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Hydrogen from Natural Gas via Steam Methane Reforming (SMR)

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Updated: January 4, 2015

Energy efficiency of hydrogen from natural gas

- Definition of energy efficiency
- From basic stoichiometry
  - $CH_4 + 2\ H_2O \rightarrow CO_2 + 4\ H_2$
  - Fuel to satisfy the heat requirements
- From “real” processes
  - SMR – Steam methane reforming
  - Water shift reactions
  - Heat integration
  - CO_2 removal or PSA?

Energy Efficiency

- Usable energy out of a process compared to all energy inputs

$$\eta = \frac{\dot{E}_{out}}{\sum\left(\dot{E}_{in}\right)_i}$$

- Energy values could be heat, work, or chemical potential (heating value)
  - HHV (Gross): Fuel + $O_2 \rightarrow CO_2 + H_2O$ (liquid)
  - LHV (Net): Fuel + $O_2 \rightarrow CO_2 + H_2O$ (vapor)

Compound	**GPSA Data Book**		**Derived from Aspen Plus 2006.5**			
	HHV	**LHV**	**HHV**		**LHV**	
	Btu/scf	**Btu/scf**	**kcal/g.mol**	**Btu/scf**	**kcal/g.mol**	**Btu/scf**
Hydrogen	324.2	273.8	68.7	325.9	57.7	273.9
Methane	1010.0	909.4	213.6	1013.1	191.7	909.1
Carbon Monoxide	320.5	320.5	67.6	320.6	67.6	320.6
Carbon Dioxide	0.0	0.0	0.0	0.0	0.0	0.0

- Energy values may have to be discounted when combining different types
  - Should the HHV be discounted when combining with heat values?

Basic Stoichiometery – $CH_4 + 2\ H_2O \rightarrow CO_2 + 4\ H_2$

- Production:

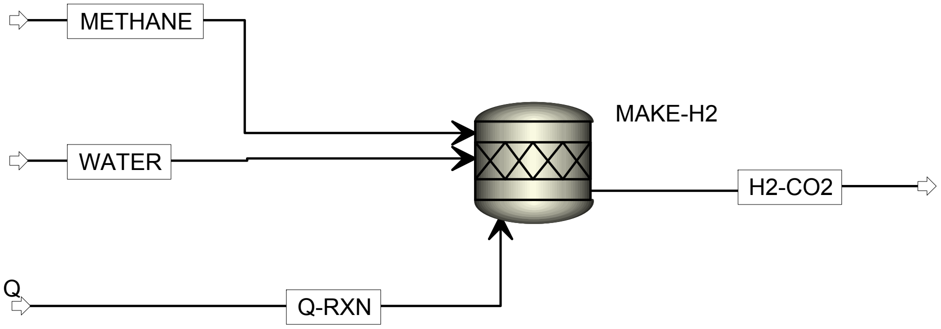
$$\frac{N_{H_2}}{N_{CH_4}} = 4\ \frac{\text{mol}}{\text{mol}}$$

- Apparent efficiency (HHV basis)
  - Just from stoichiometry:

$$\eta = \frac{4 \times 68.7}{1 \times 213.6} = 1.29$$

  - Include heat of reaction:

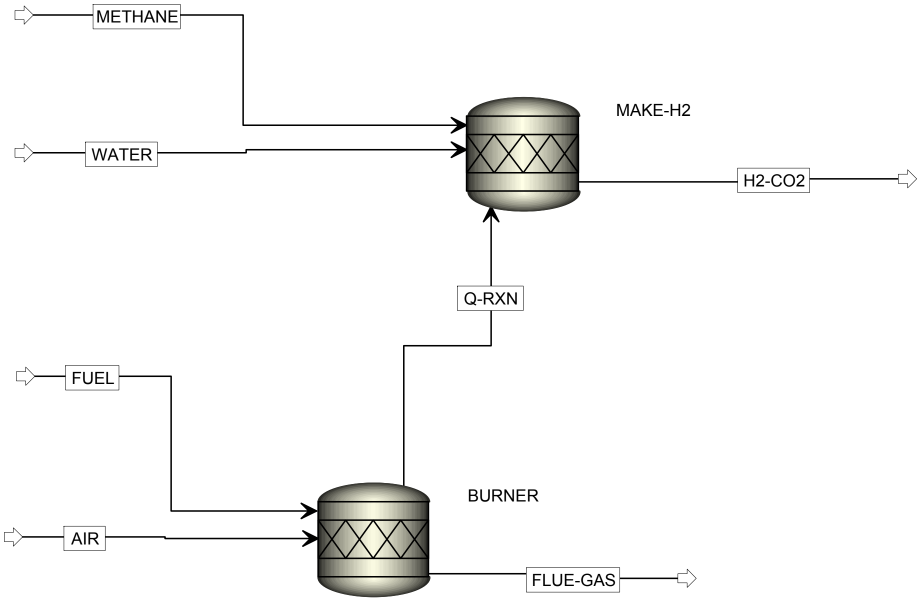
$$\eta = \frac{4 \times 68.7}{1 \times 213.6 + 61.3} = 1.00$$



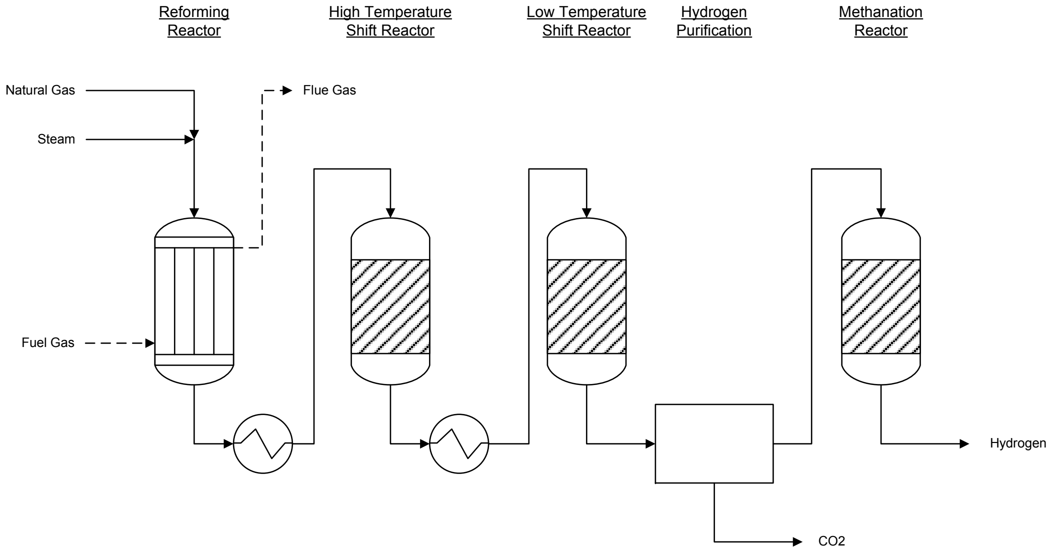
How do we provide the heat of reaction?

- Could use additional methane – 0.29 mol fuel/mol reactant (HHV basis)
- Production: $$\frac{N_{H_2}}{N_{CH_4}} = \frac{4}{1+0.29} = 3.1\,\frac{\text{mol}}{\text{mol}}$$
- Efficiency including fuel (HHV basis)

$$\eta = \frac{4\times 68.7}{1.29\times 213.6} = 1.0$$



Steam Methane Reforming & Water Gas Shift



- *Reforming*. Endothermic catalytic reaction, typically 20-30 atm & 800-880° C (1470-1615° F) outlet.

$$CH_4 + H_2O \leftrightarrow CO + 3\ H_2$$

- *Shift conversion*. Exothermic fixed-bed catalytic reaction, possibly in two steps.

