



COLORADO SCHOOL OF MINES



Hydrogen from Natural Gas via Steam Methane Reforming (SMR)

John Jechura – jjechura@mines.edu
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Energy efficiency of hydrogen from natural gas

- Definition of energy efficiency
- From basic stoichiometry
 - $\text{CH}_4 + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4 \text{H}_2$
 - 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

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

- Energy values could be heat, work, or chemical potential (heating value)
 - HHV (Gross): Fuel + O₂ → CO₂ + H₂O (liquid)
 - LHV (Net): Fuel + O₂ → CO₂ + H₂O (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 Stoichiometry – $\text{CH}_4 + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4 \text{H}_2$

- Production:

$$\frac{N_{\text{H}_2}}{N_{\text{CH}_4}} = 4 \frac{\text{mol}}{\text{mol}}$$

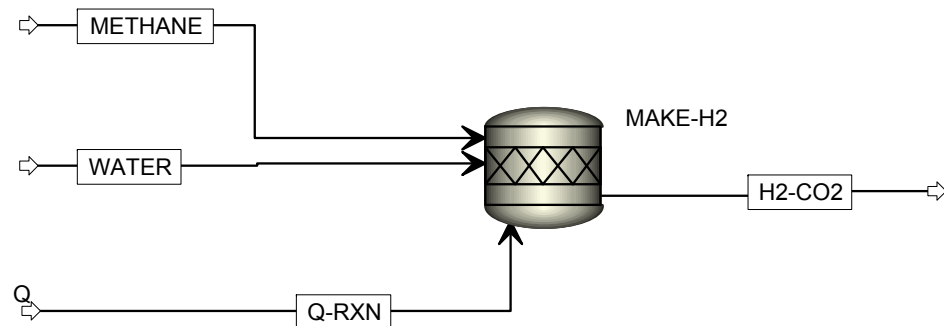
- Apparent efficiency (HHV basis)

- Just from stoichiometry:

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

- Include heat of reaction:

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



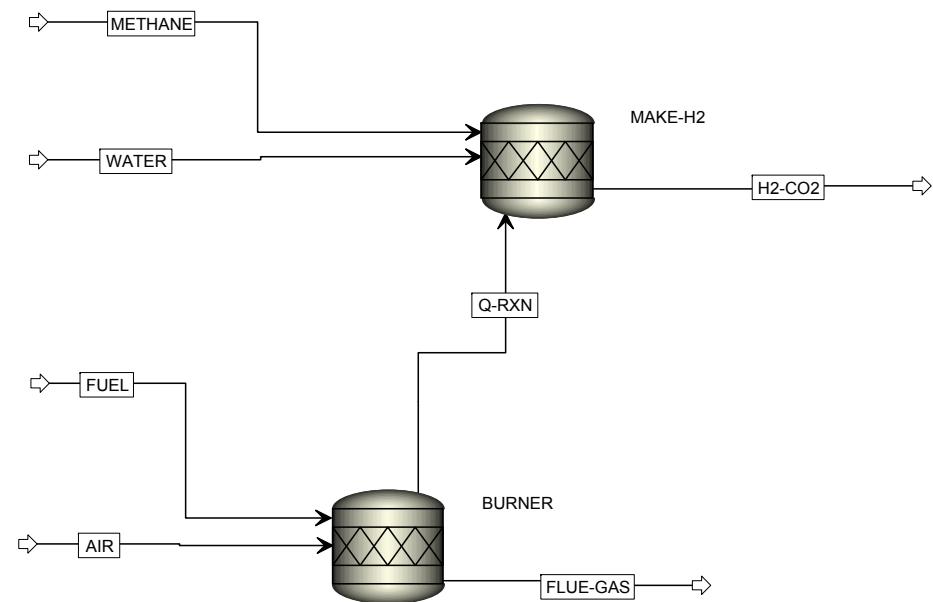
How do we provide the heat of reaction?

- Could use additional methane – 0.29 mol fuel/mol reactant (HHV basis)

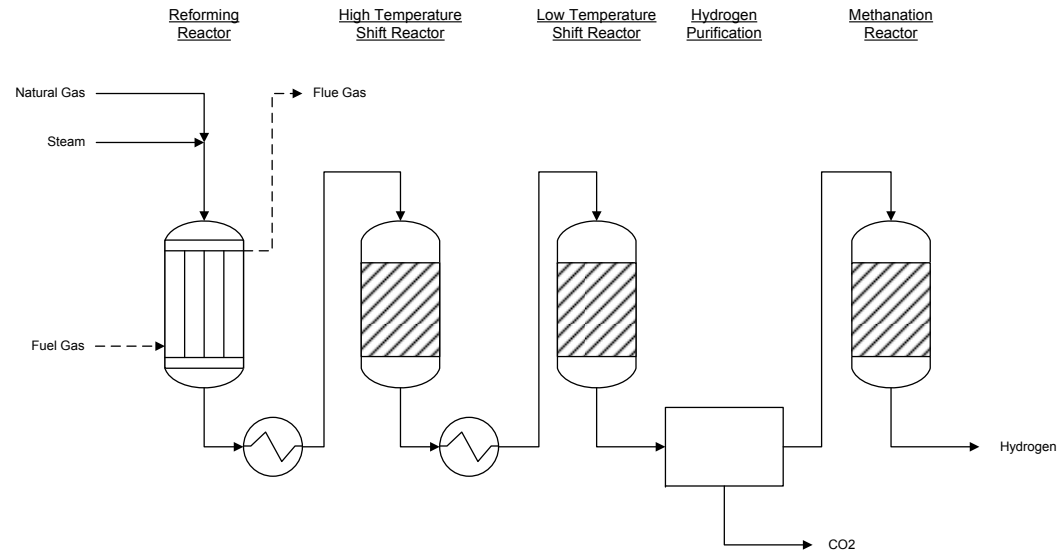
- Production:
$$\frac{N_{\text{H}_2}}{N_{\text{CH}_4}} = \frac{4}{1 + 0.29} = 3.1 \frac{\text{mol}}{\text{mol}}$$

- Efficiency including fuel (HHV basis)

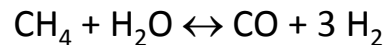
$$\eta = \frac{4 \times 68.7}{1.29 \times 213.6} = 1.0$$



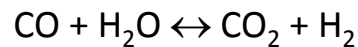
Steam Methane Reforming & Water Gas Shift



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



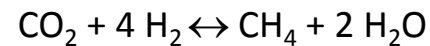
- **Shift conversion.** Exothermic fixed-bed catalytic reaction, possibly in two steps.



