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Scale-up of Hydrogen Transport Membranes for IGCC and FutureGen Plants

Presented by

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#PD15

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Overview

Timeline

- Phase I Start 1 Oct 2005
- Phase II Start 1 Oct 2008
- Phase II End 30 Sept 2011

Budget ($000)

➢ Phase I Funding	$ 2,900
✓ DOE share:	$ 2,300
✓ Contractor share:	$ 600
➢ Funding for FY06/07	$ 2,300
➢ Phase II Funding	$40,000
✓ DOE Share	$31,000
✓ Contractor share	$ 9,000

Barriers Addressed

- Reducing hydrogen cost
- Hydrogen production from diverse pathways
- Hydrogen of sufficient purity for fuel cells

Technical Targets

- Low-cost system to produce H_2 from coal-derived synthesis gas and enable cost effective capture of CO_2 for sequestration
- Obtain engineering scale-up data in 220 lb H_2 /day unit
- Design, build and operate 4 ton/day unit
- Tolerant to syn gas contaminants

Partners

- NORAM Engineering
- CoorsTek
- Praxair

DOE Contract DE-FC26-05NT42469

Objectives

- Develop high-throughput, low-cost H_2 separation system suitable for application with coal-based synthesis gas, including improved tolerance to contaminants (S, Hg, etc.) and enabling cost effective capture of CO_2 for sequestration
- Select candidate mechanical configuration (tube vs. plate; metallic alloy vs. cermet) considering cost, performance, & manufacturability of membrane and system
- Scale up membrane & system from 0.45 lb/day of H_2 using lab gases to 220 lb/day in coal-derived syn gas
- Integrate membrane design into a 4 ton/day H_2 production unit
- Determine optimum process design & cost and compare vs. other systems

Plan and Approach

- Materials Development
  - ✓ Examine membrane and catalyst compositions
  - ✓ Develop preparation techniques
- Performance Screening
  - ✓ Evaluate flux, life, impurities effects using WGS composition
  - ✓ Establish range of operating conditions
- Mechanical Design
  - ✓ Evaluate tubular versus planar configurations
  - ✓ Assess manufacturing costs and maintenance issues
- Process Design and Economics
  - ✓ Integrate into IGCC flow sheets – with and without co-production of H2 & power
  - ✓ Determine methods for impurity management
  - ✓ Compare economics, including capex & opex, versus other technologies
- Scale-up steps
  - ✓ 1.5 lbs/day H2 production – lab scale using simulated gas compositions
  - ✓ 220 lbs/day H2 production – using coal-based SG slipstream
  - ✓ 4 tons/day H2 production – complete engineering data package
  - ✓ Commercial module expected to be ~ 35 TPD H2 Production

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Technology Development Highlights

- Developed membrane system that meets or exceeds the 2010 DOE targets for flux and selectivity
- Focus on establishing better understanding of these systems
  - ✓ Optimization
  - ✓ Robustness
  - ✓ Scale-up for manufacturing

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Technology Development Highlights

- Developed cermet materials with comparable performance to Pd membranes
  - ✓ Tested for more than 500 hours without loss in permeability
- Identified lower cost route for fabrication of these materials
- Preliminary design and cost estimating work indicate they are competitive with El100 membranes
- Work underway to scale up manufacturing procedures

Technology Development Highlights

- Results from process economic studies show HTM system is competitive with conventional technology
  - ✓ Cost of electricity basis
  - ✓ 2% improvement on HHV basis
- Further optimization cases being examined
  - ✓ 1000 psig gasifier
  - ✓ Warm gas cleaning
  - ✓ Higher CO_2 capture cases
- Future work on co-production of H_2 and power

Technology Development Highlights

- Construction of 1.3 lbs/day high pressure unit completed
  - ✓ Initial operations demonstrated at 1.46 lbs/day at full WGS conditions
- Adding reactor capacity
  - ✓ High pressure reactor system for life studies
  - ✓ Impurity management reactor system
- Increasing focus on analytical capabilities
  - ✓ Understanding decay mechanism(s)
  - ✓ Improving membrane performance

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Key Technical HTM Issues

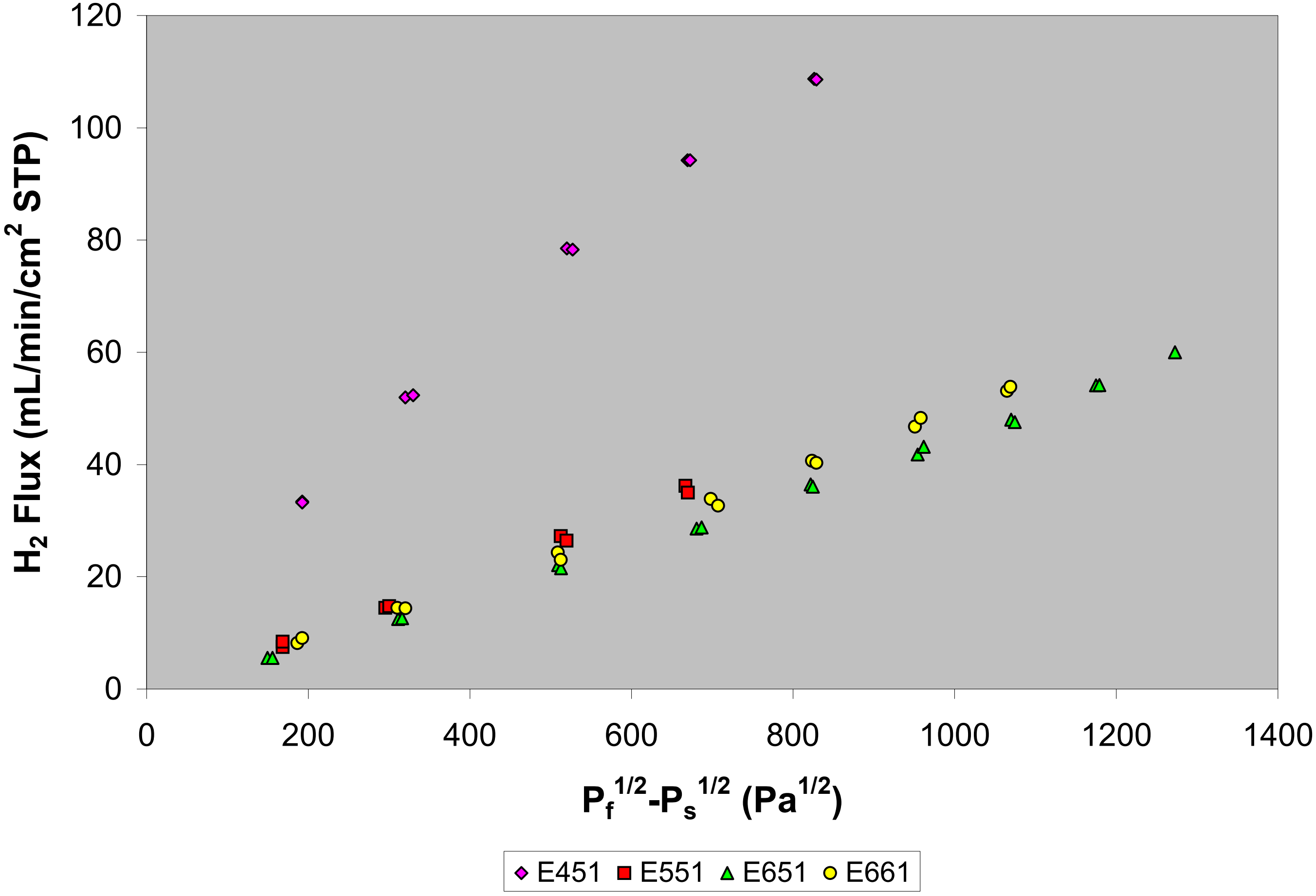
- Understanding Embrittlement
  - ✓ Further Alloy Development
  - ✓ Testing
- Catalyst Development
  - ✓ Electrodeposition / Electroless Deposition
- Full WGS Testing
  - ✓ Sweep
  - ✓ No Sweep
- Scale-Up Testing
  - ✓ Reactor Baseline Testing
  - ✓ Scale-up Unit