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

HTS: 345-370° C (650 – 700°F)
LTS: 230° C (450°F)

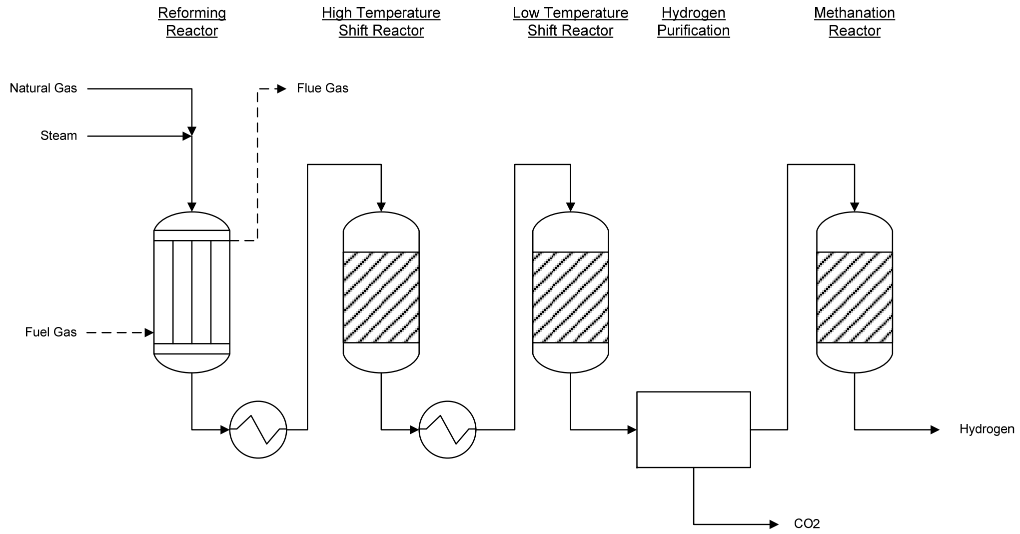
- *Gas Purification*. Absorb CO_2 (amine) or separate into pure H_2 stream (PSA or membrane).
- *Methanation*. Convert residual CO & CO2 back to methane. Exothermic fixed-bed catalytic reactions at 370-425° C (700 – 800°F).

$$CO + 3\ H_2 \leftrightarrow CH_4 + H_2O$$

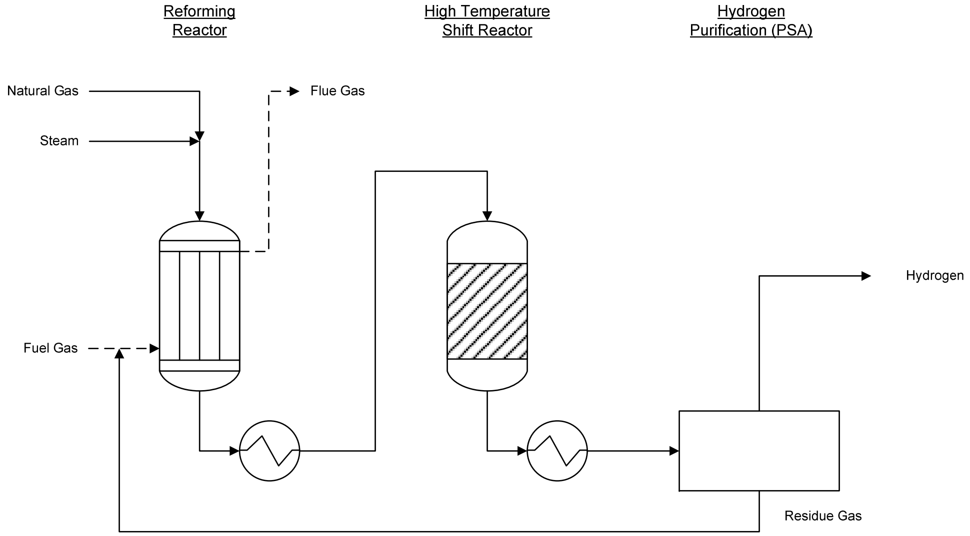
$$CO_2 + 4\ H_2 \leftrightarrow CH_4 + 2\ H_2O$$

SMR Alternate Designs

- Traditional with 2 stages shift reactors – 95% to 98% purity



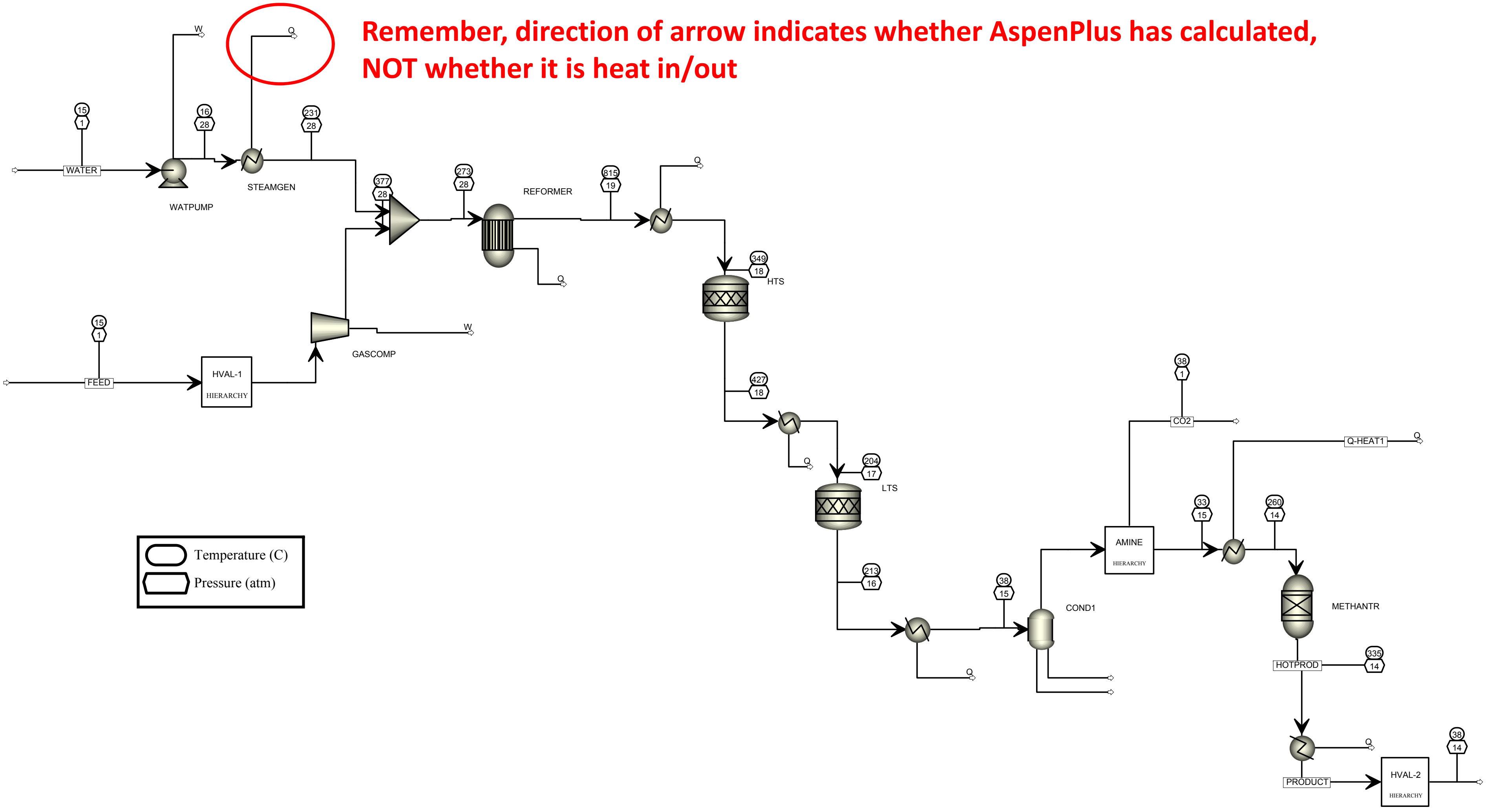
- Newer designs with PSA (Pressure Swing Adsorption) – lower capital costs, lower conversion, but very high purity (99%+)



