50%**
CO: **40%**
CH4: **10%**
100.0%

approx. (xyz) values
1.00
0.40
1.40

approx. n value for C
0.35

Char Hopper

Char/Ash flowrate [kg/hr]: 86.24

Resulting Char Composition [%w]

approx. n value for C	Carbon	72.58%
5.15	Hydrogen	5.14%
approx. (xyz) values	Oxygen	11.44%
1.00	Ash(all)	10.71%
0.85		99.9%
0.12		

NG SOURCE

Flare
[kg/hr]
55.06
? [scfh]
1519.89

Spliter
Flared Fraction
10%

Boiler
Required Flow [kg/hr]
for Pyrolysis: **0.0**
for Eductor: **481.1**

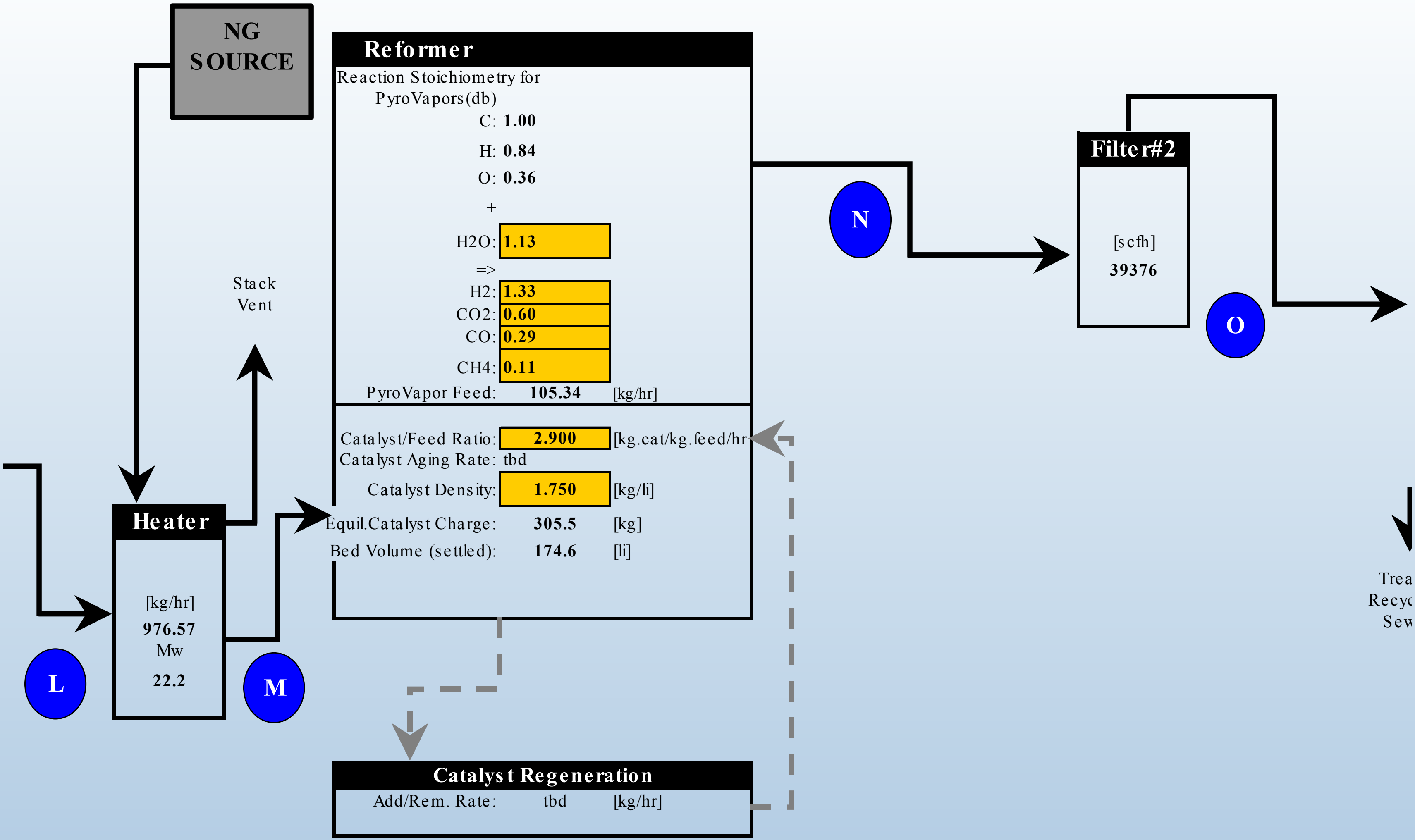
Super Heater
for Pyrolysis: **100%**
for Eductor:
100% transfer eff.