Hydrogen "Embrittlement"

- Precipitation of a metal hydride within the bulk metal as the H/M ratio becomes too high resulting in membrane failure.
- Complex Alloy Formation
  - ✓ Binary – non hydride forming element
  - ✓ Ternary – grain growth inhibitor
  - ✓ Quaternary – oxygen getter
- Hydrogen concentration in the metal
- Complex – not just a problem that can be solved with alloys

Alloy Testing – No Sweep

- 420°C
- 0.25 mm
- 90% H_2 Feed
- No Sweep



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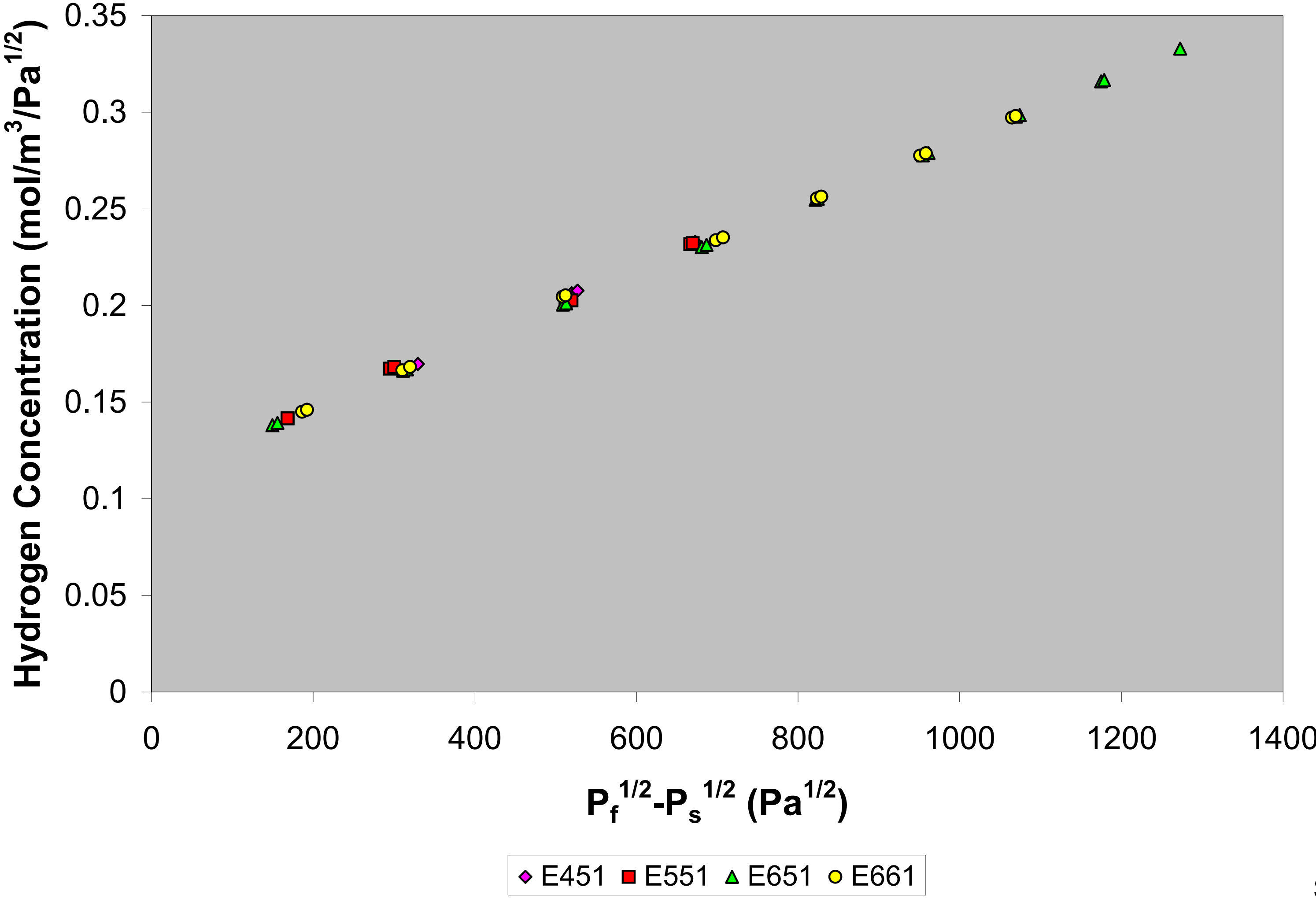
Alloy Hydrogen Concentration – No Sweep



Membrane Pre-Treatment

- Four Different Pre-Treatments Evaluated
  - ✓ Applied Individually or Combined
  - ✓ Improve Membrane Performance / Lifetime / Resistance to Embrittlement
- Method A
  - ✓ Purposely Break Membranes (40% H_2 Feed, No Sweep)
    - ❖ Membrane #1: No Pre-treatment with Method A
      - – Membrane Broke at 151 psig
    - ❖ Membrane #2: Pre-treated with Method A
      - – Membrane Did Not Break Up to 1000 psig

Membrane Pretreatment (cont.)