Process Considerations

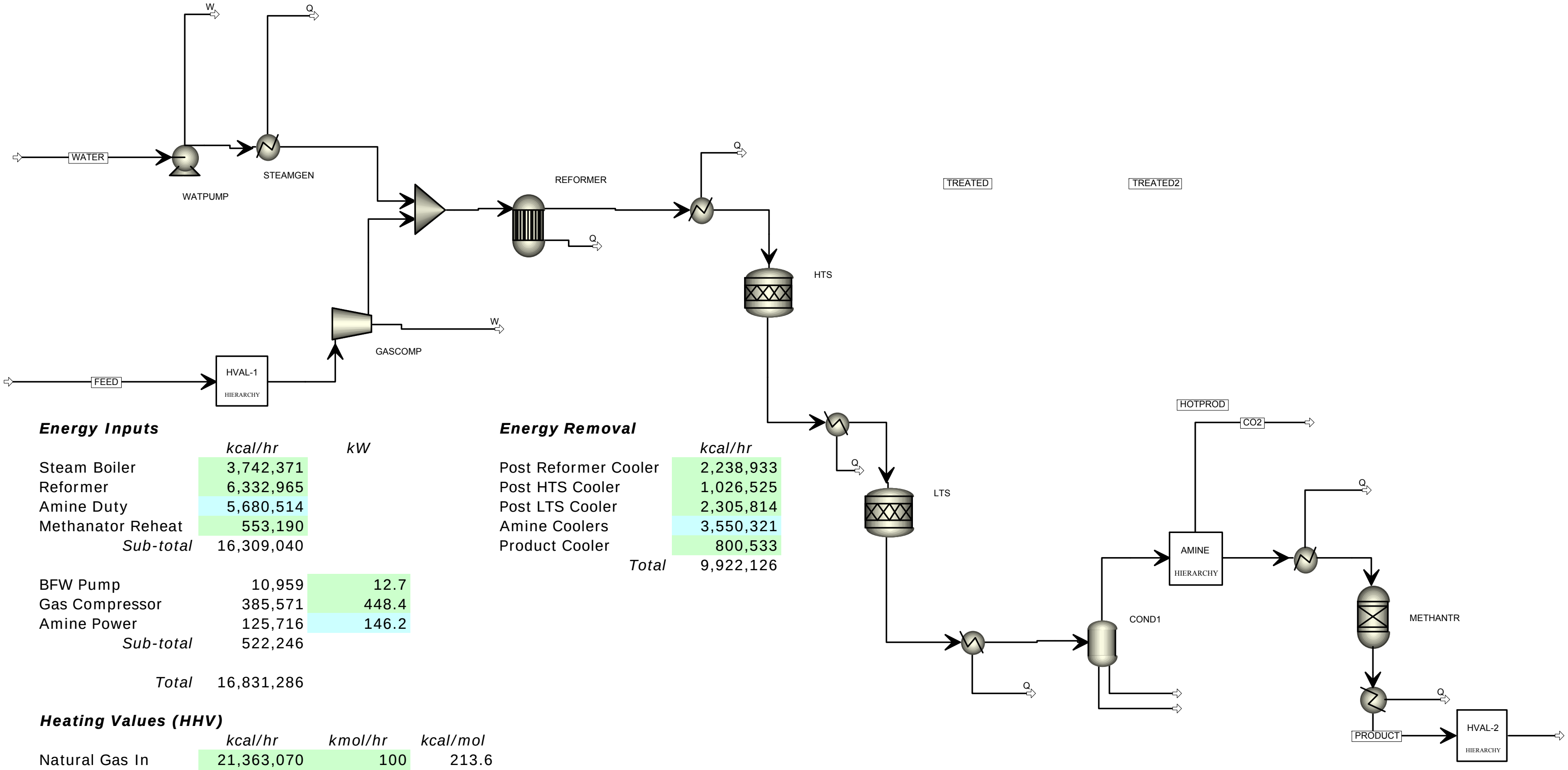
	Kaes [2000]	**Molburg & Doctor [2003]**	**Nexant Report [2006]**	**Other**
Desulfurization Reactors	Model as conversion reactor Small temperature increase	Model as equilibrium reactor. Sulfur compounds converted to H_2S & adsorbed in ZnO bed. 500 - 800°F depending on technology. 700°F most typical. Typically up to 725 psi (50 bar)		
Reformer	1450 - 1650°F exit Equilibrium Gibbs reactor with 20°F approach (for design).	1500°F Model as equilibrium reactor.	20 - 30 atm (295 - 440 psia) 850-1000°F (455-540°C) inlet 1470-1615°F (800-880°C) outlet	
High Temperature Shift Reactor	650 - 700°F entrance for HTS + LTS 500 - 535°F entrance when no LTS Equilibrium Gibbs reactor All components inert except CO, H_2O, CO_2, & H_2.	660°F entrance Fixed 90% CO conversion	940°F (504°C) inlet	
Low Temperature Shift Reactor	400 - 450°F entrance Equilibrium Gibbs reactor All components inert except CO, H_2O, CO_2, & H_2.	400°F entrance Fixed 90% CO conversion	480-525°F (249-274°C) outlet	
Methanation	500 - 550°F entrance Equilibrium Gibbs reactor All components inert except CH_4, CO, H_2O, CO_2, & H_2.			
Amine Purification	Model as component splitter Treated gas 10 - 15°F increase, 5 - 10 psi decrease, water saturated	Model as component splitter Treated gas 100°F & 230 psi (16 bar) exit 95% CO_2 recovery		MDEA circulation, duty, & work estimates from GPSA Data Book Rejected CO_2 atmospheric pressure & water saturated
PSA	Model as component splitter 100°F entrance H_2 purity as high as 99.999%	Model as component splitter 90% H_2 recovered H_2 contains 0.001% product stream as contaminant		75 - 85% recovery for "reasonable" capital costs (higher requires more beds) 200 - 400 psig feed pressure for refinery applications 4:1 minimum feed:purge gas ratio. Purge gas typically 2 - 5 psig.

Basic SMR Process



Remember, direction of arrow indicates whether AspenPlus has calculated, NOT whether it is heat in/out

SMR Basic Process Energy Requirements



Energy Inputs

	kcal/hr	*kW*
Steam Boiler	3,742,371	
Reformer	6,332,965	
Amine Duty	5,680,514	
Methanator Reheat	553,190	
Sub-total	16,309,040	
BFW Pump	10,959	12.7
Gas Compressor	385,571	448.4
Amine Power	125,716	146.2
Sub-total	522,246	
Total	16,831,286	

Energy Removal

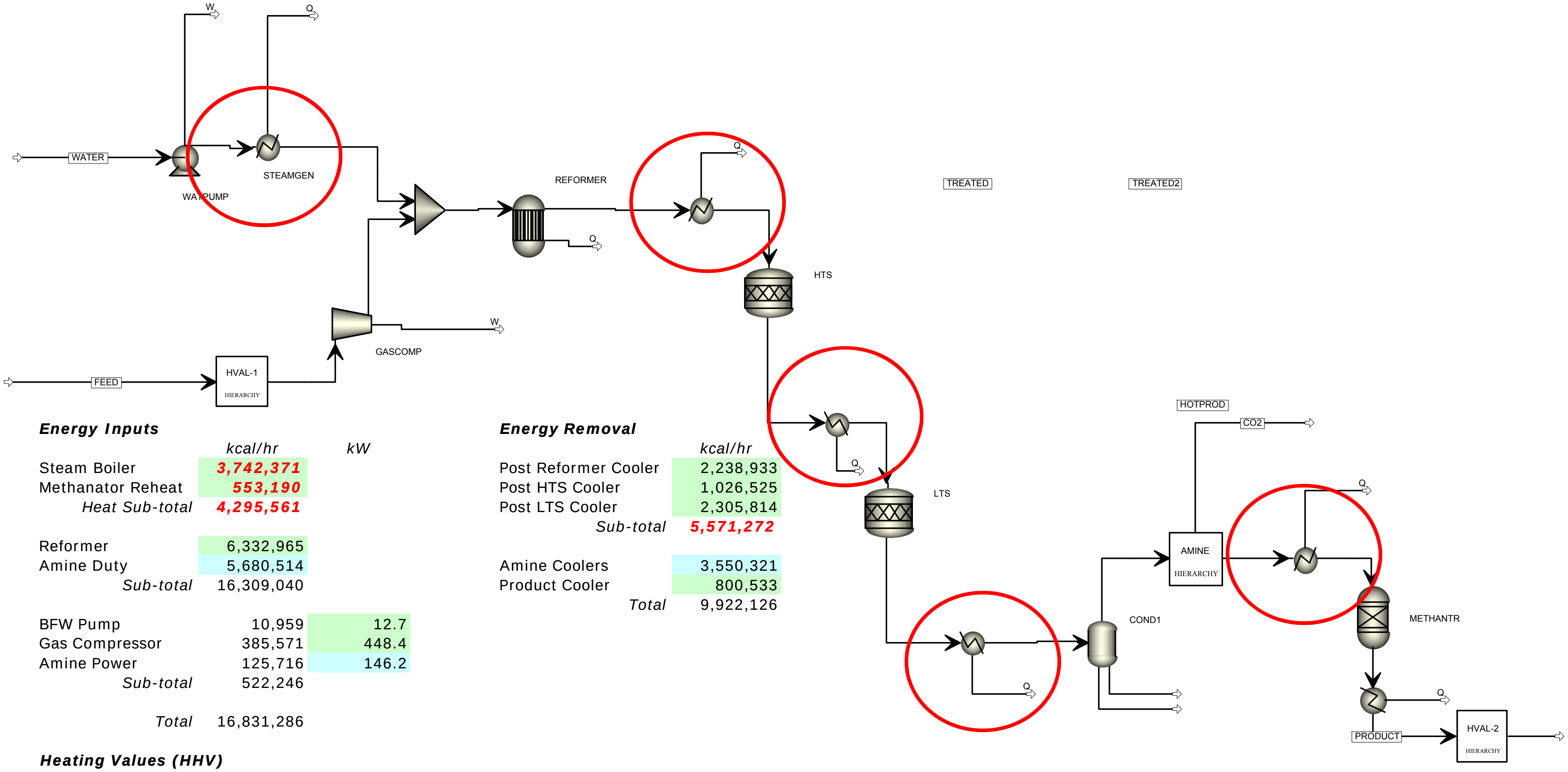
	kcal/hr
Post Reformer Cooler	2,238,933
Post HTS Cooler	1,026,525
Post LTS Cooler	2,305,814
Amine Coolers	3,550,321
Product Cooler	800,533
Total	9,922,126

