Evaluation of Hydrogen Production Cycles Based on Efficiency

Ch E 4273
Senior Design
Spring 2007

Purpose

Develop and implement a method of ranking water-splitting cycles

Outline

- Importance of Hydrogen
- Thermochemical/Hybrid Cycles
- Current Methods of Evaluation
- Our Methodology based on Efficiency
- Results

Hydrogen Economy

- Advantages
- Disadvantages
- Methods for producing hydrogen
- Other suggested economy types

Hydrogen Economy

- The current U.S. demand †
  - – 11 MM tons/yr total
    - Crude lightening
    - Produce cleaner-burning fuels
    - Methanol/Ammonia production
  - – Steam reformation of methane
- Demand in Hydrogen Economy †
  - – 200 MM tons/yr for transportation
  - – 450 MM tons/yr for all other energy needs

† K. R. Schultz 2003, General Atomics, DOE grant

Water-Splitting Cycles

$$H_2O \Leftrightarrow H_2 + \frac{1}{2}O_2$$

- Only products are hydrogen and oxygen
- Only reactant is water
- Other species form and breakdown in a cyclic manner, non-effluent

Water Splitting Cycles

- Thermochemical Cycles
  - Thermochemical reactions only
- Hybrid Cycles
  - Thermochemical reactions
  - Electrochemical reactions
- Some could benefit from nuclear plant heat sources
- Over 200 known cycles

Water Splitting Cycles

- Thermochemical Reactions
  - Established equipment in industry
  - Often require high temperatures
- Electrochemical Reactions
  - More rare in industry
  - Difficult to implement
  - Occur at lower temperatures

Water Splitting Cycle Examples

- Hallett Air Products (hybrid)

$$Cl_2 + H_2O \xrightarrow{1123K} 2HCl + \frac{1}{2}O_2$$

$$2HCl \xrightarrow{298K} Cl_2 + H_2$$

- US Chlorine (thermochemical)

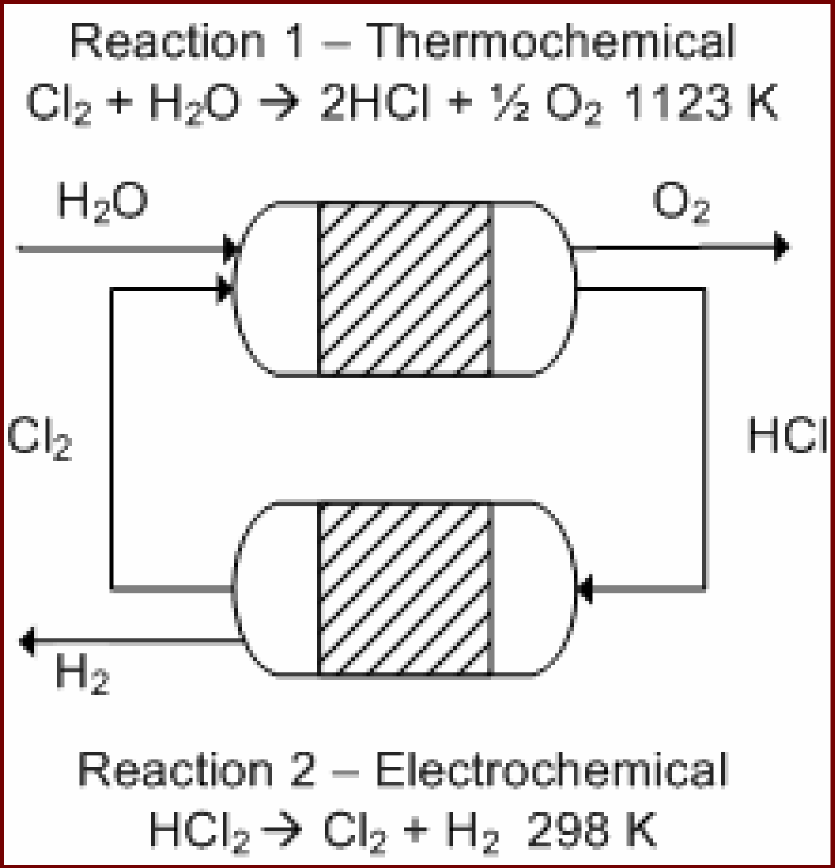
$$Cl_2 + H_2O \xrightarrow{1123K} 2HCl + \frac{1}{2}O_2$$