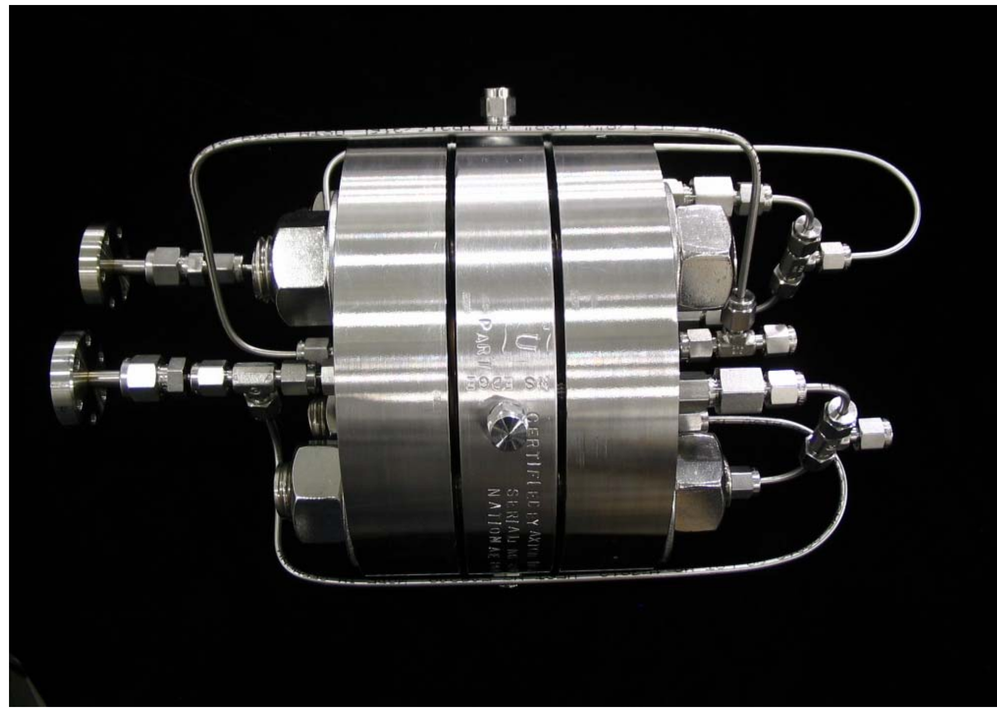
- Method B
  - ✓Higher initial flux
  - ✓Lower rate of decay
- Method C
  - ✓Initial flux increase
  - ✓No long-term benefits
- Method D
  - ✓Slightly higher initial flux
  - ✓No decay in activity after 300 hours

Scale-up of Catalyst Deposition

- Current deposition method is magnetron sputtering onto planar membranes
- Catalyst deposition techniques being evaluated for scale-up include:
  - ✓ Electroless
  - ✓ Electrodeposition
- Other variables under investigation:
  - ✓ Catalyst Composition
  - ✓ Catalyst Thickness

Scale-Up Testing: Goal 1.3 lbs H_2 / day

- Reactor Conditions:
  - ✓ 390°C
  - ✓ Feed (22 L/min.)
    - ❖ 41% H_2
    - ❖ 3% CO
    - ❖ 17% CO_2
    - ❖ 37% Steam
    - ❖ Balance He
  - ✓ N_2 Sweep (30 L/min.)
  - ✓ ΔP = 400 psig
  - ✓ 63 cm^2



1.3 lbs H_2 / day Separation Unit Designed by NORAM

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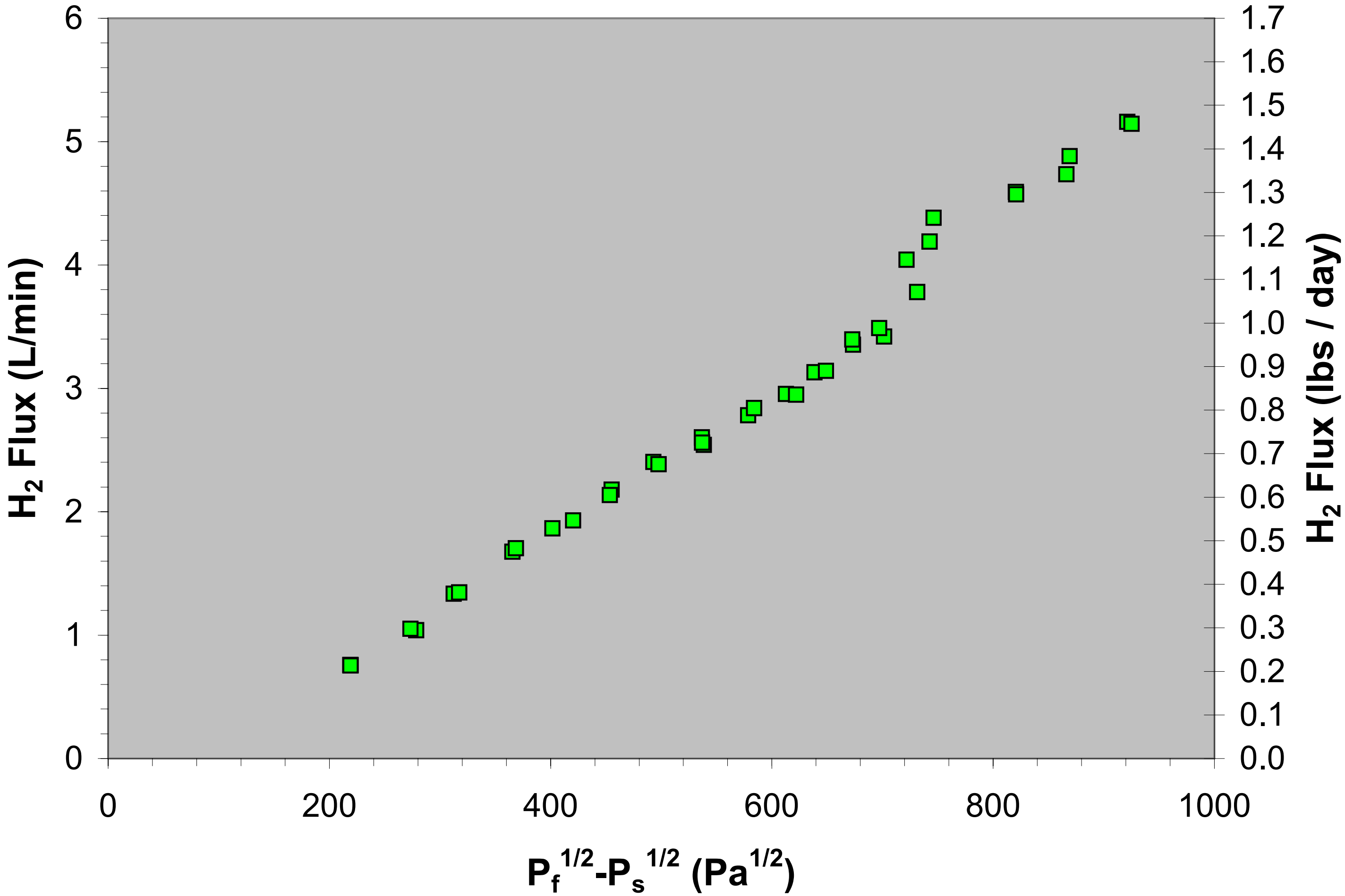
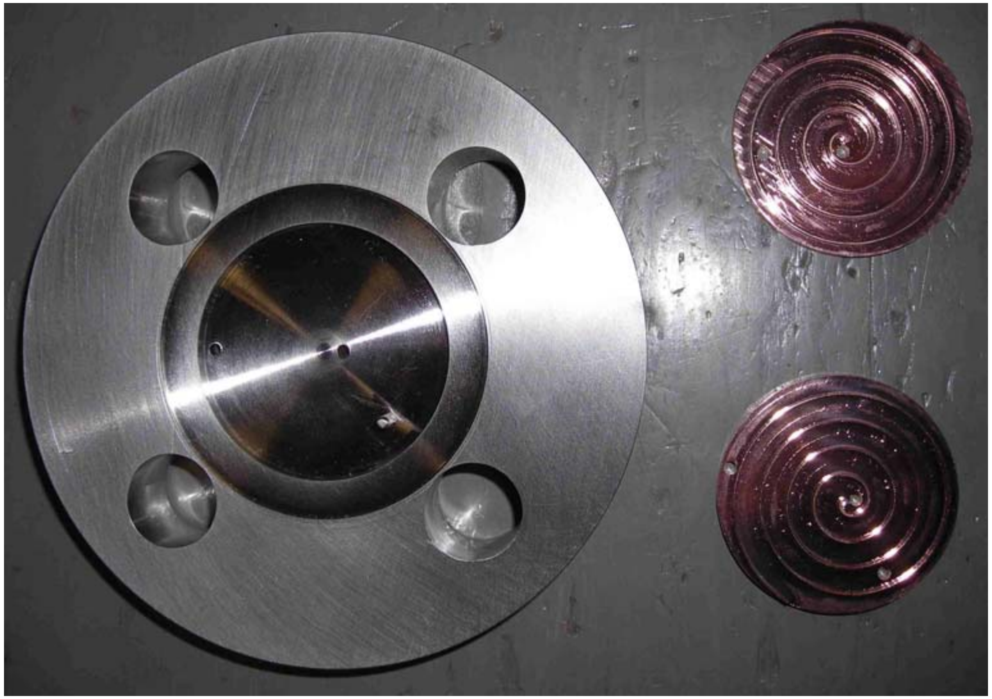
Scale-Up Testing Results