HTS: 345-370° C (650 – 700°F)

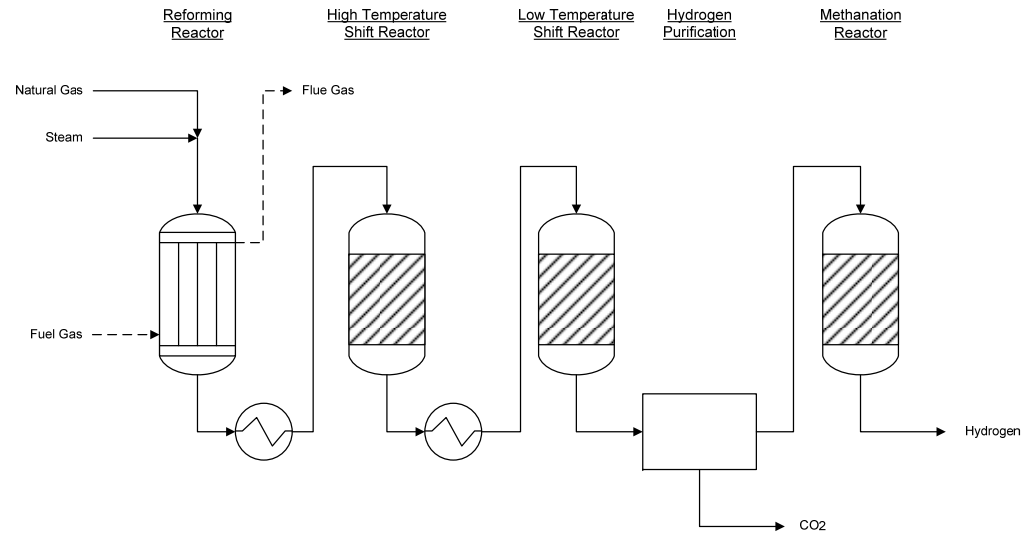
LTS: 230° C (450°F)

- **Gas Purification.** Absorb CO₂ (amine) or separate into pure H₂ stream (PSA or membrane).
- **Methanation.** Convert residual CO & CO₂ back to methane. Exothermic fixed-bed catalytic reactions at 370-425° C (700 – 800°F).

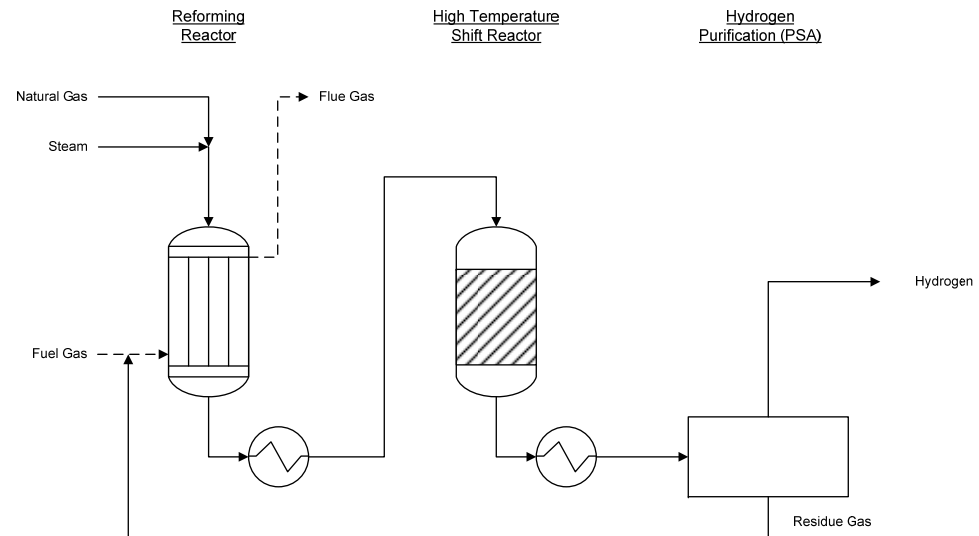


SMR Alternate Designs

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



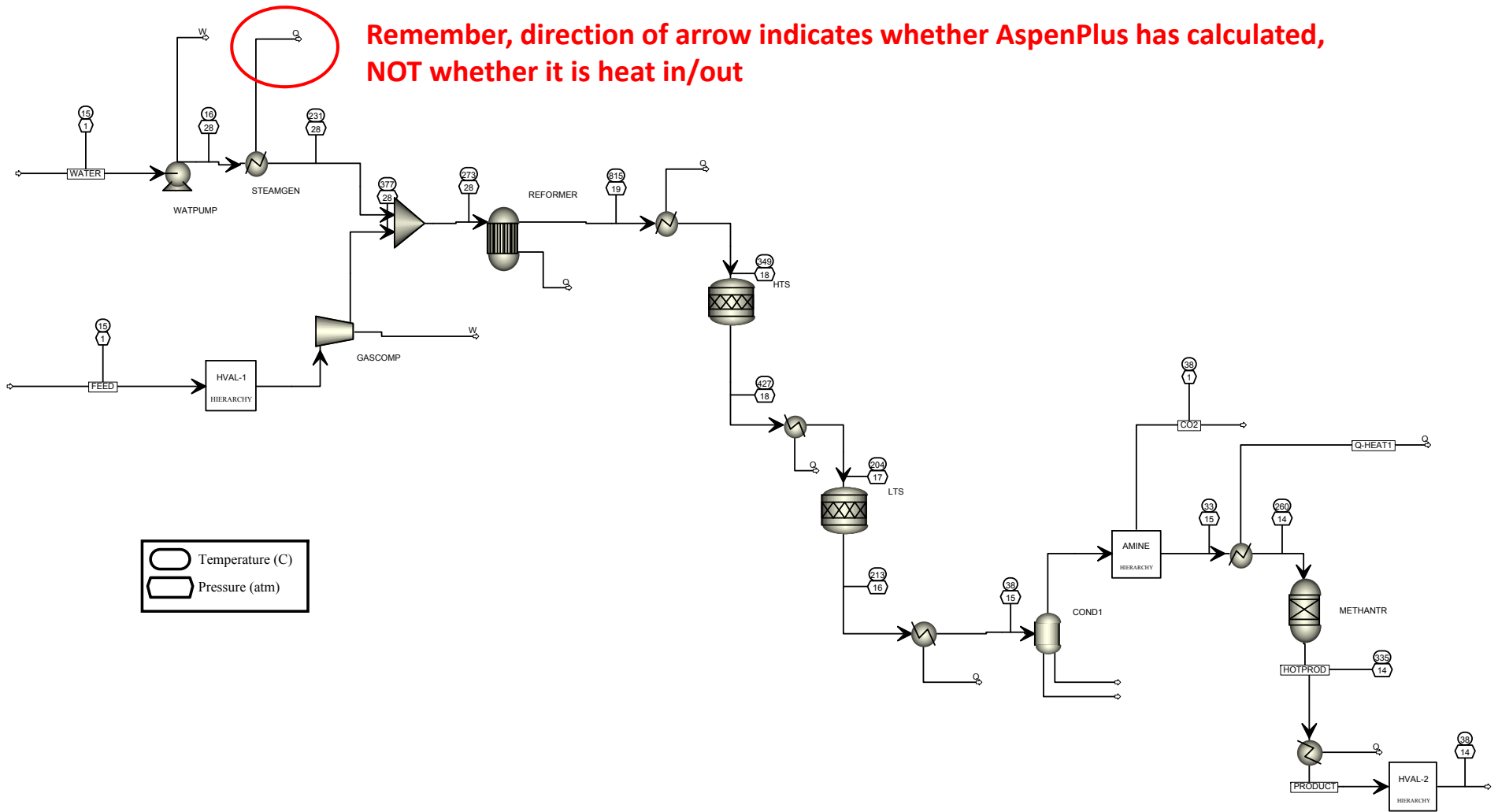
- Newer designs with PSA (Pressure Swing Adsorption) – lower capital costs, lower conversion, but very high purity (99%+)