$$2CuCl_2 \xrightarrow{773K} 2CuCl + Cl_2$$

$$2CuCl + 2HCl \xrightarrow{473K} 2CuCl_2 + H_2$$

Water Splitting Cycle Example

Hallett Air Products (hybrid)



Reaction 1 – Thermochemical

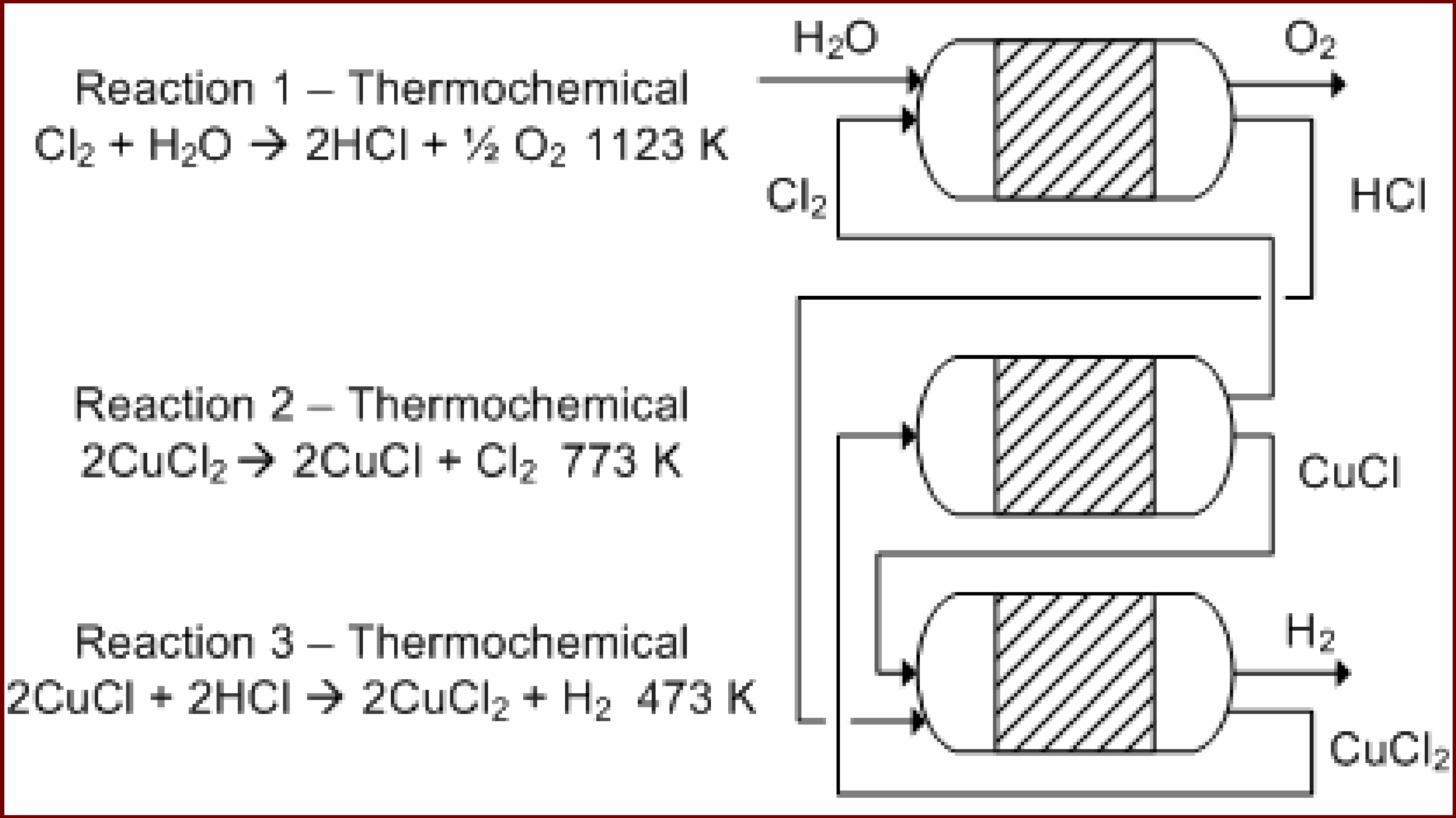
$Cl_2 + H_2O \rightarrow 2HCl + \frac{1}{2} O_2$ 1123 K