Heating Values (HHV)

	kcal/hr	*kmol/hr*	*kcal/mol*
Natural Gas In	21,363,070	100	213.6
Product Out	25,938,163	328.6	78.9
H2 Out		292.7	
	H2 Purity:	**89%**	
	H2 Production:	**2.9**	

Total Product	**25,938,163**
Total Inputs	**38,194,356**
Efficiency	**68%**

SMR – Heat Recovery for Steam Generation



Energy Inputs

	kcal/hr	*kW*
Steam Boiler	***3,742,371***	
Methanator Reheat	***553,190***	
Heat Sub-total	***4,295,561***	
Reformer	6,332,965	
Amine Duty	5,680,514	
Sub-total	16,309,040	
BFW Pump	10,959	12.7
Gas Compressor	385,571	448.4
Amine Power	125,716	146.2
Sub-total	522,246	
Total	16,831,286	

Energy Removal

	kcal/hr
Post Reformer Cooler	2,238,933
Post HTS Cooler	1,026,525
Post LTS Cooler	2,305,814
Sub-total	***5,571,272***
Amine Coolers	3,550,321
Product Cooler	800,533
Total	9,922,126

Heating Values (HHV)

	kcal/hr	*kmol/hr*	*kcal/mol*
Natural Gas In	21,363,070	100	213.6
Product Out	25,938,163	328.6	78.9
H2 Out		292.7	
	H2 Purity:	**89%**	
	H2 Production:	**2.9**	

Total Product	**25,938,163**
Net Inputs	**33,898,795**
Efficiency	***77%***

Reformer Furnace Design

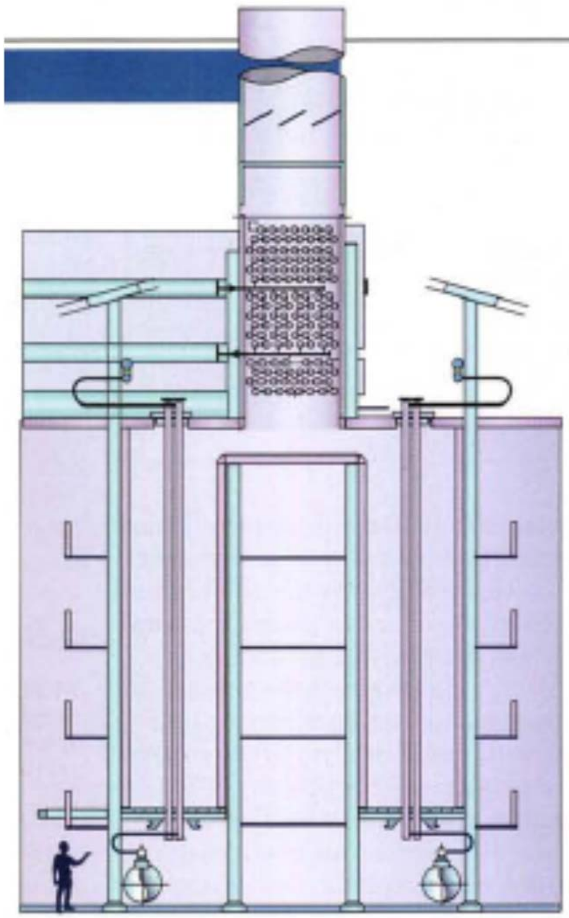


FIGURE 3. A typical reformer furnace could have over 300 burners

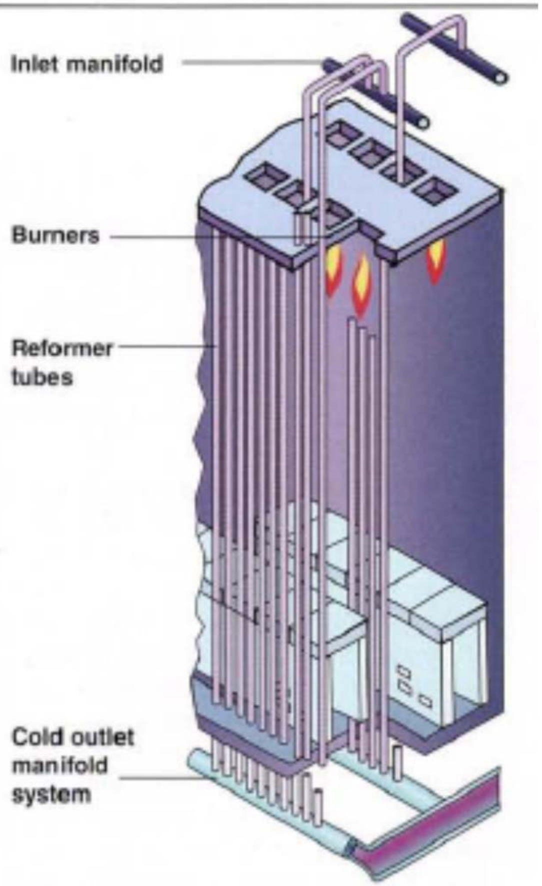
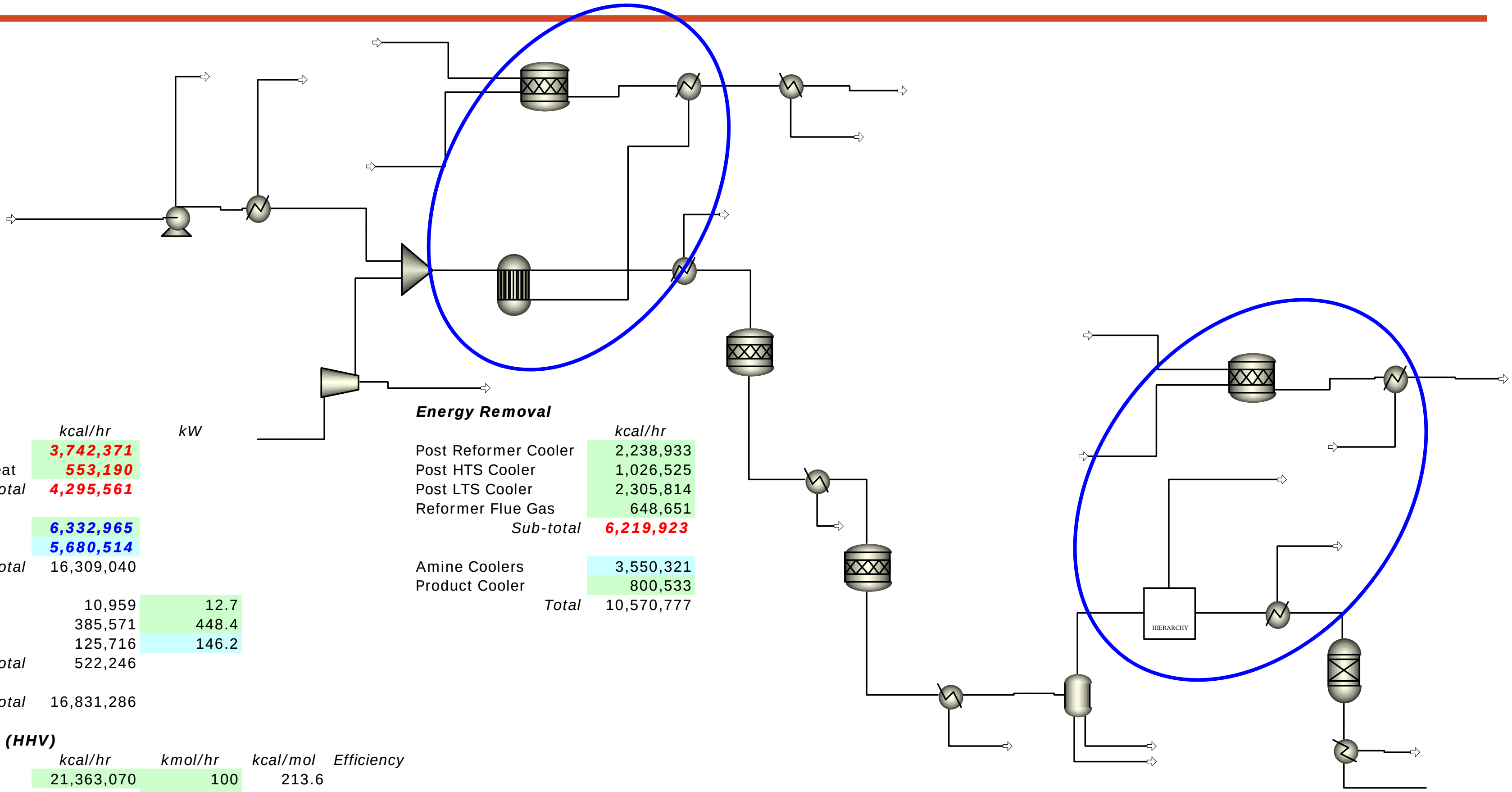