to Pyrolysis Unit

Eductor
Motive Steam Flow Ratio
[kg.steam/kg.feed]
0.9709
C/steam (mol)
target: 5
actual: **6.00**

Filter #1
[scfh]
34812.9

Char/Ash Waste?



NG SOURCE

Stack
Vent

Heater

[kg/hr]
976.57
Mw
22.2

L

M

Reformer

Reaction Stoichiometry for
PyroVapors(db)

C: **1.00**
H: **0.84**
O: **0.36**
+
H2O: **1.13**
=>
H2: **1.33**
CO2: **0.60**
CO: **0.29**
CH4: **0.11**

PyroVapor Feed: **105.34** [kg/hr]

Catalyst/Feed Ratio: **2.900** [kg.cat/kg.feed/hr
Catalyst Aging Rate: tbd
Catalyst Density: **1.750** [kg/li]
Equil.Catalyst Charge: **305.5** [kg]
Bed Volume (settled): **174.6** [li]

Catalyst Regeneration

Add/Rem. Rate: tbd [kg/hr]

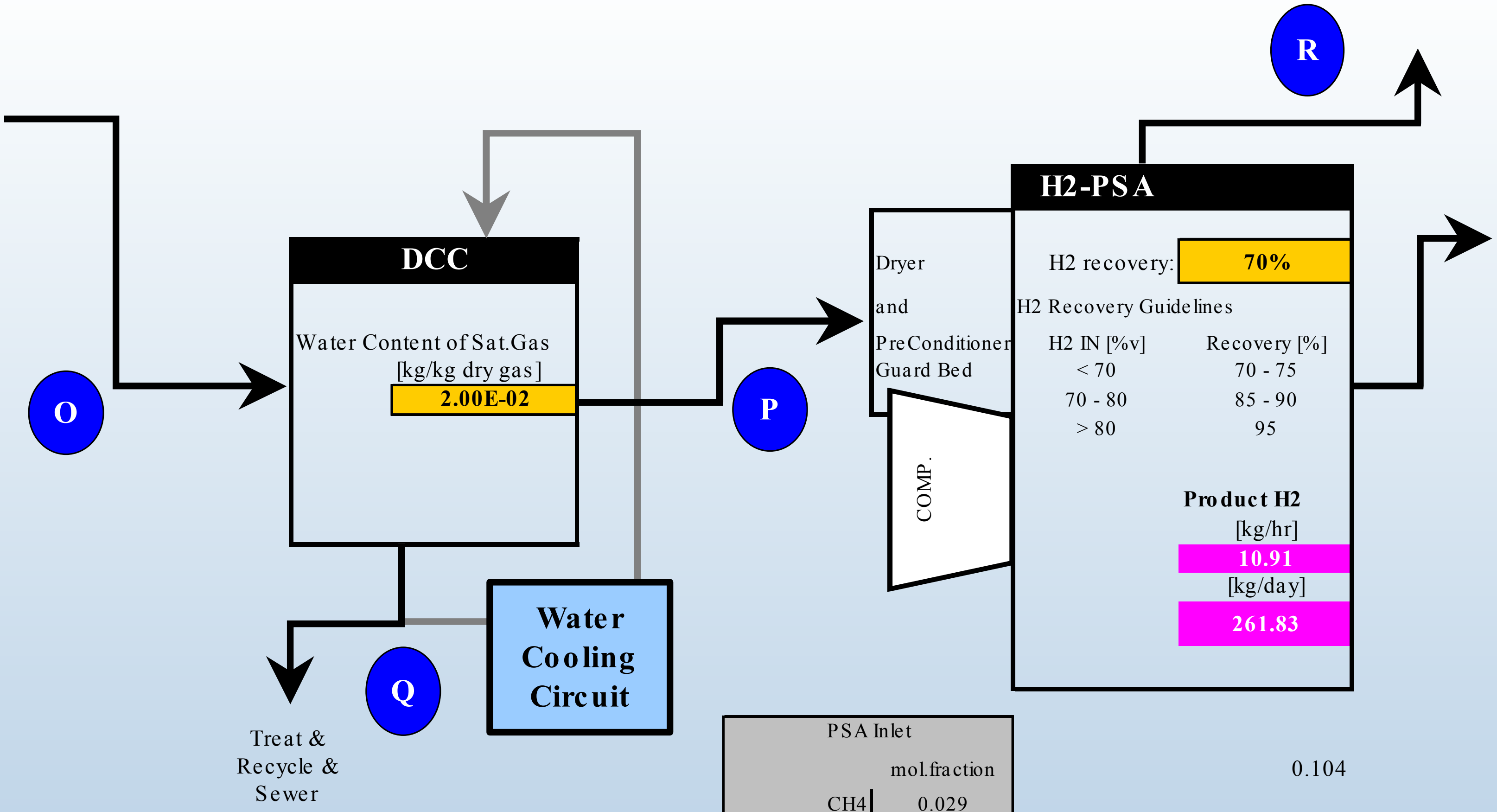
N

Filter#2

[scfh]
39376

O

Trea
Recyc
Sew



DCC

Water Content of Sat.Gas
[kg/kg dry gas]
2.00E-02

Water Cooling Circuit