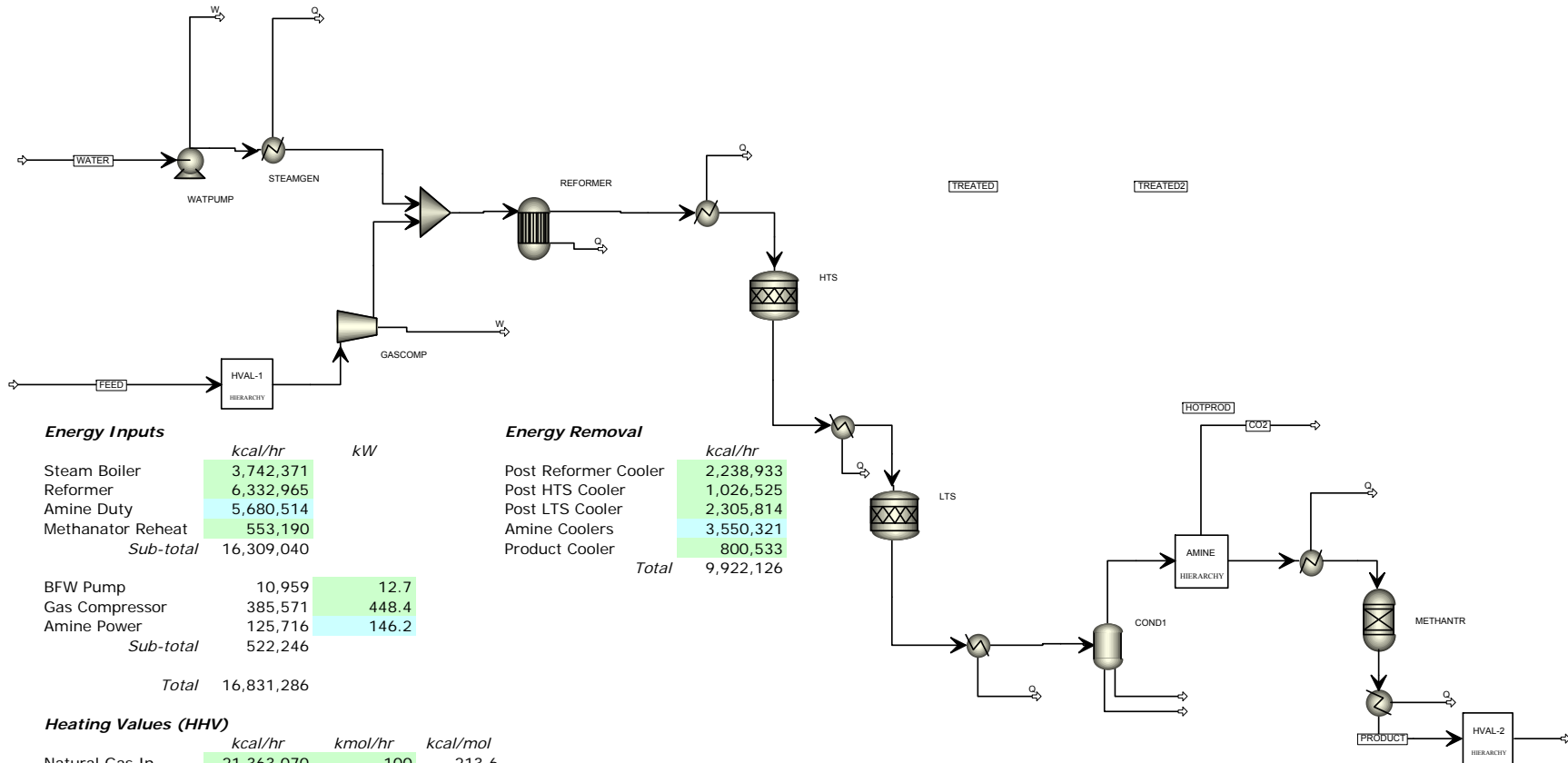
Process Considerations

	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 ₂ S & 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 ₂ O, 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 ₂ O, 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 ₂ O, 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