- 1.46 lbs H_2 / day
- Full WGS Conditions



Final 1.3 lb/day Separator Design



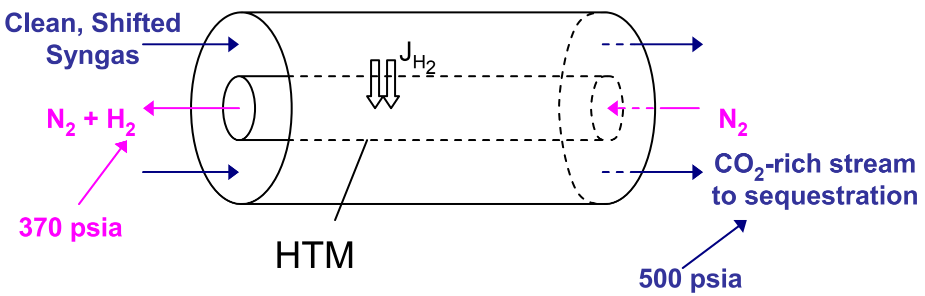
HTM Model

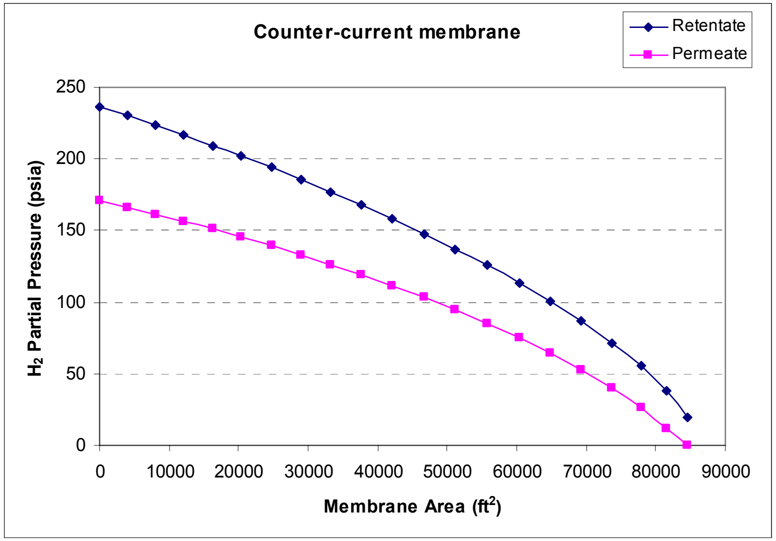
- Modeled as a subflowsheet of unit operations in Hysys

$$Flow_{H_2} = J_{H_2} A_{HTM}$$

$$J_{H_2} = \frac{P_0}{l} \exp\left(\frac{-E_A}{RT}\right)\left(P_{H_2,\mathrm{Ret}}{}^{1/2} - P_{H_2,Perm}{}^{1/2}\right)$$

- Model parameters derived from Eltron membrane data



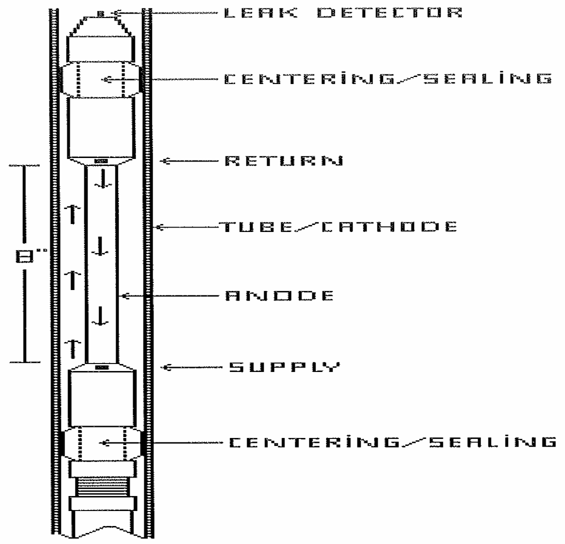


Membrane Scale-Up

Tubular Membrane Component Development

- Tube Manufacture
- Weld Procedure Specification
- Catalyst Coating
- Tubesheet to Tube Joint Development
- Support Material Specification
- Material Physical Properties

Tube Catalyst Coating



- *Existing Process for Boiler Tube Repair*
- *Gun Barrel Repair – 0.556"*
- *Select Prototype Tube OD to Suit Coating Development*

