DOE Hydrogen Program

Reactor Cost Analysis

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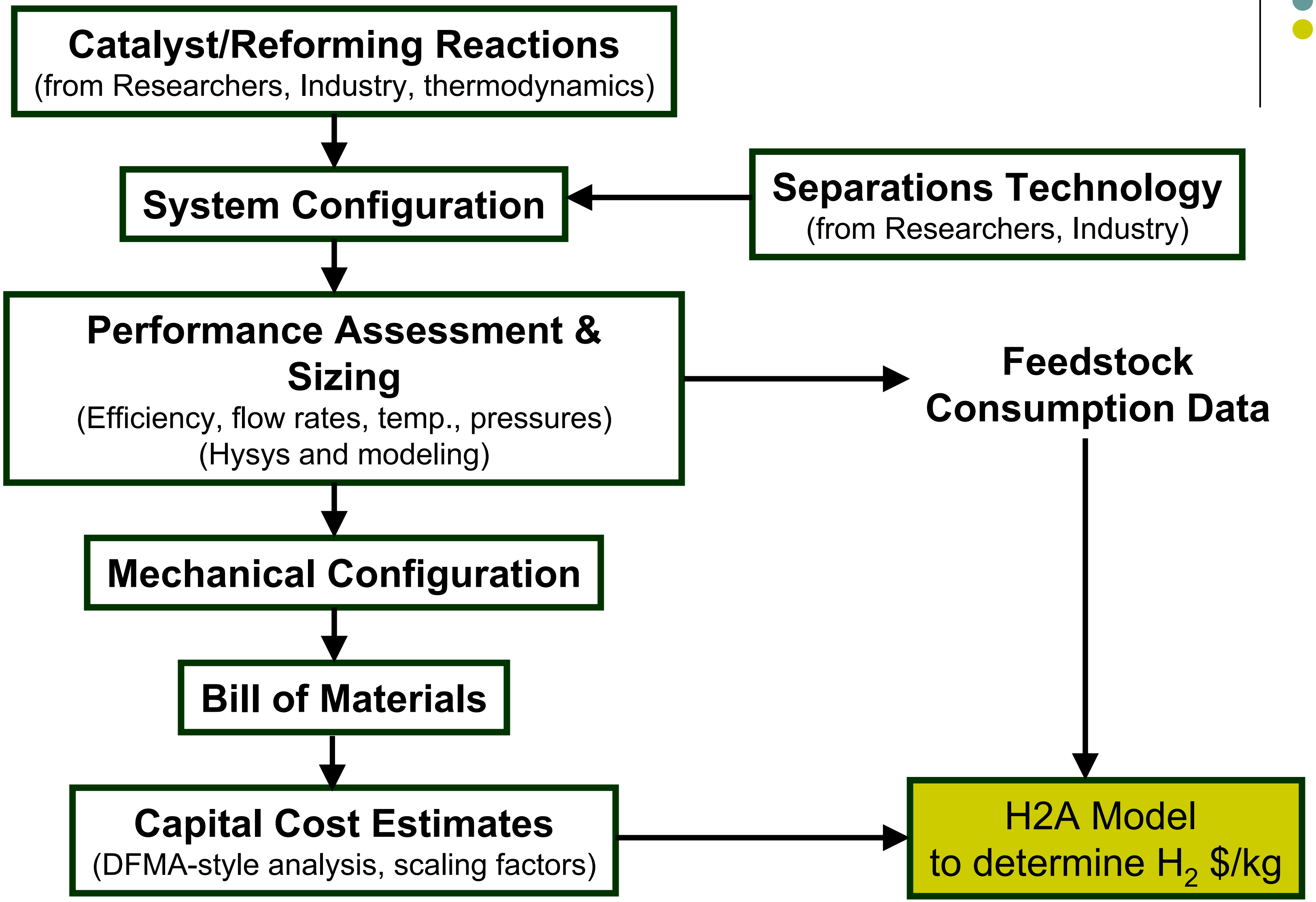
Objective

- Assess cost of H_2 from bio-derived liquids
  - Looking at forecourt scale systems: 100-1500+kg/day
  - Emphasis on Ethanol
  - Looking at both "conventional" and "advanced" systems
- Interaction with the Researchers is bi-directional
  - Researchers help me with catalysts, performance, configurations
  - I can assist Researchers with system studies, configurations, and system performance estimates
- Output of my work will be:
  - System/Configuration Definition
  - Performance specification & optimization
  - Capital cost estimation
  - Projected hydrogen $/kg