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

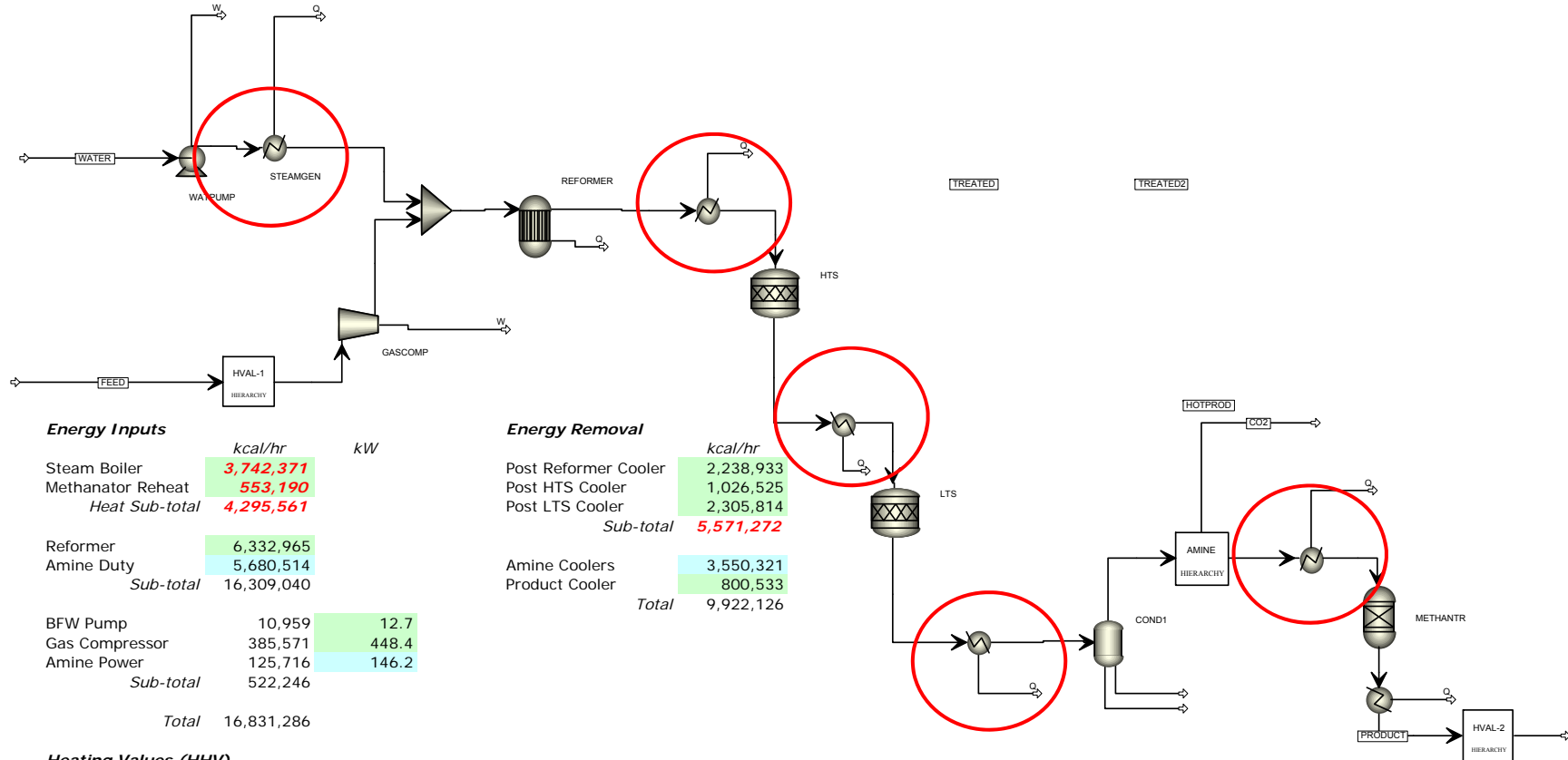
	kcal/hr
Post Reformer Cooler	2,238,933
Post HTS Cooler	1,026,525
Post LTS Cooler	2,305,814
Amine Coolers	3,550,321
Product Cooler	800,533
Total	9,922,126