Economic Results for Power-only Cases

- Results from process economic studies show HTM system is competitive with conventional technology
  - ✓ Reduced cost of electricity
  - ✓ Improvement in HHV efficiency
  - ✓ CO_2 compression costs minimized
- Guidance from optimization cases examined to date
  - ✓ Driving HTM to high recovery (~95%)
  - ✓ Use of ASU N_2 as sweep gas improves recovery and eliminates H_2 compression for turbine (turbine requires nitrogen dilution anyhow)
  - ✓ Use of medium-temperature shift catalyst minimizes steam requirements
- Further optimization cases being examined
  - ✓ 1000 psig gasifier
  - ✓ Warm gas cleaning
  - ✓ Higher CO_2 capture cases
- Work on co-production of H_2 and power underway

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Results: Membrane vs. Base case

Case	Base	Membrane
Power Gen and Consumption		
Gas turbine power (MW)	230.0	230.0
Steam turbine power (MW)	103.1	137.1
Generator Losses (MW)	4.1	4.4
Gross Power (MW)	**329.0**	**363.9**
AGR power	11.9	0.7
CO2 compression power	15.3	7.8
Other auxiliary loads	59.8	73.2
Total auxiliary loads	**87.1**	**81.7**
Net Power (MW)	**241.9**	**282.1**
Inputs and Consumables		
Coal (tpd)	2942	3217
O2 (tpd)	2119	2671
Plant Outputs		
CO2 (tpd)	5786	6394
Sulfur (tpd)	130	143
Slag Ash (tpd)	440	483
Heat rate (BTU/kWh)	11141	10447
HHV Efficiency	30.6%	32.7%
Other Parameters		
WGS Steam/CO	2.5	1.7
HP Steam to HRSG (kpph)	532.3	802.8
IP Steam to HRSG (kpph)	161.2	215.9
LP Steam to HRSG (kpph)	59.2	0.0

Steam turbine power increases because more process steam is made and less superheated steam is extracted from the turbine

Auxiliary power load decreases even though coal and O_2 flow increase. Savings from CO_2 compression and AGR power.

Net Result: Decrease in Aux. load and increase in ST output gives HHV efficiency increase of 2.1 percentage points

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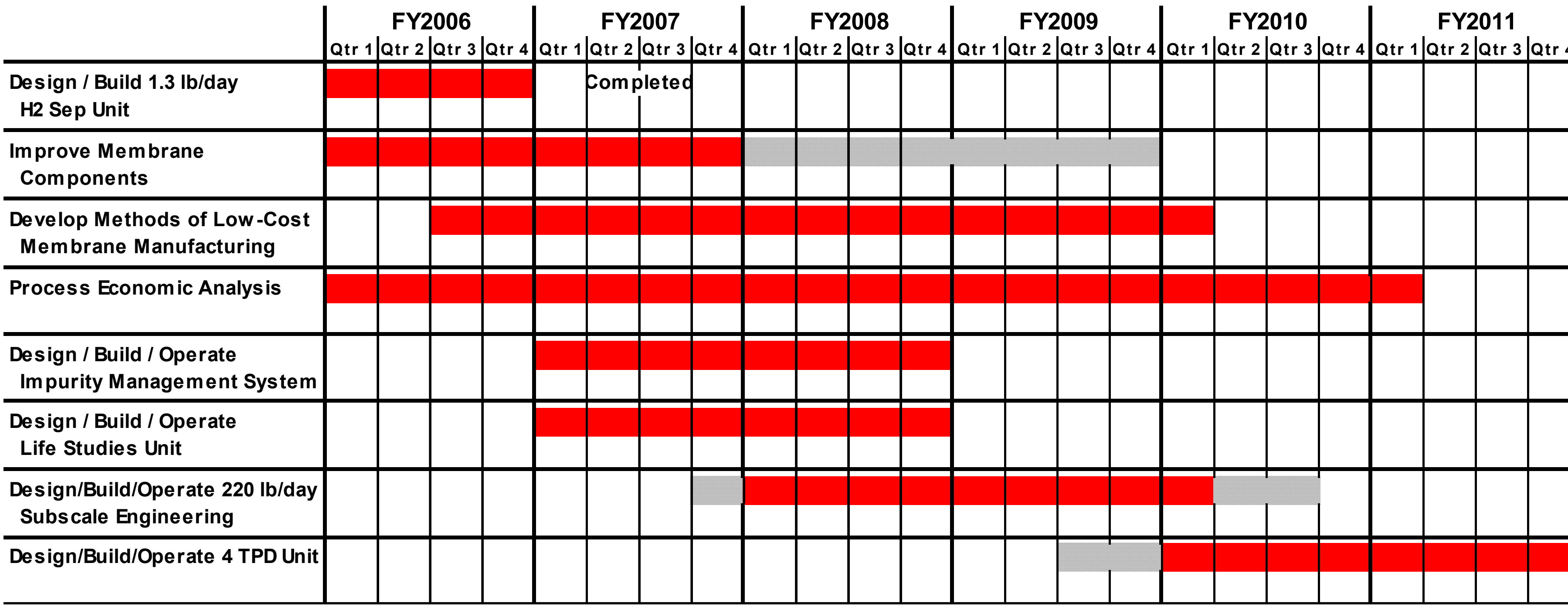
Simplified Project Schedule

Scale Up Hydrogen Transport Membranes for IGCC and FutureGen Coal to Hydrogen Production Plants



DOE Contract #DE-FC26-05NT42469

Business Development Challenges

- Contract between Eltron & DOE is for first 2 years only. Last 4 years will be committed after commercialization partner(s) have been identified.
  - ✓ Advanced discussions with likely major partner
  - ✓ In discussions with material suppliers and fabricators wanting preferred supply arrangements
  - ✓ Early discussions with several other potential partners
- Utilizing stage gate process based on technical & economic criteria
  - ✓ First gate at end of Phase I
  - ✓ Next gate after successful operation of 220 lb/day unit ~end 2009
  - ✓ Final gate after successful operation of 4 TPD unit ~end 2011
- Entering discussions with potential sites for 220 lb/day unit

Summary

- Achieved first scale-up step under full WGS conditions
- Improving knowledge of impact of membrane materials and preparation techniques on degradation and embrittlement
- Developing more sophisticated process engineering and economic tools for system optimization
- Economics show that system is competitive with conventional technology in power only case
  - ✓ Reduction in cost of electricity
  - ✓ Lower compression costs for hydrogen and CO_2
  - ✓ Higher CO_2 capture possible
  - ✓ Co-production of hydrogen and power underway
- Scale-up efforts underway through work with:
  - ✓ Materials suppliers and fabricators
  - ✓ Warm gas cleaning technology provider
  - ✓ Potential sites for scale-up
- The project is on schedule and budget.