Methodology



Ethanol Reforming Hierarchy

Reforming Options

- **Gas Phase**
  - **Steam Reforming**
    - **High Temp** >550°C
      - **"2-Step" Ref.** (ie. methanation followed by SMR)
        - H_2Gen
        - **With WGS**
    - **Med. Temp** 300-550°C
      - **"1-Step" Ref.**
        - PNNL
        - OSU
        - MRT/Linde (fluidized bed)
        - **With or Without WGS**
  - **Partial Oxidation**
    - GE (SCPO)
    - **With WGS**
  - **OTM/ Water-Splitting**
    - ANL
    - **With WGS**
- **Liquid Phase**
  - Virent (sorbitol, glucose, glycerol feedstocks)

H_2 Purification

- **PSA**
- **Separate Membrane Section**
- **Membrane/WGS**
- **Membrane Reactor**

Potential Ethanol SR Reactions

1) C_2H_5OH dehydration to ethylene (C_2H_4) and water

dehydration $C_2H_5OH \rightarrow C_2H_4 + H_2O$

polymerization $C_2H_4 \rightarrow$ coke

2) C_2H_5OH decomposition/cracking to methane (CH_4)

decomposition $C_2H_5OH \rightarrow CH_4 + CO + H_2$

steam reforming $CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$

3) C_2H_5OH dehydrogenation to acetaldehyde (C_2H_4O)

dehydrogenation $C_2H_5OH \rightarrow C_2H_4O + H_2$

decarbonylation $C_2H_4O \rightarrow CH_4 + CO$

steam reforming $CH_4 + H_2O \rightarrow 3H_2 + 2CO$

4) C_2H_5OH decomposition into acetone (CH_3COCH_3)

decomposition $2\ C_2H_5OH \rightarrow CH_3COCH_3 + CO + 3H_2$

steam reforming $CH_3COCH_3 + 2H_2O \rightarrow 5H_2 + 3CO$

5) Steam reforming of C_2H_5OH to syngas ($CO + H_2$)

steam reforming $C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$

6) Water gas shift

7) Methanation

8) Coking from CH_4 (methane)

coking $CH_4 \rightarrow 2H_2 + C$

9) Coking from boudouard reaction

coking $CO_2 \rightarrow O_2 + C$

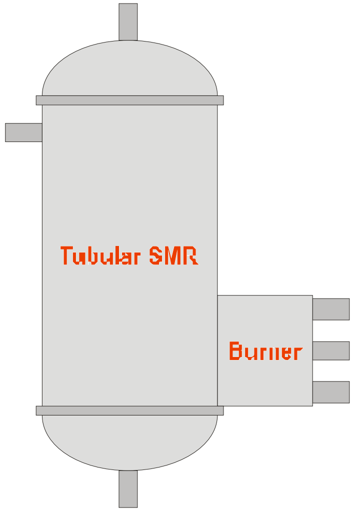
10) Dissociative adsorption of water to form acetic acid (CH_3COOH)

water adsorption $C_2H_5OH + H_2O \rightarrow CH_3COOH + 2H_2$

Neat EtOH or E85/E95?

Reactor Configurations

Tubular Reactor



Annular
Heat Exchange Reactor (HER)

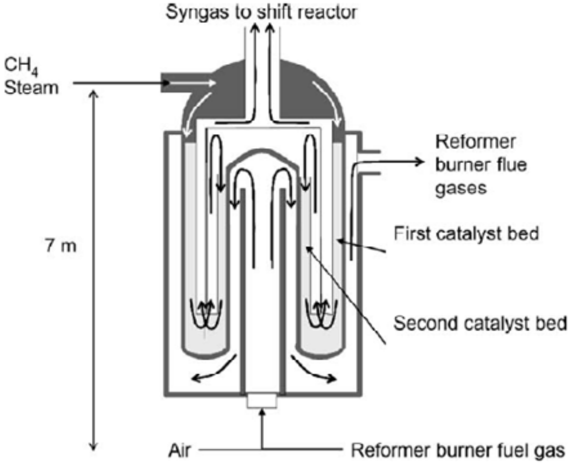
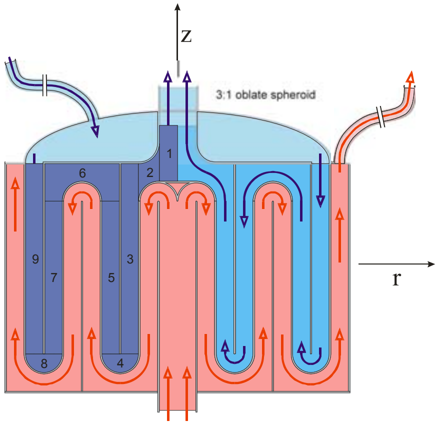


Figure 18: Heat exchange reformer (HER) with annular concentric catalyst bed (170).