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

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%

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

Reformer Furnace Design

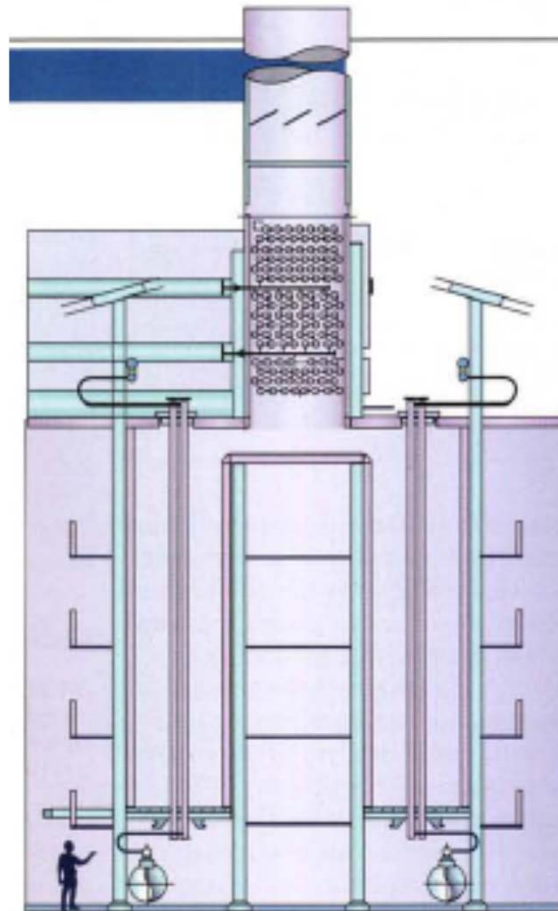


FIGURE 3. A typical reformer furnace could have over 300 burners

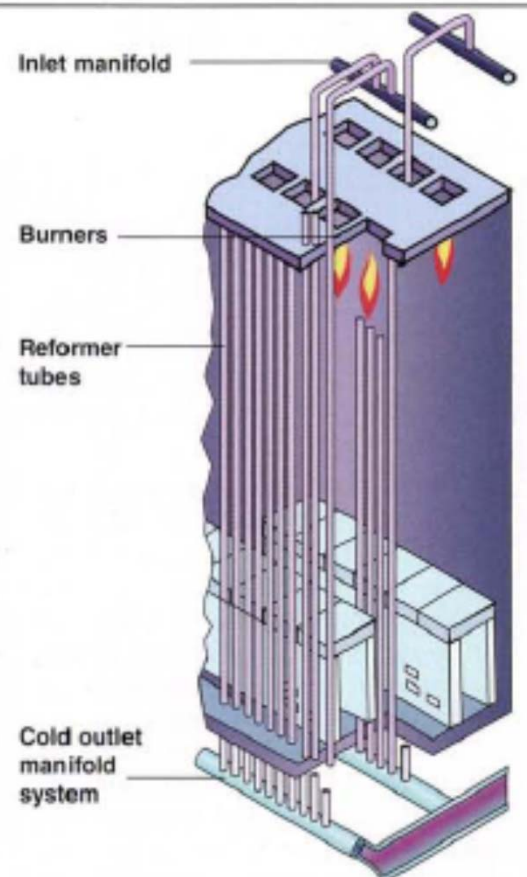
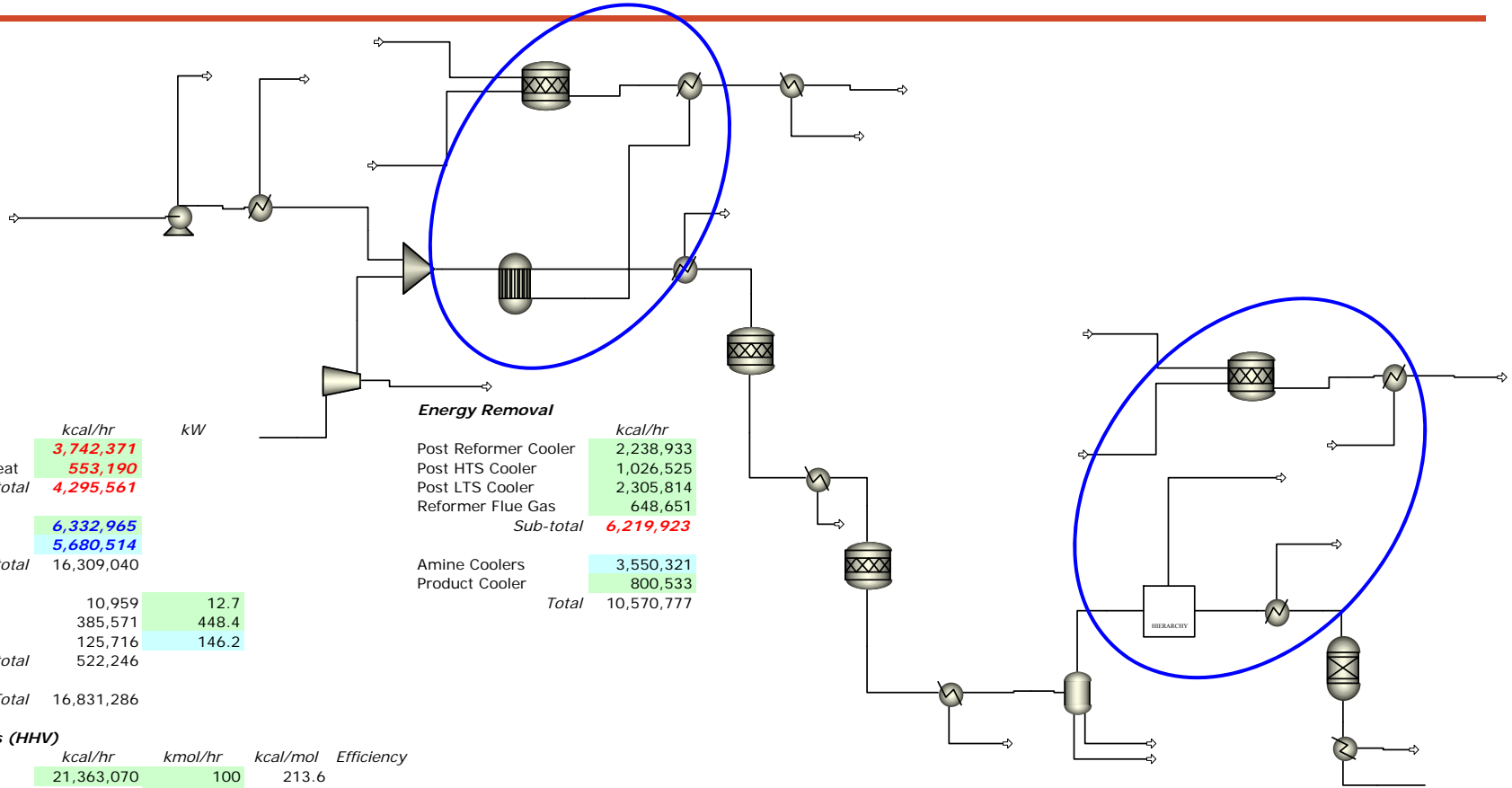


FIGURE 4. Hydrogen plants with single heaters and capacities up to 100,000

“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

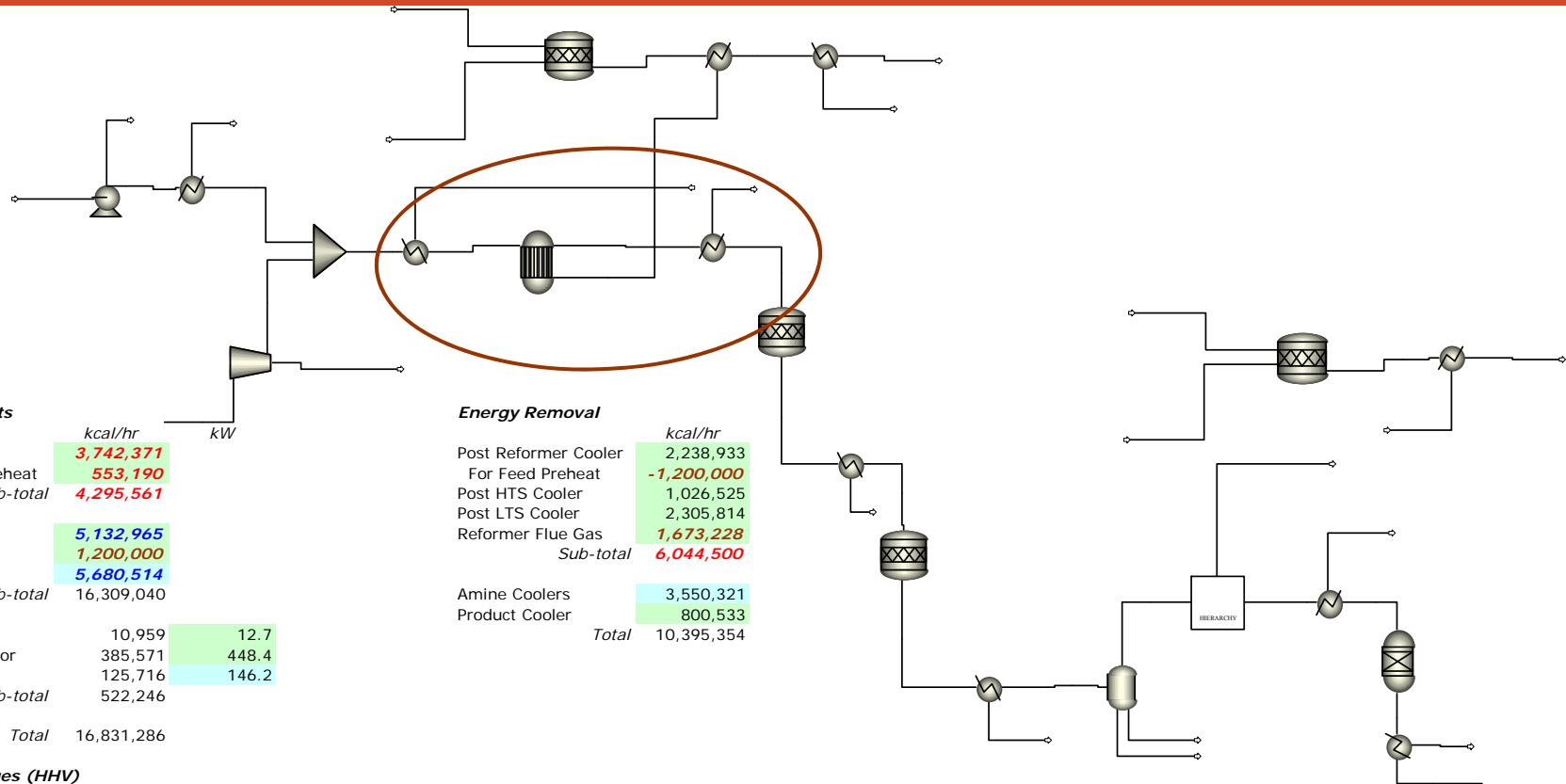
Heating Values (HHV)

	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%

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)