FIGURE 4. Hydrogen plants with single heaters and capacities up to 100,000

"Hydrogen Production by Steam Reforming"
Ray Elshout, *Chemical Engineering*, May 2010

Direct Fired Heaters for Reformer & Amine Unit



Energy Inputs

	kcal/hr	*kW*
Steam Boiler	***3,742,371***	
Methanator Reheat	***553,190***	
Heat Sub-total	***4,295,561***	
Reformer	***6,332,965***	
Amine Duty	***5,680,514***	
Sub-total	16,309,040	
BFW Pump	10,959	12.7
Gas Compressor	385,571	448.4
Amine Power	125,716	146.2
Sub-total	522,246	
Total	16,831,286	

Energy Removal

	kcal/hr
Post Reformer Cooler	2,238,933
Post HTS Cooler	1,026,525
Post LTS Cooler	2,305,814
Reformer Flue Gas	648,651
Sub-total	***6,219,923***
Amine Coolers	3,550,321
Product Cooler	800,533
Total	10,570,777

Heating Values (HHV)

	kcal/hr	*kmol/hr*	*kcal/mol*	*Efficiency*
Natural Gas In	21,363,070	100	213.6	
Reformer Fuel Gas	***8,184,406***	38.3	213.6	77%
Amine Unit Fuel Gas	***6,659,083***	31.2	213.6	85%
Total	36,206,559	169.5		
Product Out	25,938,163	328.6	78.9	
H2 Out		292.7		
	H2 Purity:	**89%**		
	H2 Production:	**1.7**		

Total Product	**25,938,163**
Net Inputs	**36,728,805**
Efficiency	***71%***

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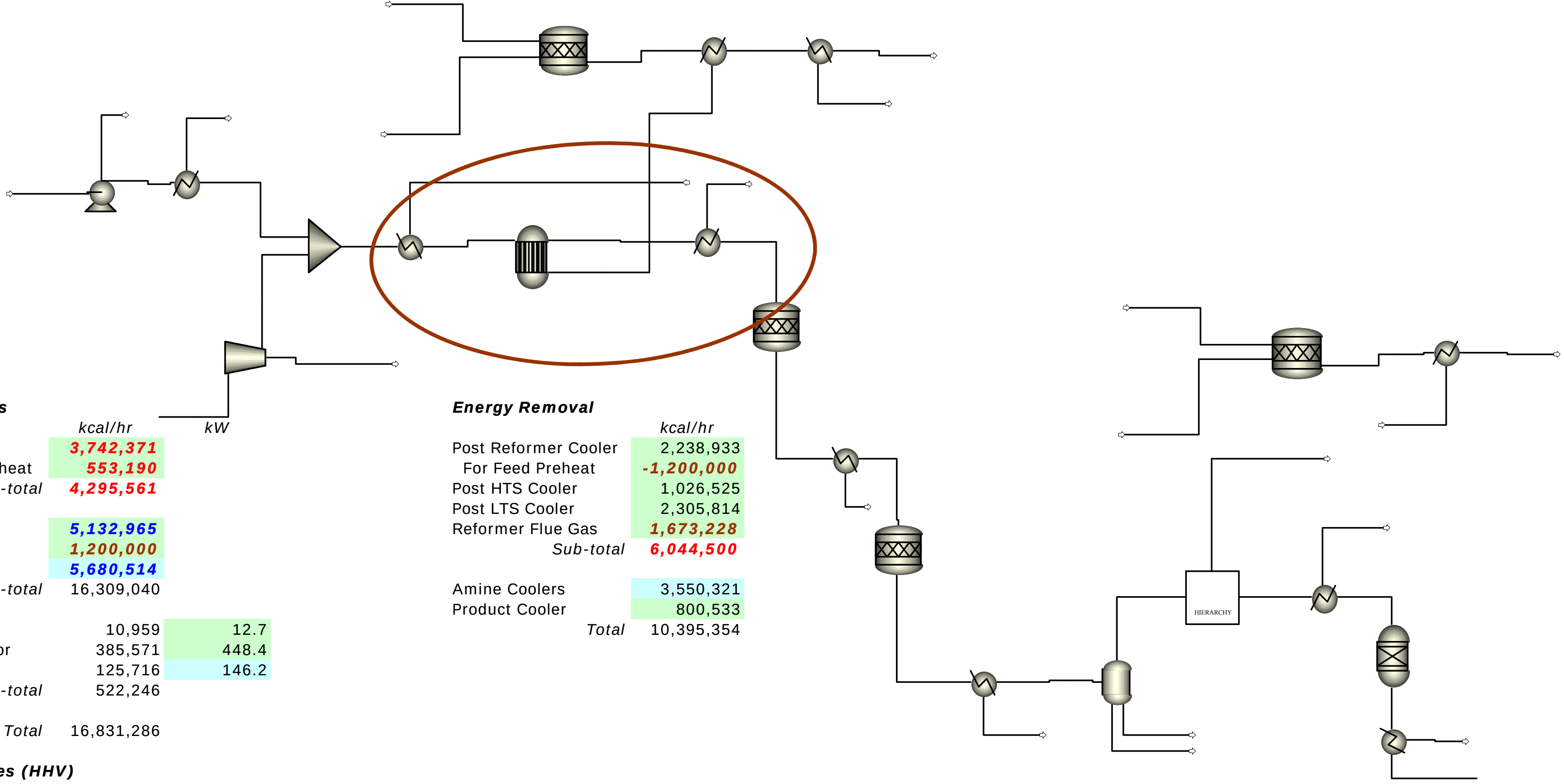
Pre-Heat the Reformer Feed?