Treat &
Recycle &
Sewer

Dryer
and
PreConditioner
Guard Bed

COMP.

H2-PSA

H2 recovery: **70%**

H2 Recovery Guidelines

H2 IN [%v]	Recovery [%]
< 70	70 - 75
70 - 80	85 - 90
> 80	95

Product H2

[kg/hr]
10.91
[kg/day]
261.83

PSA Inlet

	mol.fraction
CH4	0.029
H2	**0.352**
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
- O2 vs. Air in Pyrolyzer, Preheater and FBR
  - Impact on Reactor Size

Catalyst Management Plan

- Low Deactivation Rate ~ 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

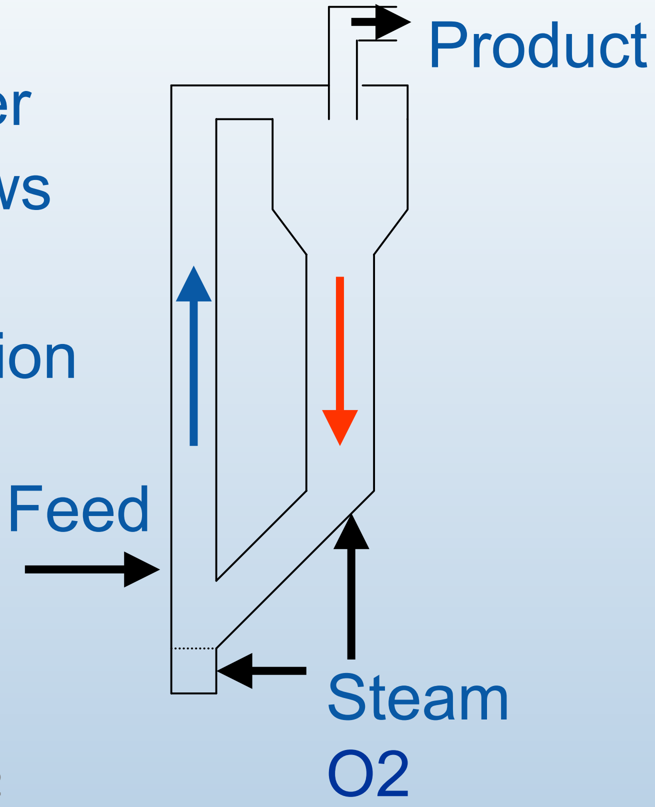
Circulating Fluid Bed

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

Reforming $C_xH_yO_z + H_2O \rightarrow H_2 + CO_x$

Water gas shift: $CO + H_2O \rightarrow CO_2 + H_2$

Coke Gasification: $C + H_2O \rightarrow CO + H_2$



Product

Feed

Steam

O2