Back-Up Slides

- See following slides

Development Pathways

- Tubular –unsupported
- Pros
  - ✓ Proven Mech Design
  - ✓ Proven Fabrication
  - ✓ Maintainable
  - ✓ Inherent Manifold
- Cons
  - ✓ Thicker Membrane
  - ✓ Lower Pressure
  - ✓ Larger Equipment
  - ✓ Coating Inside Tube

- Planar – Supported
- Pros
  - ✓ Thinner Material
  - ✓ Higher Pressure
  - ✓ Smaller Equipment
- Cons
  - ✓ Complex Mech Design
  - ✓ Material Interaction
  - ✓ Fabrication Development
  - ✓ Manifold
  - ✓ Planar Maintainability

FutureGen Technical Targets*

- Approximately 275 MW plant capacity
- 90% CO_2 sequestration
  - ✓ 95% purity
  - ✓ 2200 psia
- 99% S and ≤ 0.05 lb/MMBTU NO_x
- 7884 operating hours per year w/ 90% availability

* *FutureGen: Integrated Hydrogen, Electric Power Production and Carbon Sequestration Research Initiative*, US DOE Office of Fossil Energy, March 2004

Financial Assumptions

- Levelized COE is the metric used to compare casework
- Use DOE IGCC Project Analysis Financial Model v3.0
  - ✓ 100% equity financing
  - ✓ 10% IRR
  - ✓ $35/ton Illinois #6 coal
  - ✓ 20 year plant life
  - ✓ 4 year construction period starting in Jan 2010
  - ✓ No escalation or inflation
  - ✓ 15 year 150% declining balance depreciation
  - ✓ Working capital as 7% of 1st year revenues
  - ✓ 38% Federal and state taxes
  - ✓ Start-up at 2% of EPC
  - ✓ Development fees at 4% of EPC
  - ✓ 5% and 0.6% of EPC/year for fixed and variable O&M, respectively
- The *differences* in the COE are used to compare the cases

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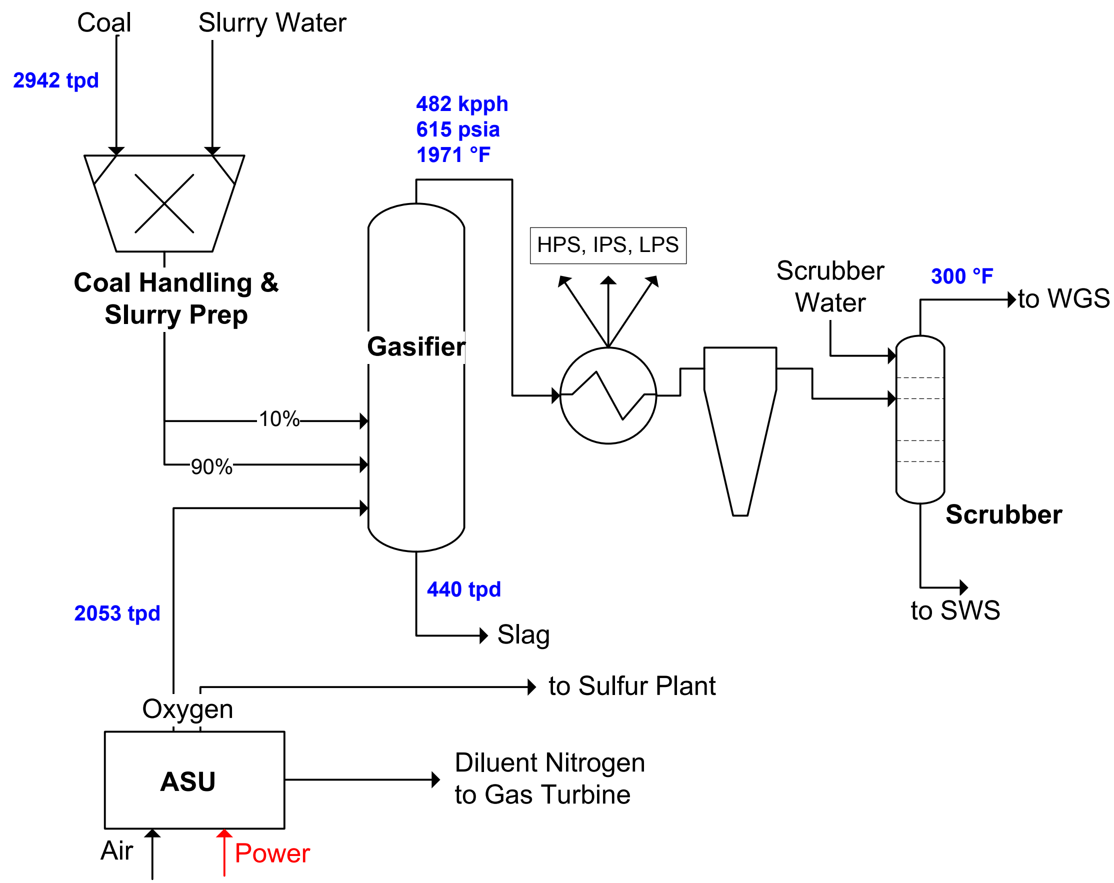
Baseline Case: Gasification

- Conoco-Phillips E-Gas gasifier w/ 90/10% staged feed to minimize CH_4
- 615 psia operating pressure
- No air side ASU integration w/ the gas turbine
- Use Illinois #6 coal