Energy Inputs

	kcal/hr	*kW*
Steam Boiler	***3,742,371***	
Methanator Reheat	***553,190***	
Heat Sub-total	***4,295,561***	
Reformer	***5,132,965***	
Feed Preheat	***1,200,000***	
Amine Duty	***5,680,514***	
Sub-total	16,309,040	
BFW Pump	10,959	12.7
Gas Compressor	385,571	448.4
Amine Power	125,716	146.2
Sub-total	522,246	
Total	16,831,286	

Energy Removal

	kcal/hr
Post Reformer Cooler	2,238,933
For Feed Preheat	***-1,200,000***
Post HTS Cooler	1,026,525
Post LTS Cooler	2,305,814
Reformer Flue Gas	***1,673,228***
Sub-total	***6,044,500***
Amine Coolers	3,550,321
Product Cooler	800,533
Total	10,395,354

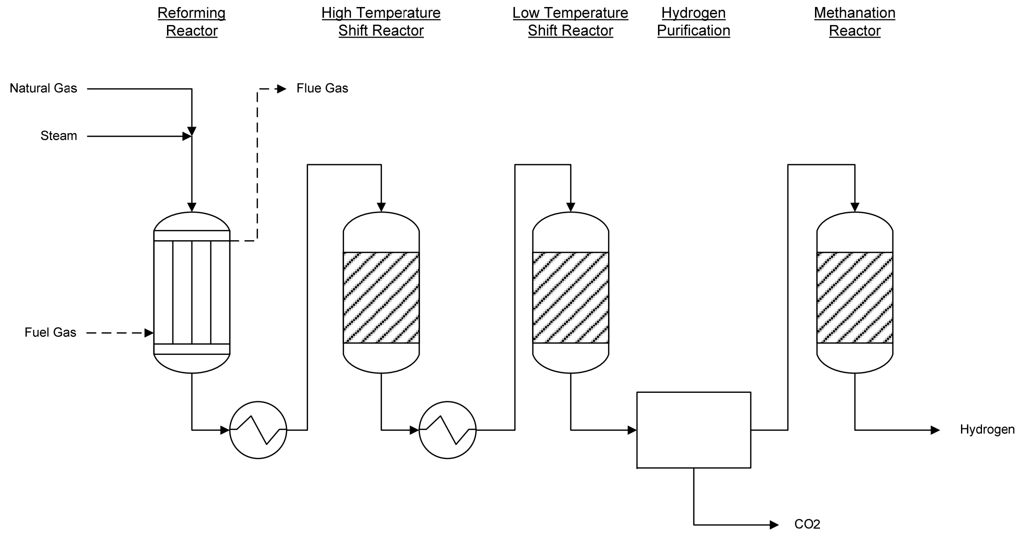
Heating Values (HHV)

	kcal/hr	*kmol/hr*	*kcal/mol*	*Efficiency*
Natural Gas In	21,363,070	100	213.6	
Reformer Fuel Gas	***7,978,680***	37.3	213.6	***64%***
Amine Unit Fuel Gas	***6,659,083***	31.2	213.6	85%
Total	36,000,833	168.5		
Product Out	25,938,163	328.6	78.9	
H2 Out		292.7		
H2 Purity:		**89%**		
H2 Production:		**1.7**		

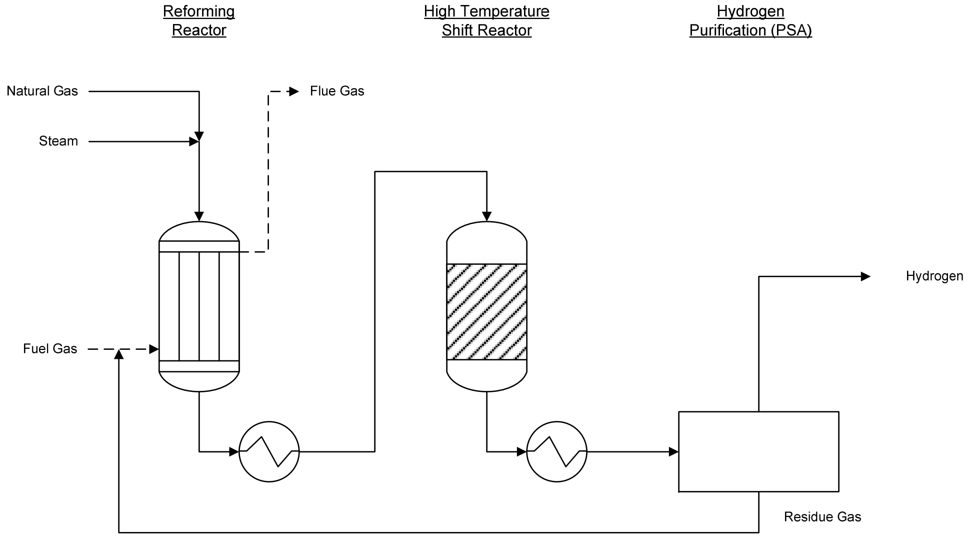
Total Product	**25,938,163**
Net Inputs	**36,523,078**
Efficiency	***71%***

SMR Alternate Designs

- Traditional with 2 stages shift reactors – 95% to 98% purity



- Newer designs with PSA (Pressure Swing Adsorption) – lower capital costs, lower conversion, but very high purity (99%+)



Alternate Hydrogen Purification Processes

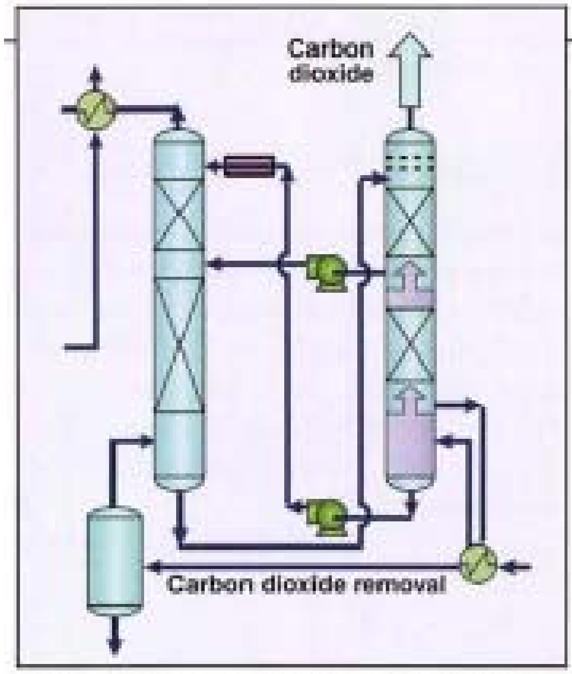


FIGURE 5. Most older units remove carbon dioxide from the hydrogen-rich gas with a solvent