Reaction 2 – Electrochemical

$HCl_2 \rightarrow Cl_2 + H_2$ 298 K

Water Splitting Cycle Example

US Chlorine (thermochemical)



Reaction 1 – Thermochemical

$Cl_2 + H_2O \rightarrow 2HCl + \frac{1}{2} O_2$ 1123 K

Reaction 2 – Thermochemical

$2CuCl_2 \rightarrow 2CuCl + Cl_2$ 773 K

Reaction 3 – Thermochemical

$2CuCl + 2HCl \rightarrow 2CuCl_2 + H_2$ 473 K

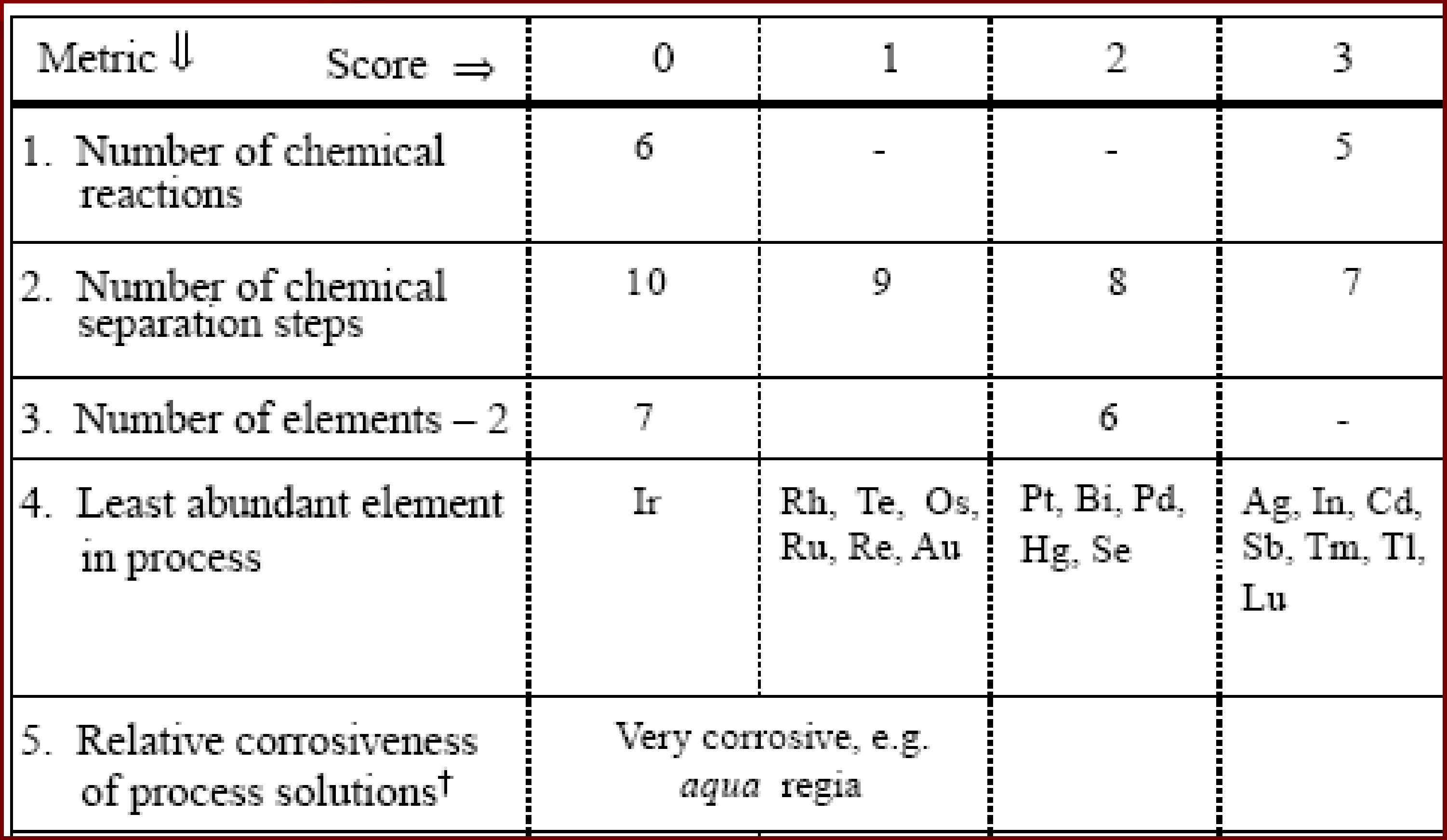
Issues

- Coupled reactions
  - Cyclic Process- Degrees of freedom
- Special reaction methods (high $\Delta G>0$)
  - Electrolysis
  - Continuous product removal
- Reaction Equilibrium
  - Reversibility
  - Equilibrium conversion
- Separation Energy (heat and work) may complicate the flowsheet

Prior Evaluation Efforts

- L.C. Brown (2000, DOE) scored cycles based on known characteristics
  - Qualitative approach
  - Questionable evaluation technique
    - Point system for process complexities
    - Equal weighting assigned to all criteria
    - "Judgment call" basis
    - Heavily favors well-researched cycles

Prior Evaluation Efforts



Metric ⇓ Score ⇒	0	1	2	3
1. Number of chemical reactions	6	-	-	5
2. Number of chemical separation steps	10	9	8	7
3. Number of elements – 2	7		6	-
4. Least abundant element in process	Ir	Rh, Te, Os, Ru, Re, Au	Pt, Bi, Pd, Hg, Se	Ag, In, Cd, Sb, Tm, Tl, Lu
5. Relative corrosiveness of process solutions†	Very corrosive, e.g. *aqua* regia			

Prior Evaluation Efforts

- Lewis (2005, DOE) evaluated cycles based on efficiency
  - Quantitative approach
  - Considers equilibrium
  - Assumes 50% efficiency for all work processes
    - Actual efficiency may be better or worse
    - Different processes have different efficiencies

Our Proposed Solution

Efficiency Based Ranking System:

- Find maximum possible efficiency
  - Pinch technology to determine hot utility
    - Stream analysis
    - Heat of reaction
  - Estimate work required
- Consider reaction equilibrium
- DOF: optimize flow rates and temperatures

Cycle Efficiency

$$\eta = -\frac{\Delta H_{H_2O}°(298K)}{Q+W}$$

- Enthalpy of formation of water is minimum energy required for water-splitting

Cycle Efficiency

- Only heat and work transferred across system boundary included
- Heat term
  - Hot utility
  - Heat for separations
- Work term
  - Pump/compressor work
  - Electrical work in electrolysis