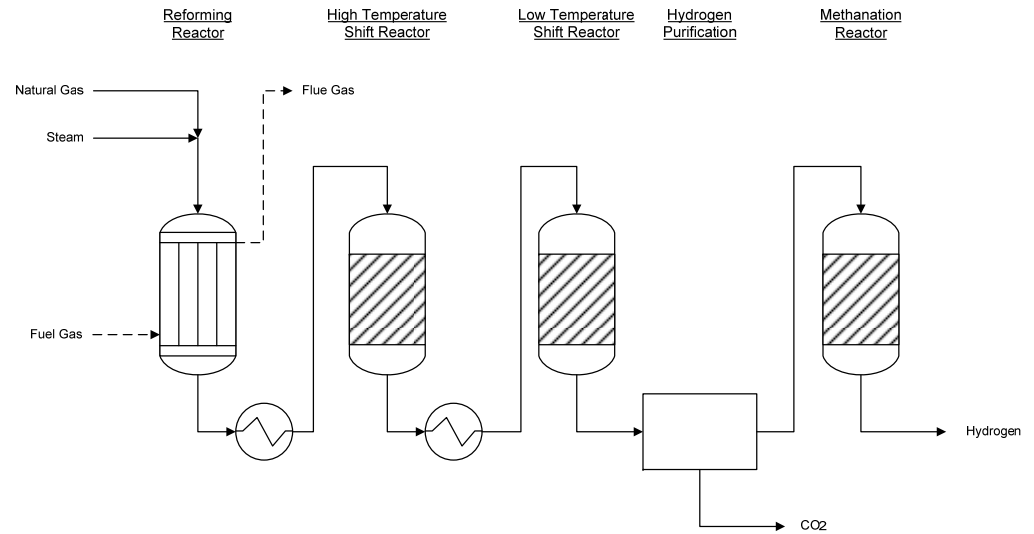
	kcal/hr	kmol/hr	kcal/mol	Efficiency
Natural Gas In	21,363,070	100	213.6	
Reformer Fuel Gas	7,978,680	37.3	213.6	64%
Amine Unit Fuel Gas	6,659,083	31.2	213.6	85%
Total	36,000,833	168.5		

Product Out	25,938,163	328.6	78.9
H2 Out		292.7	
H2 Purity:		89%	
H2 Production:		1.7	

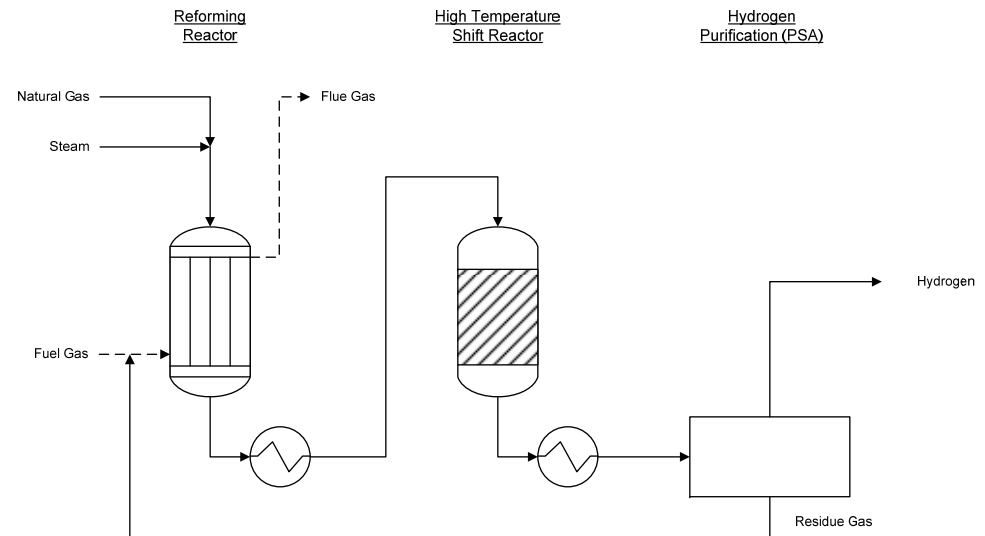
Total Product	25,938,163
Net Inputs	36,523,078
Efficiency	71%

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

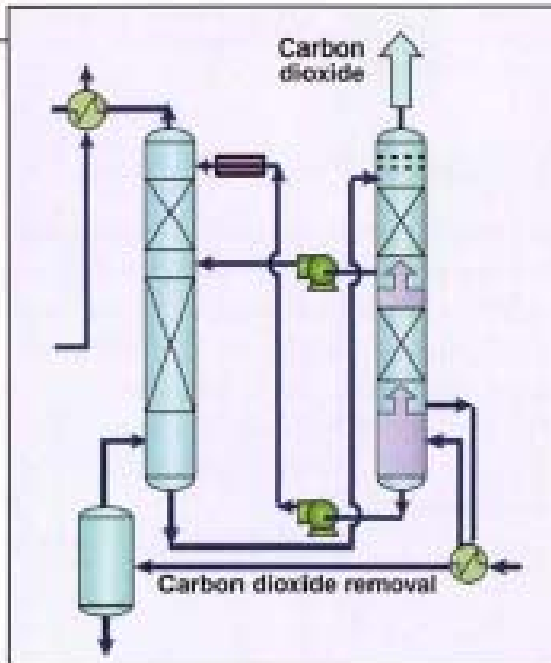


FIGURE 5. Most older units remove carbon dioxide from the hydrogen-rich gas with a solvent