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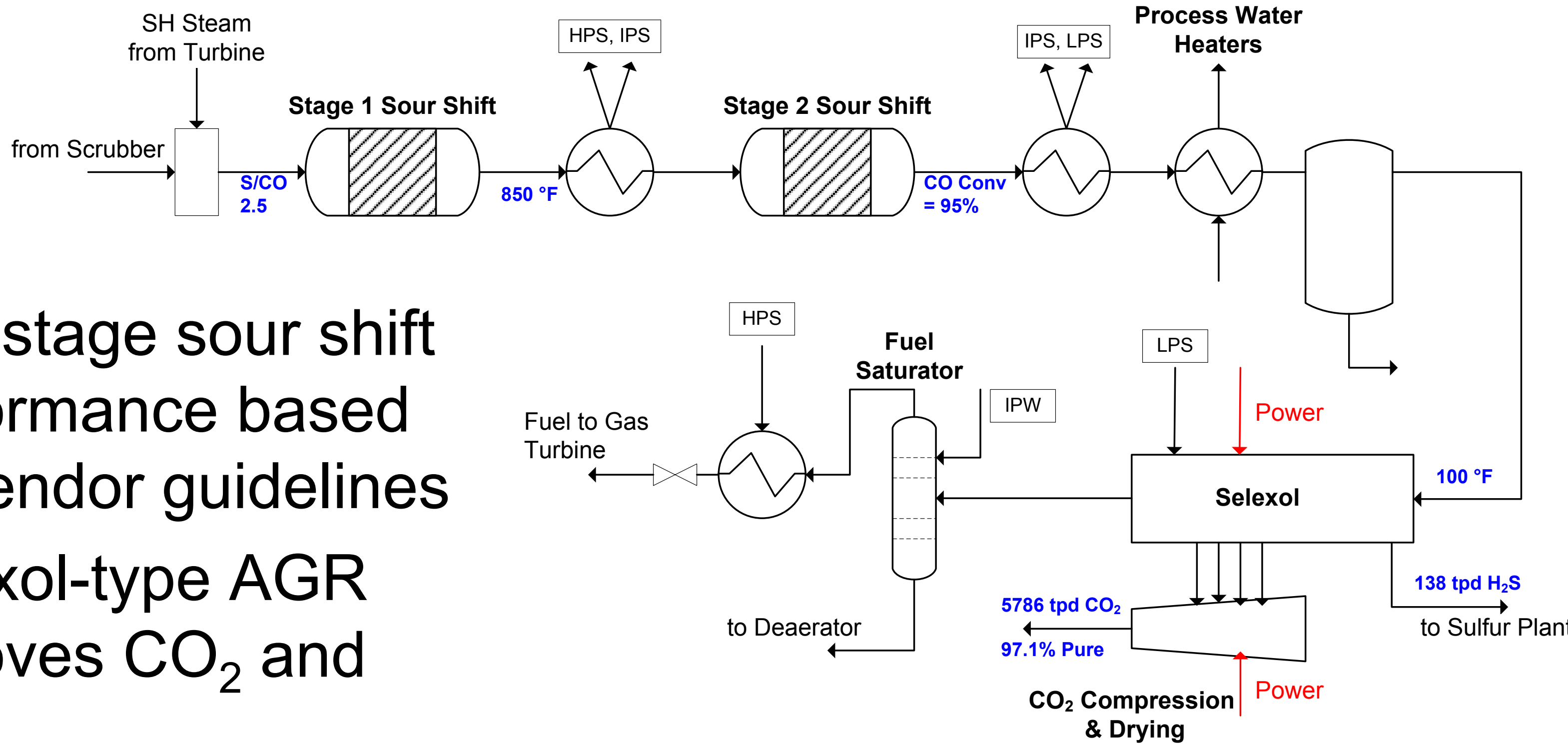
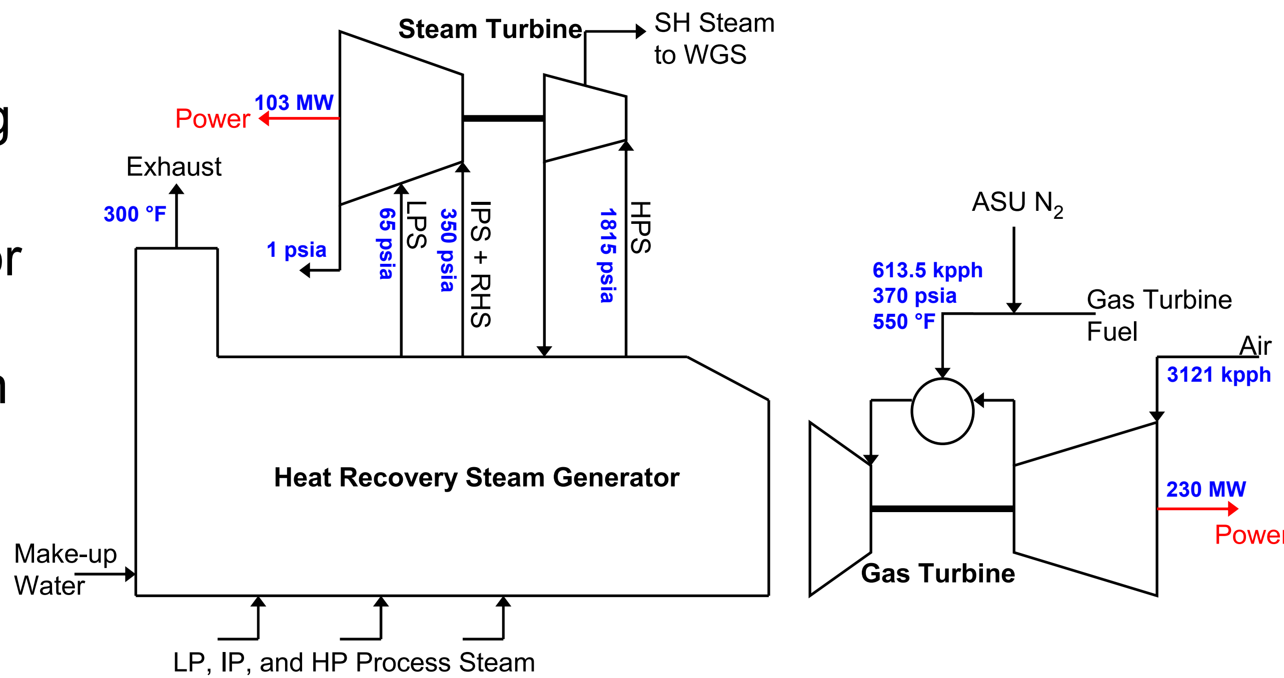
Baseline Case: Syngas



- Two-stage sour shift performance based on vendor guidelines
- Selexol-type AGR removes CO_2 and H_2S
- CO_2 compressed to 2200 psia from 18 – 350 psia

Baseline Case: Power Island

- GE 7251FB gas turbine w/ diffusion combustor operating at maximum output
- N_2 dilution of feed for NO_x control and power augmentation
- 3-pressure HRSG
- 1815 psia/ 1050 °F/ 1050 °F reheat steam turbine