[170] Topsoe HTCR Compact Hydrogen Units. Haldor Topsoe A/S. www.haldortopsoe.com (accessed Dec. 2004).



DOE Technical Targets for Dense Metallic Membranes

Flux Rate:	2006 Status	2010 Target	2015 Target
	>200 scfh/ft^2	250 scfh/ft^2	300 scfh/ft^2

Based on:

- 20 psi partial pressure difference
- 15 psig permeate minimum total pressure (preferably >50 psig) (assumed to be pure H_2)
- 400°C

Sievert's Law

$$D = A \cdot \mathcal{P} \cdot (P^{0.5}_{\mathrm{H_2\,Reformate}} - P^{0.5}_{\mathrm{H_2\,Permeate}}) \qquad \text{where permeability } \mathcal{P} = \frac{a}{t} \cdot \exp\left(\frac{-b}{RT}\right)$$

where

D is the hydrogen permeation rate in **scfh**

$\mathcal{P}$ is the permeability, in **scfh/ft^2/atm$^{0.5}$**

A is the membrane effective surface area in **ft^2**

P_{H2} is the hydrogen partial pressure (reformate or permeate streams) in **atm**

t is the thickness of the membrane in **ft**

T is the membrane temperature in °**R**

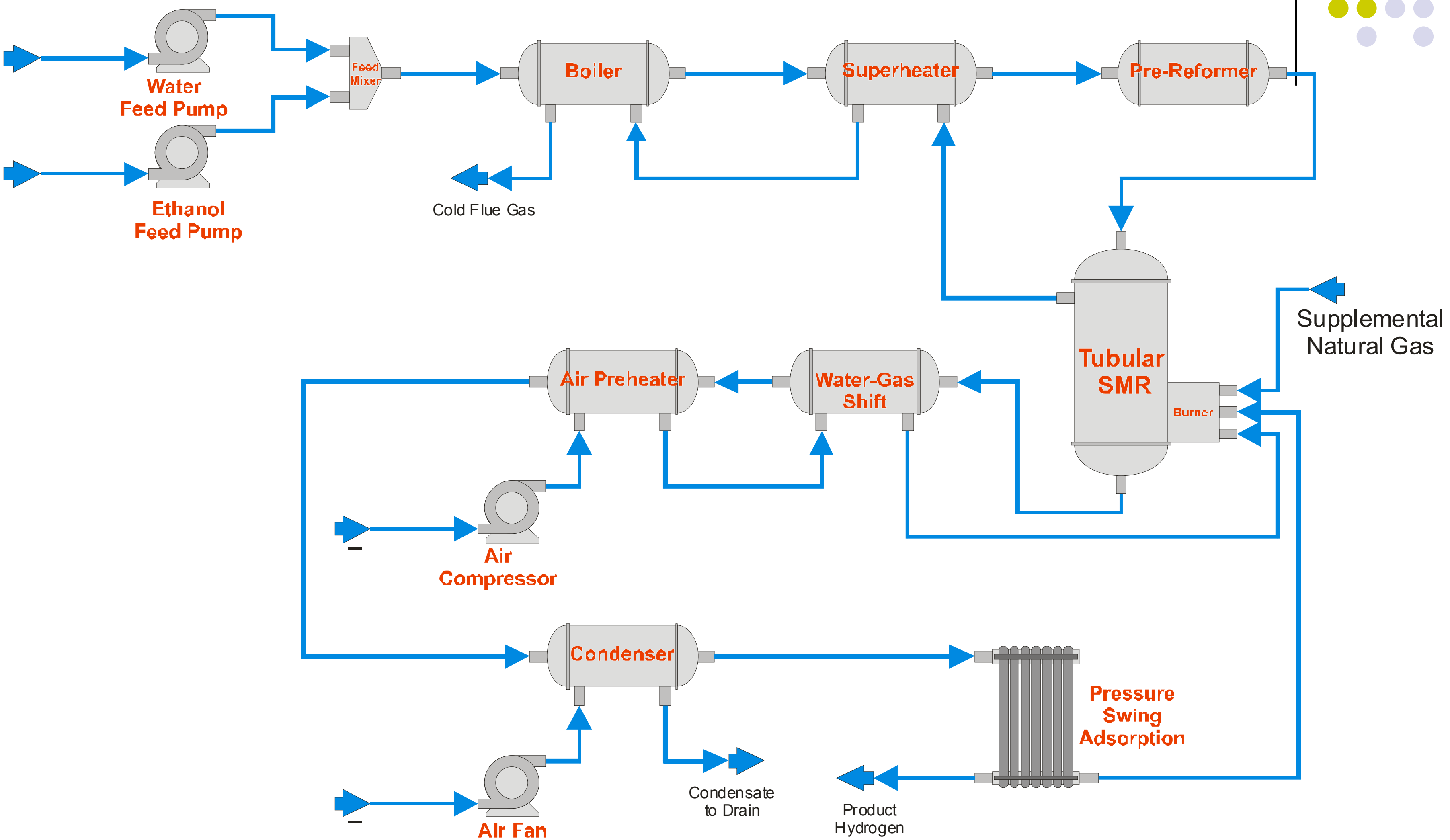
R is the ideal gas constant in **ft^3-atm/°R/lb-mol**