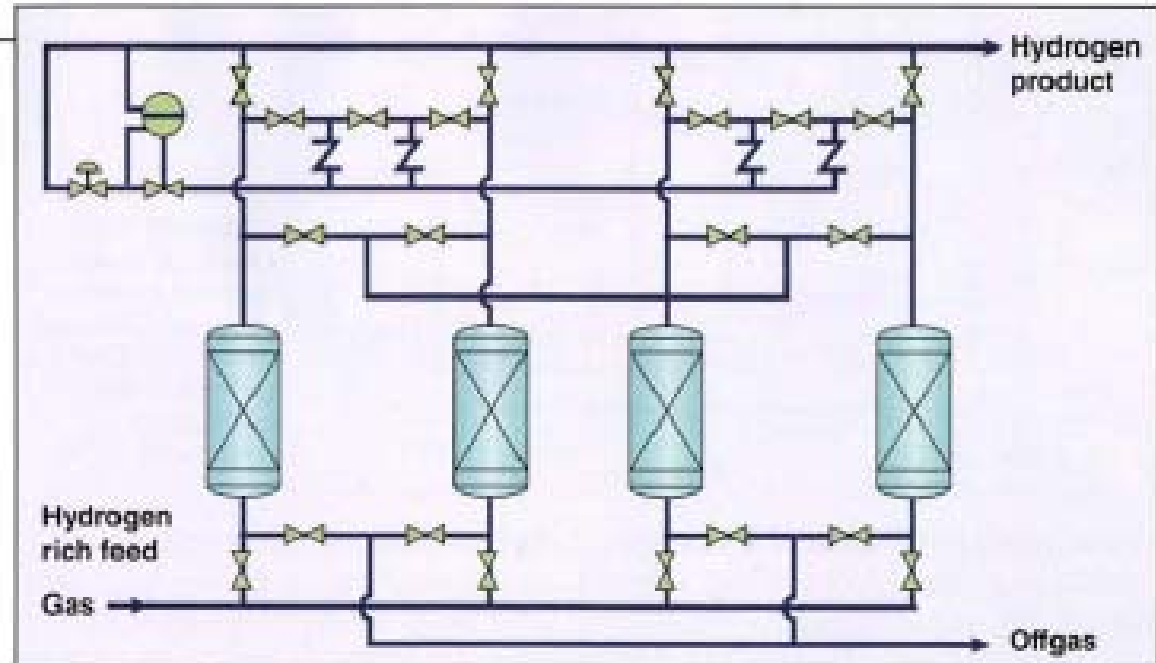
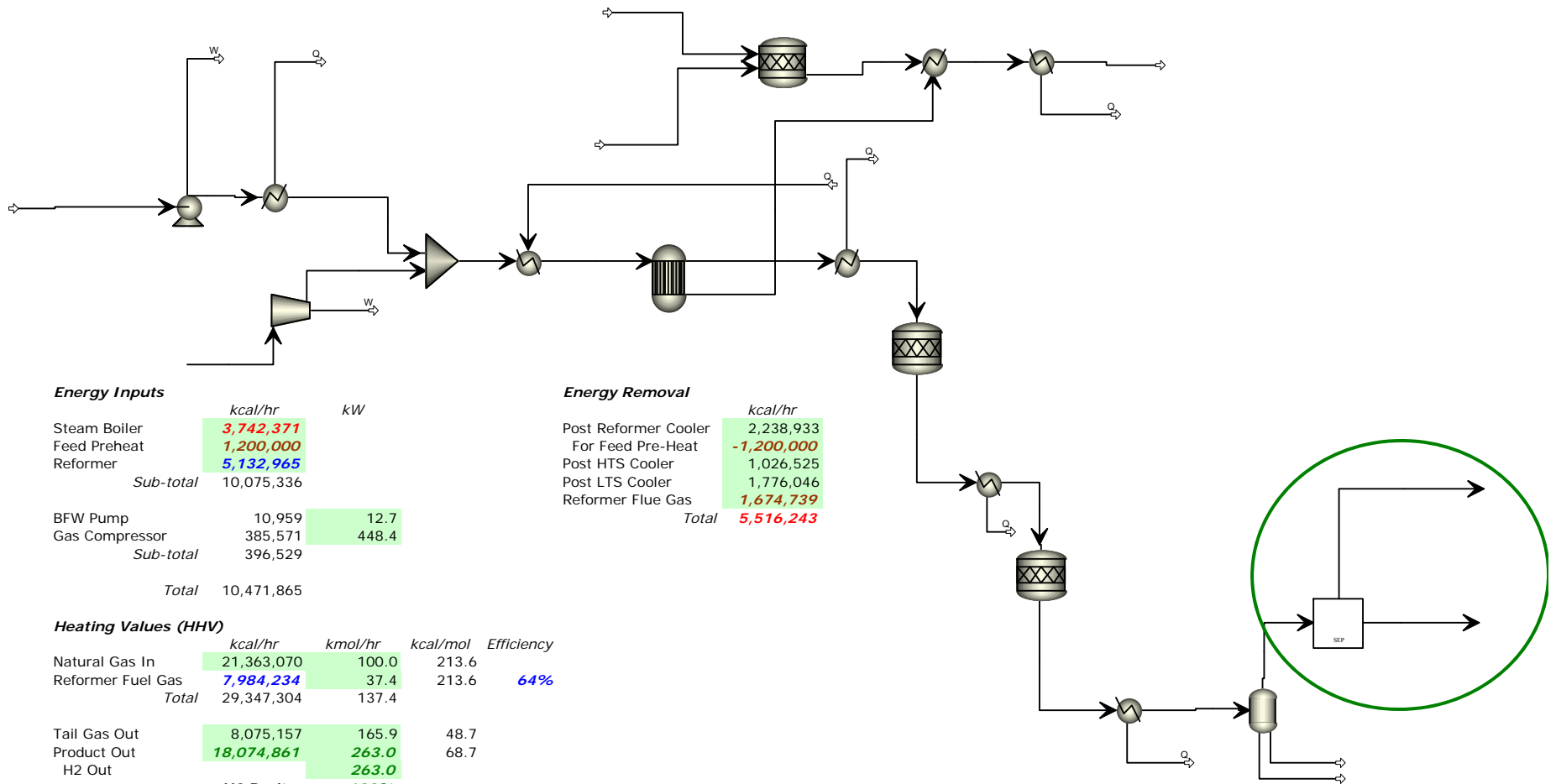


FIGURE 6. A PSA unit separates carbon monoxide, carbon dioxide and unconverted hydrocarbons from hydrogen. Adsorbers operate in a high-pressure to low-pressure cycle to adsorb and then release contaminants