Equilibrium

$$\Delta G = \sum \nu_i \left(\mu_i^\circ + RT \ln a_i \right)$$

Setting ΔG_{RXN} equal to zero gives the following,

$$K_{EQ} = \exp\left(-\frac{\Delta G_{Rxn}^\circ}{RT} \right)$$

$$K_{EQ} = \prod a_i^{\nu_i}$$

Equilibrium

- Sulfur Iodine – Reaction 1 (1123 K)

$$H_2SO_4(v) \xrightarrow{1123K} SO_2(v) + H_2O(v) + \frac{1}{2}O_2(v)$$

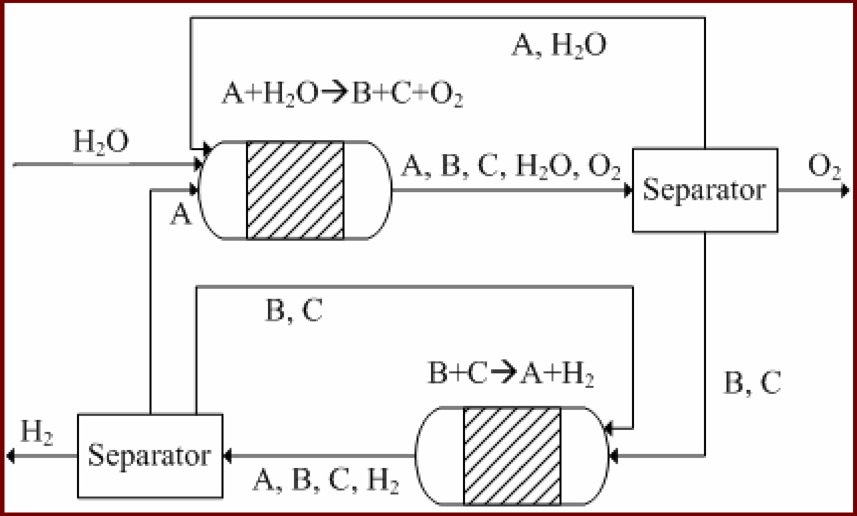
$$K_1(T_1) = \frac{n_{SO_2} n_{H_2O} n_{O_2}^{.5} \cdot P^{1.5}}{n_{H_2SO_4}(n_{H_2SO_4} + n_{SO_2} + n_{H_2O} + n_{O_2})^{1.5}}$$

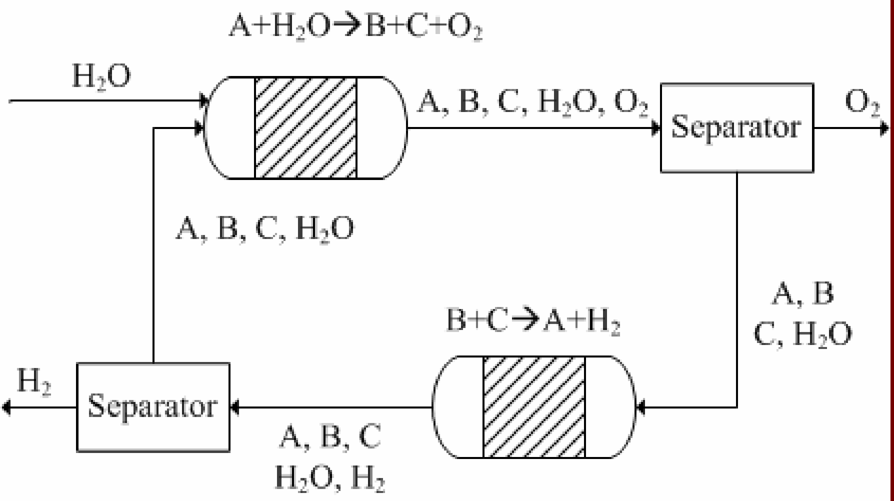
- Relate number of moles to conversion

  $n_i = n_{i,o} + \nu_i X_i \quad \Rightarrow K_1(T_1) = f(X)P^{1.5}$

Excess Reactants

Two primary options of handling





- Recycle
  - Increases separation requirement
  - Strategic product placement
- No Recycle
  - Increases heat requirement
  - 2 configurations for cycles with 3 or more reactions