a, b are the empirical constants dependent on the material of the membrane

Therefore implied Permeability Technical Targets are:

Permeability:	2006 Status	2010 Target	2015 Target
	>454 scfh/ft^2/atm$^{0.5}$	567 scfh/ft^2/atm$^{0.5}$	>680 scfh/ft^2/atm$^{0.5}$

Representative Flow Schematic



Configurations Planned for Modeling

Baseline Configuration:

1. Baseline Ethanol System: High temp. SR with pre-reformer & PSA

Advanced Configurations:

Baseline System:

2. - with membrane separation unit
3. - with combined WGS/membrane

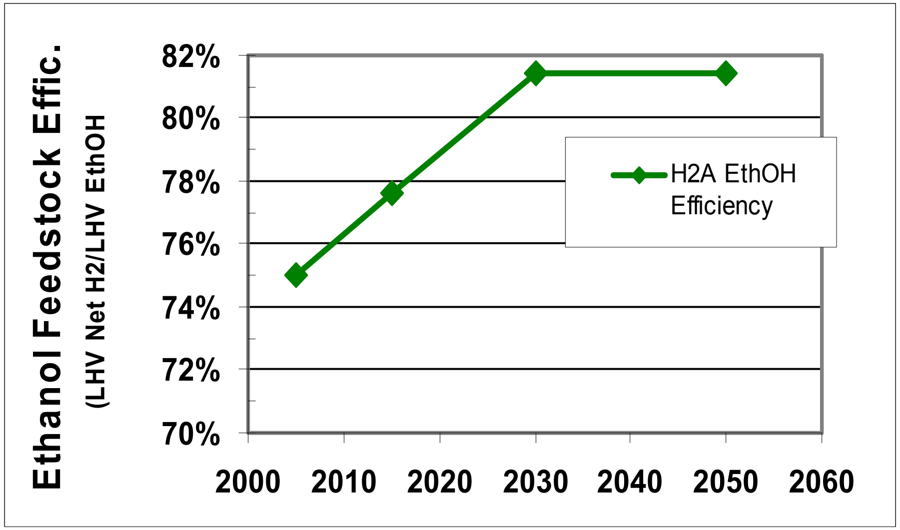
Medium Temperature System:

4. - with PSA
5. - with membrane separation unit
6. - with combined WGS/membrane
7. - with membrane reactor