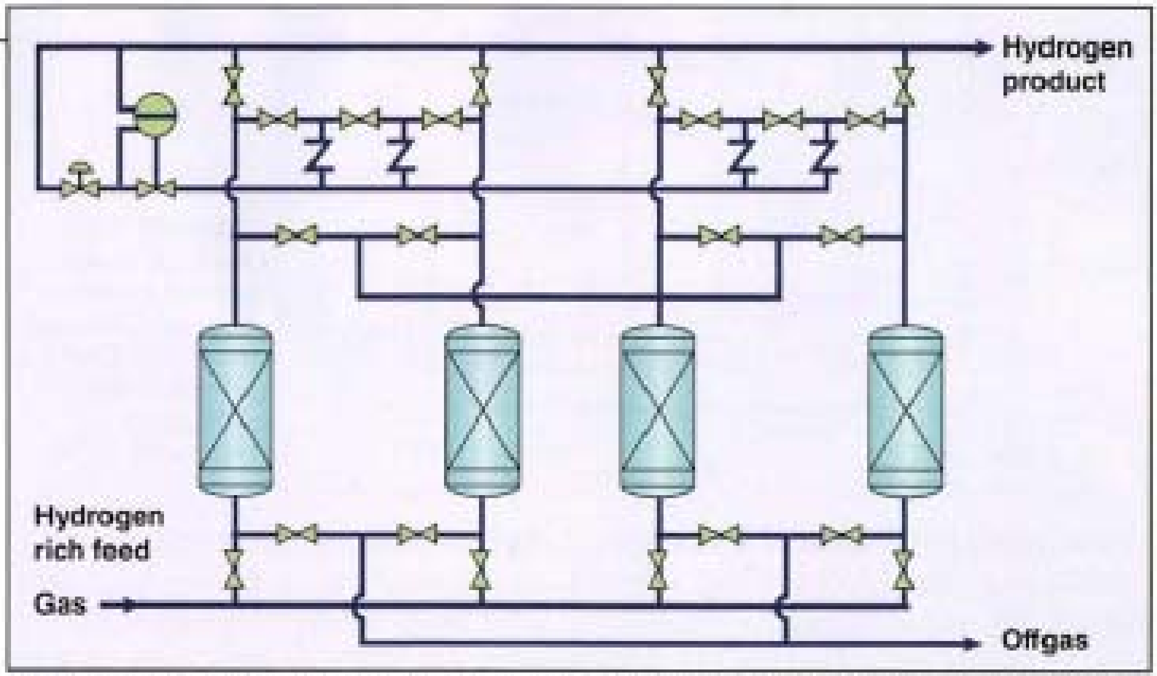
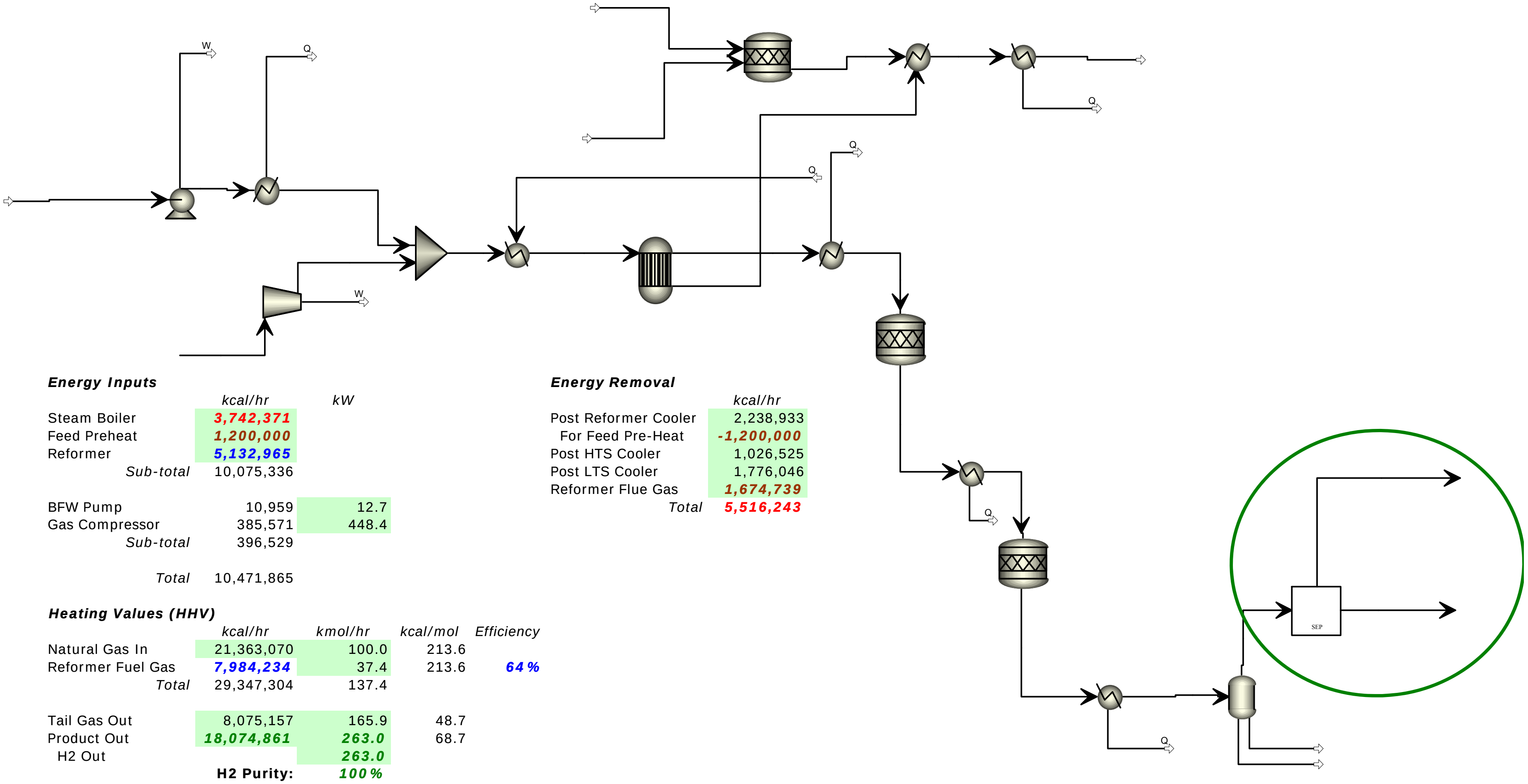


FIGURE 6. A PSA unit separates carbon monoxide, carbon dioxide and unconverted hydrocarbons from hydrogen. Adsorbers operate in a high-pressure to low-pressure cycle to adsorb and then release contaminants

"Hydrogen Production by Steam Reforming"
Ray Elshout, *Chemical Engineering*, May 2010

Use of PSA for Product Purification



Energy Inputs

	kcal/hr	*kW*
Steam Boiler	***3,742,371***	
Feed Preheat	***1,200,000***	
Reformer	***5,132,965***	
Sub-total	10,075,336	
BFW Pump	10,959	12.7
Gas Compressor	385,571	448.4
Sub-total	396,529	
Total	10,471,865	

Energy Removal

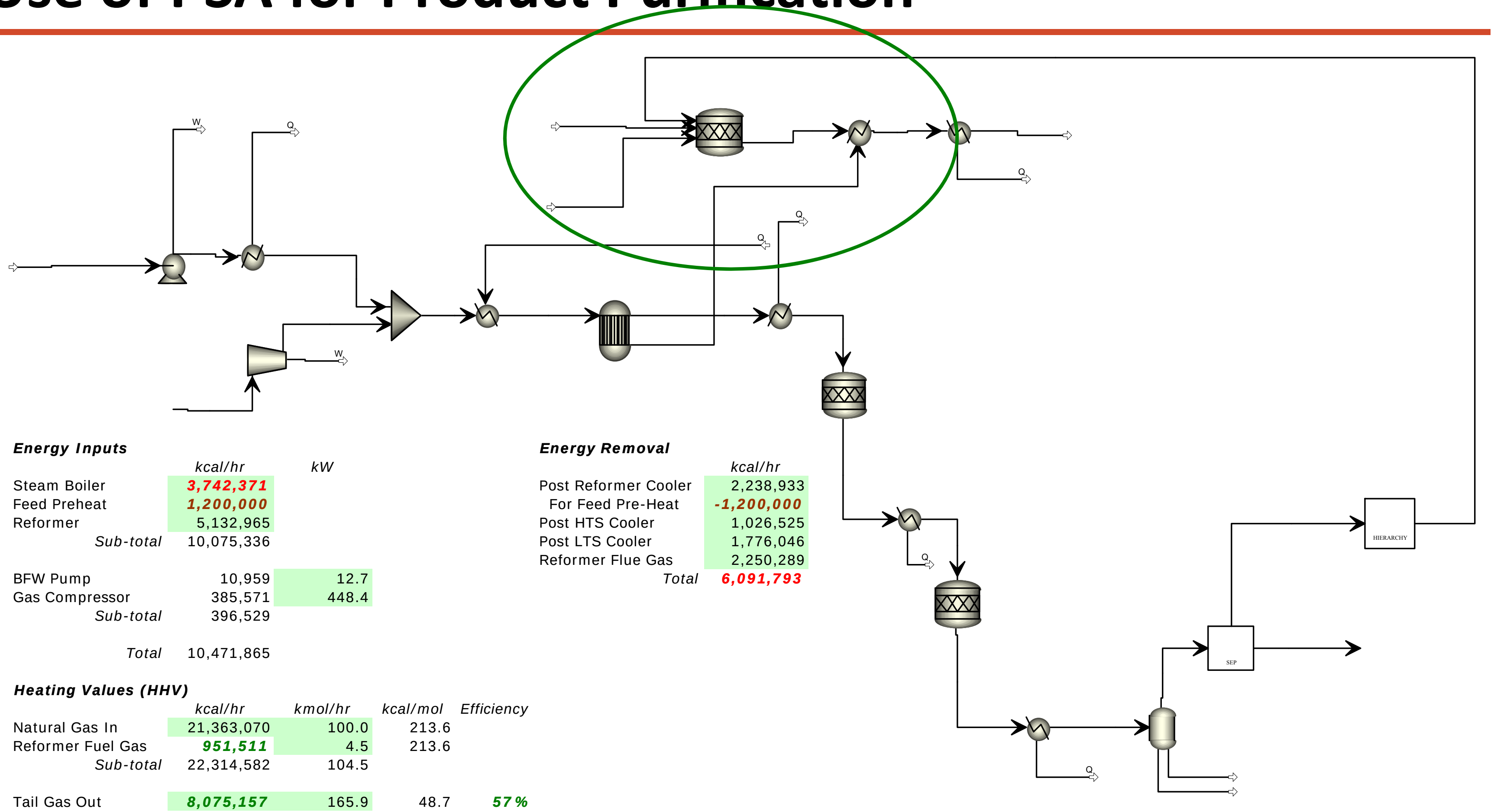
	kcal/hr
Post Reformer Cooler	2,238,933
For Feed Pre-Heat	***-1,200,000***
Post HTS Cooler	1,026,525
Post LTS Cooler	1,776,046
Reformer Flue Gas	***1,674,739***
Total	***5,516,243***