“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	

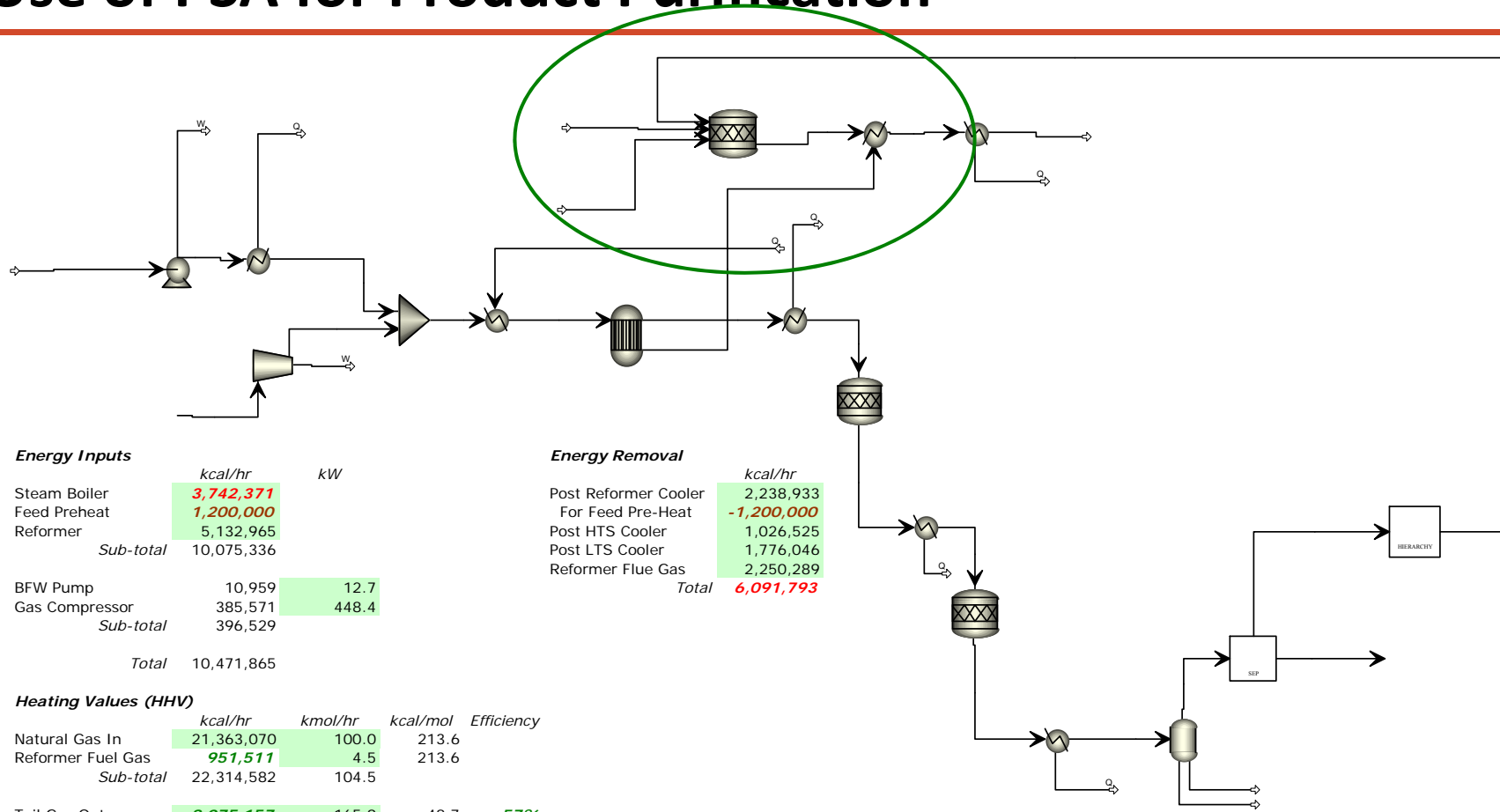
Energy Removal

	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

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			

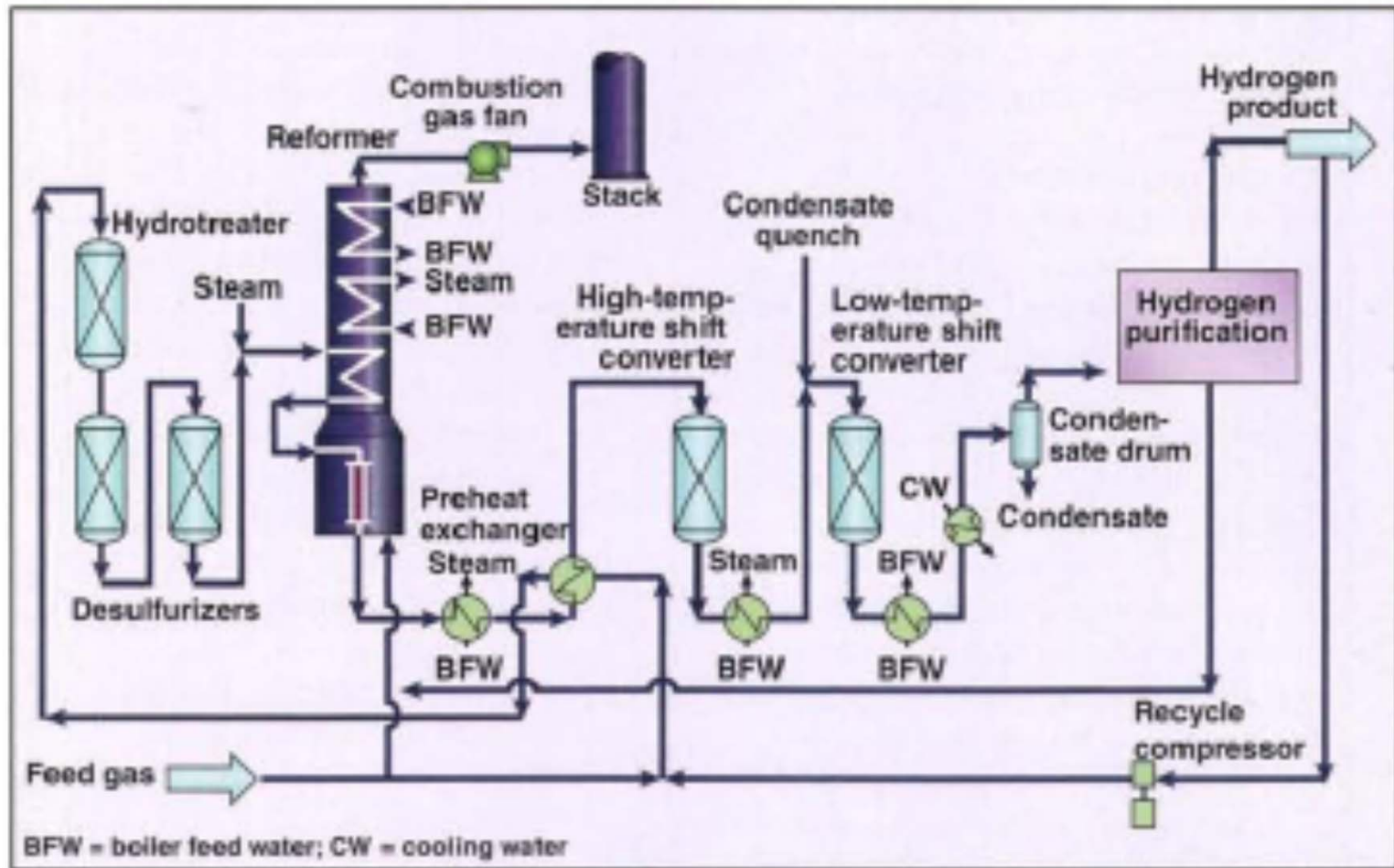
Product Out	18,074,861	263.0	68.7	
H2 Out		263.0		
H2 Purity:		100%		
H2 Production:		2.5		

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

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

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 CH₄
 - Electricity 6.79 ¢/kW-hr (for 2010 per EIA for Industrial customers)
 - PSA production scenario
 - 104.5 kmol/hr CH₄ → \$385 per hr
 - 461.1 kW → \$31 per hr
 - 263 kmol/hr H₂ → \$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
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