8. Aqueous Reformer System

Back-up Slides describing previous H2A Ethanol Analysis

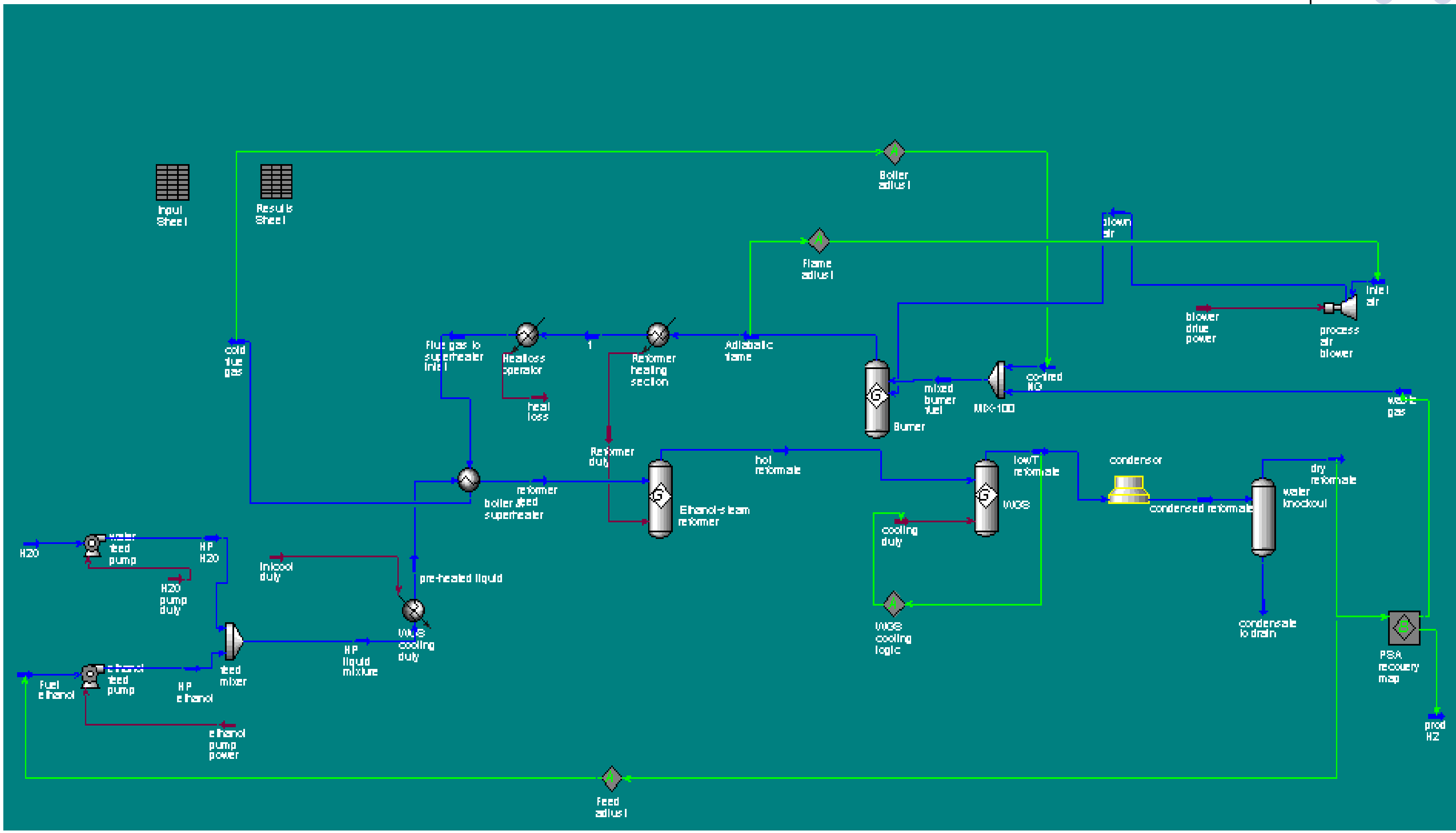
Previous H2A: System Ethanol Feedstock Efficiency (LHV)



Ethanol System Efficiency

	Current/2005 Baseline	Advanced/2015 Baseline	Long Term/2030 Baseline
Ethanol Efficiency (LHV GJH2/GJEthOH)	75.0%	77.6%	81.4%
NG Ratio (LHV GJNG/GJH2)	9.4%	10.0%	10.5%
Overall Energy Efficiciency (LHV GJH2/GJFeedstock)	70.1%	72.0%	75.0%

Previous H2A: Hysys Model of Ethanol System



Previous H2A: Other Key 1.5tpd Forecourt Ethanol Assumptions (for Current system)

Financial

- 10% real after-tax discount rate
- 70% plant utilization
- 20 year system lifetime
- 20 year analysis period
- All values in 2005$

Other Capital Costs (Current)

- H_2 Compressor: $4500/(kg/hr),1500kg/day, 20% installation factor
- H_2 Storage: steel tanks at $818/kg$H_2$, 1193 kg H_2 stored
- H_2 Dispensers: dual hose disp., $22,400 each, 3 needed
- H_2 Safety Equip.: $18,600
- Site prep, Eng. Design, Contingency: $415k

Other Costs (Current)

- Labor: 1232 hours/yr (18h/day, 50% to fueling, 3/8 to H_2 fueling)
- Rent: $0.5/ft^2, 7199ft^2 for H_2 operations
- Maintenance: 5%/3%/1% per yr of prod./compr./stor., $800/yr/dispensor
- Prod. Equip. Refurbishment; 15% of initial cost every 5 yrs, complete replacement in 10yrs
 Dispenser Lifetime: 10 yrs
- Ethanol Price: $1.07/gal

Miscellaneous (Current)

- Combination Gasoline/H2 Dispensing station (3 of 8 dispensers for H_2)

Pump Cost of H_2 from H2A Model (Forecourt EthOH)

	Levelized H_2 Price
Current	$4.40/kg
Advanced	$3.84/kg
Longer-Term	$3.60/kg