Heating Values (HHV)

	kcal/hr	*kmol/hr*	*kcal/mol*	*Efficiency*
Natural Gas In	21,363,070	100.0	213.6	
Reformer Fuel Gas	***7,984,234***	37.4	213.6	***64%***
Total	29,347,304	137.4		
Tail Gas Out	8,075,157	165.9	48.7	
Product Out	***18,074,861***	***263.0***	68.7	
H2 Out		***263.0***		
H2 Purity:		***100%***		
H2 Production:		**1.9**		

Total Product	**18,074,861**
Total Inputs	**29,743,834**
Efficiency	***61%***

Use of PSA for Product Purification



Energy Inputs

	kcal/hr	*kW*
Steam Boiler	***3,742,371***	
Feed Preheat	***1,200,000***	
Reformer	5,132,965	
Sub-total	10,075,336	
BFW Pump	10,959	12.7
Gas Compressor	385,571	448.4
Sub-total	396,529	
Total	10,471,865	

Energy Removal

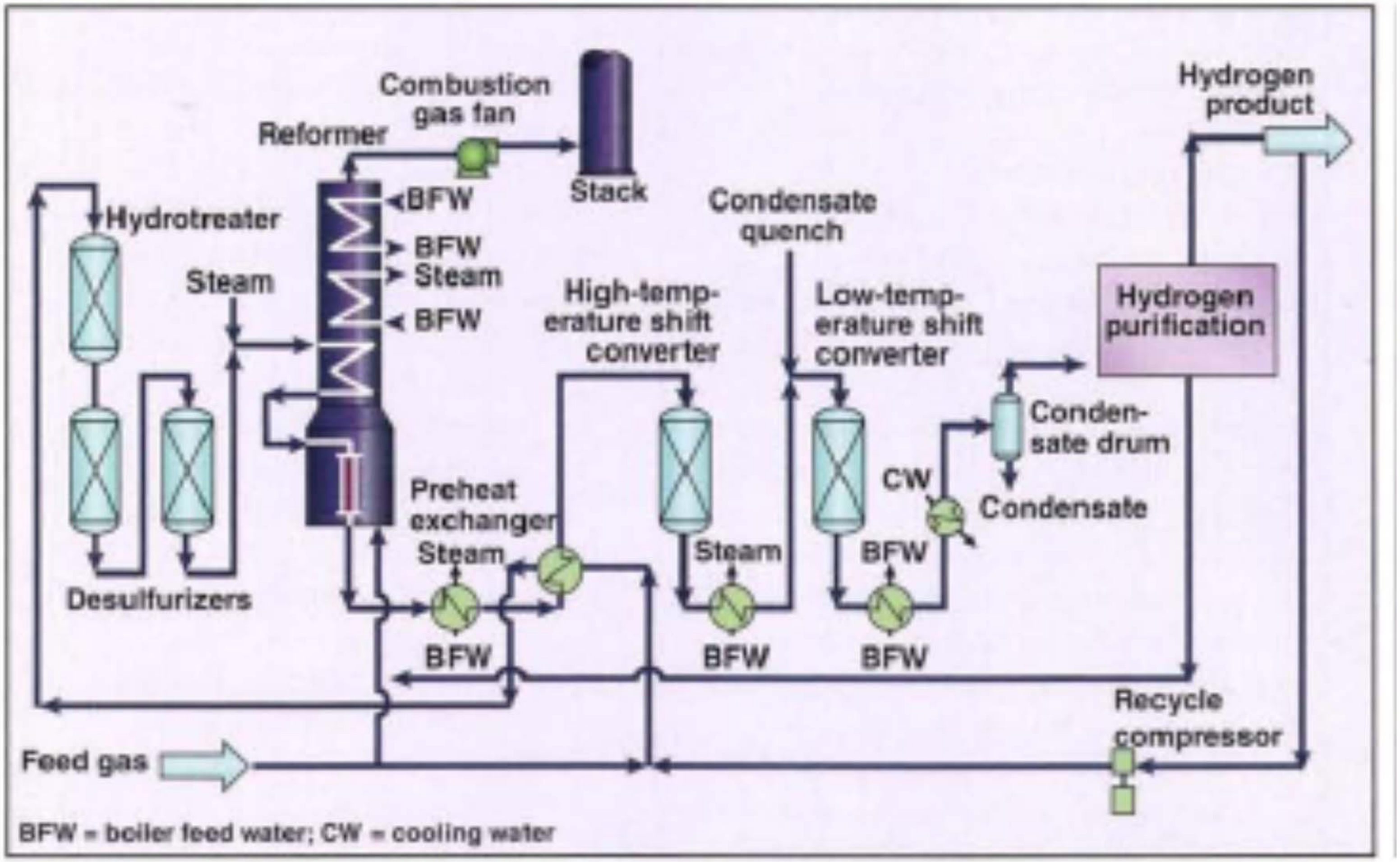
	kcal/hr
Post Reformer Cooler	2,238,933
For Feed Pre-Heat	***-1,200,000***
Post HTS Cooler	1,026,525
Post LTS Cooler	1,776,046
Reformer Flue Gas	2,250,289
Total	***6,091,793***

Heating Values (HHV)

	kcal/hr	*kmol/hr*	*kcal/mol*	*Efficiency*
Natural Gas In	21,363,070	100.0	213.6	
Reformer Fuel Gas	***951,511***	4.5	213.6	
Sub-total	22,314,582	104.5		
Tail Gas Out	***8,075,157***	165.9	48.7	***57%***
Total	30,389,739			
Product Out	18,074,861	263.0	68.7	
H2 Out		263.0		
	H2 Purity:	**100%**		
	H2 Production:	**2.5**		

Total Product	**18,074,861**
Total Inputs	**22,711,111**
Efficiency	***80%***

Integrated Process



"Hydrogen Production by Steam Reforming"
Ray Elshout, *Chemical Engineering*, May 2010

What should be the price of hydrogen?

- Hydrogen sales should cover all costs plus profit
  - Raw material costs (primarily natural gas)
  - Electricity
  - Other operating expenses (staff, …)
  - Recovery of capital invested
- Minimum is to cover cost of natural gas & power

- Example
  - Natural gas \$4.36 per million BTU (as of March 30, 2011) = \$3.68 per kmol CH_4
  - Electricity 6.79 ¢/kW-hr (for 2010 per EIA for Industrial customers)
  - PSA production scenario
    - 104.5 kmol/hr $CH_4 \rightarrow$ \$385 per hr
    - 461.1 kW $\rightarrow$ \$31 per hr
    - 263 kmol/hr $H_2 \rightarrow$ \$0.79 per kg
  - Electrolysis comparison – 80% electrolysis efficiency & 90% compression efficiency
    - \$3.80 per kg
      - \$6.80 per kg with capital costs included

A Realistic Look at Hydrogen Price Projections, F. David Doty
Mar. 11, 2004 (updated Sept 21, 2004)

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