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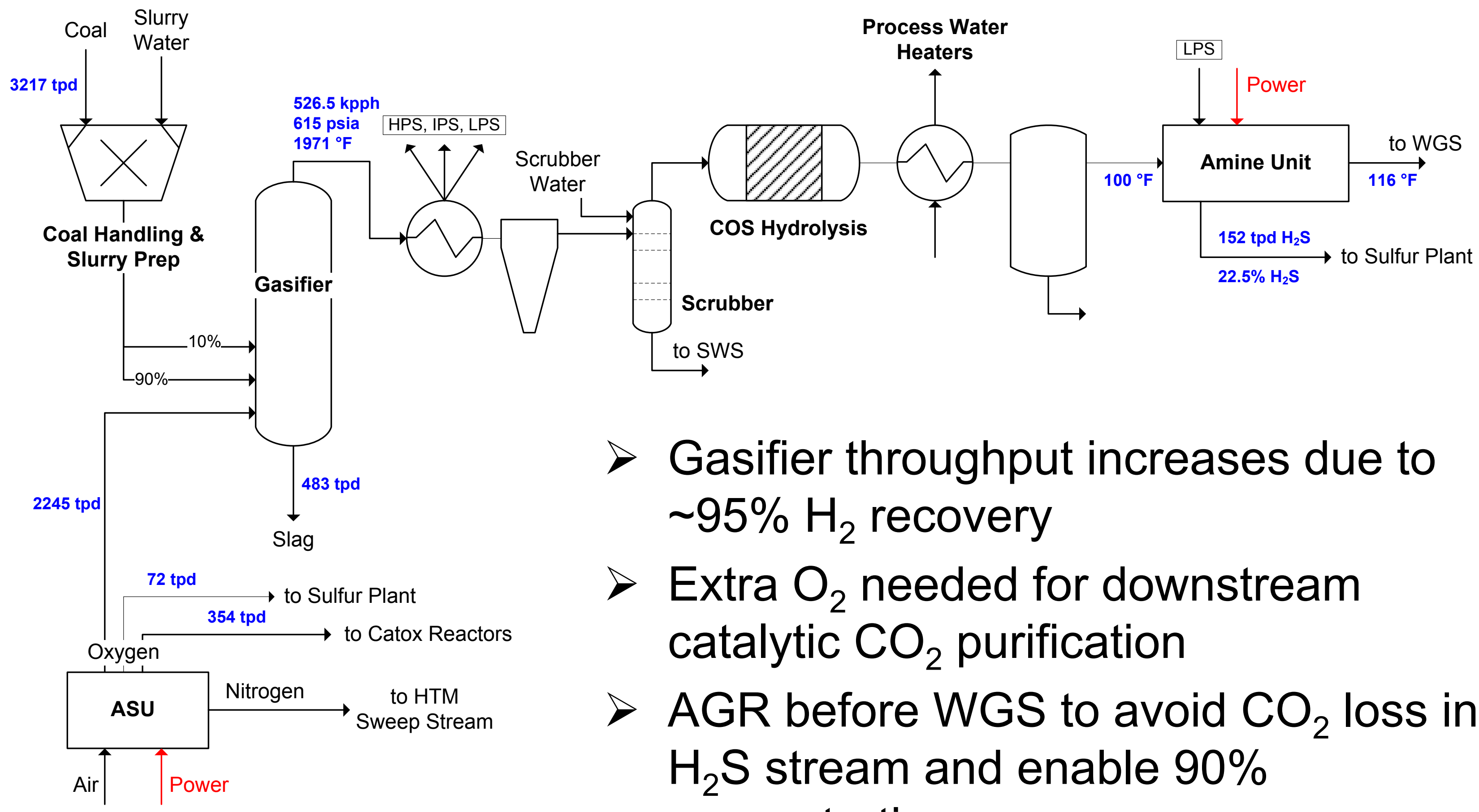
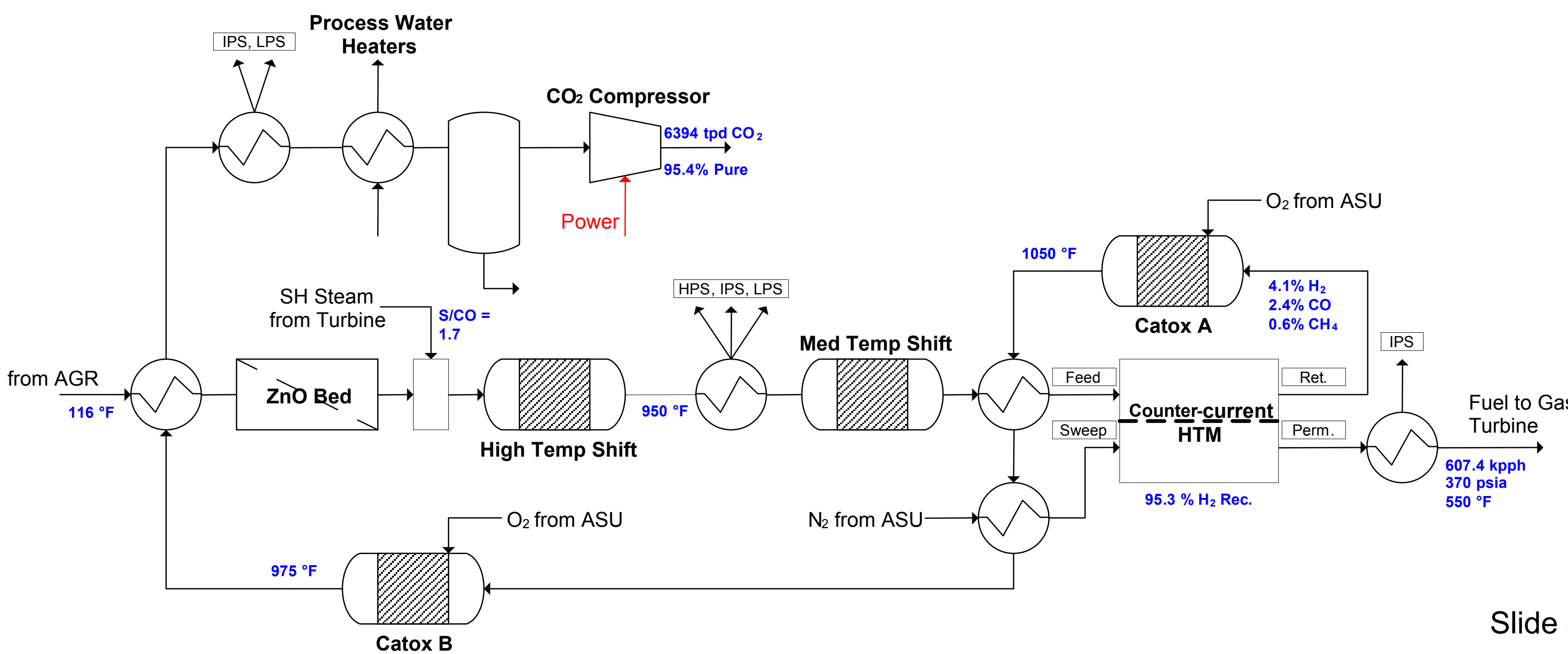
Membrane Case: Gasification



- Gasifier throughput increases due to ~95% H_2 recovery
- Extra O_2 needed for downstream catalytic CO_2 purification
- AGR before WGS to avoid CO_2 loss in H_2S stream and enable 90% sequestration
- COS hydrolysis unit necessary

Membrane Case: Syngas

- Sweet WGS replaces sour shift design
- Minimum steam/CO set by maximum HTS temperature
- ZnO guard bed for catox, MTS, and HTM protection
- 95% H_2 recovery in HTM
- Catox units use ASU O_2 to oxidize residual combustibles (CO, H_2, and CH_4) to achieve 95% CO_2 purity spec.



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Membrane Case: Power Island

- Same gas turbine/ steam turbine/ HRSG layout as the base case
- Steam turbine power output increases because less steam is extracted from the turbine (WGS S/CO)
- Also, the amount of high pressure process steam sent to the HRSG increases due to catox units