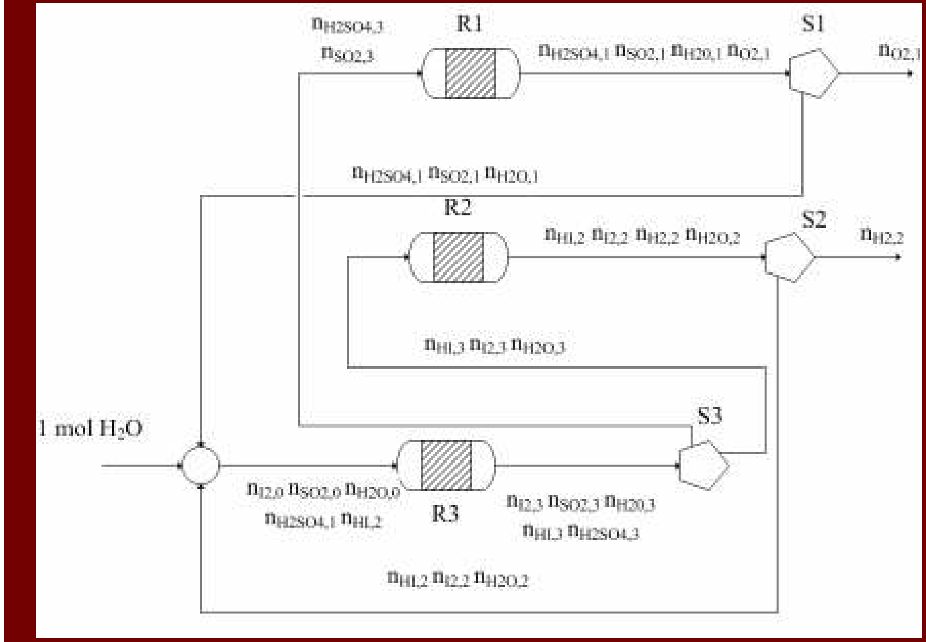
No Recycle Handling

Sulfur Iodine Cycle:

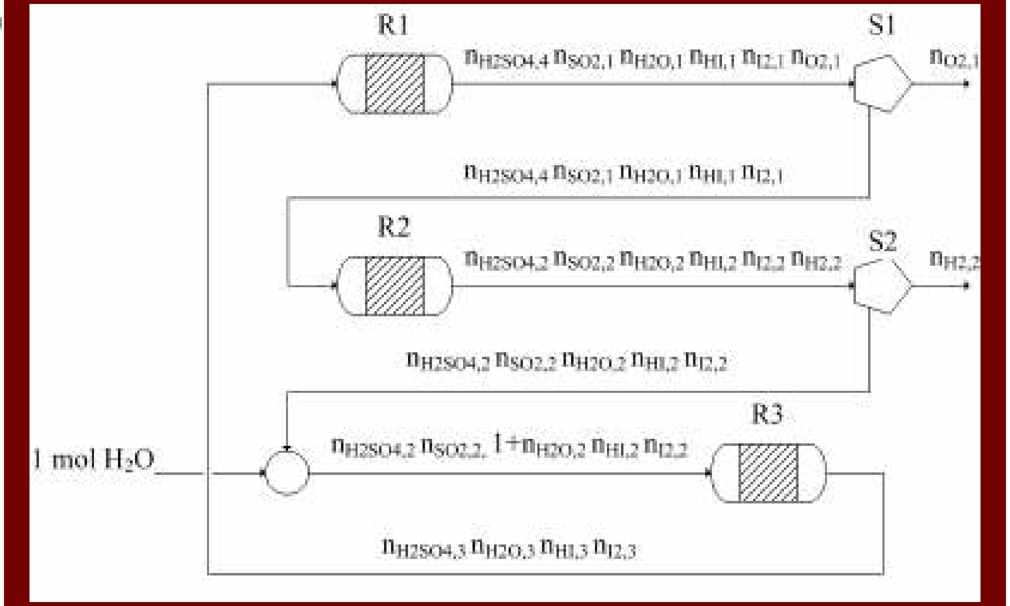
$$H_2SO_4 \xrightarrow{T=1123K} SO_2 + H_2O + \frac{1}{2}O_2$$

$$2HI \xrightarrow{T=723K} I_2 + H_2$$

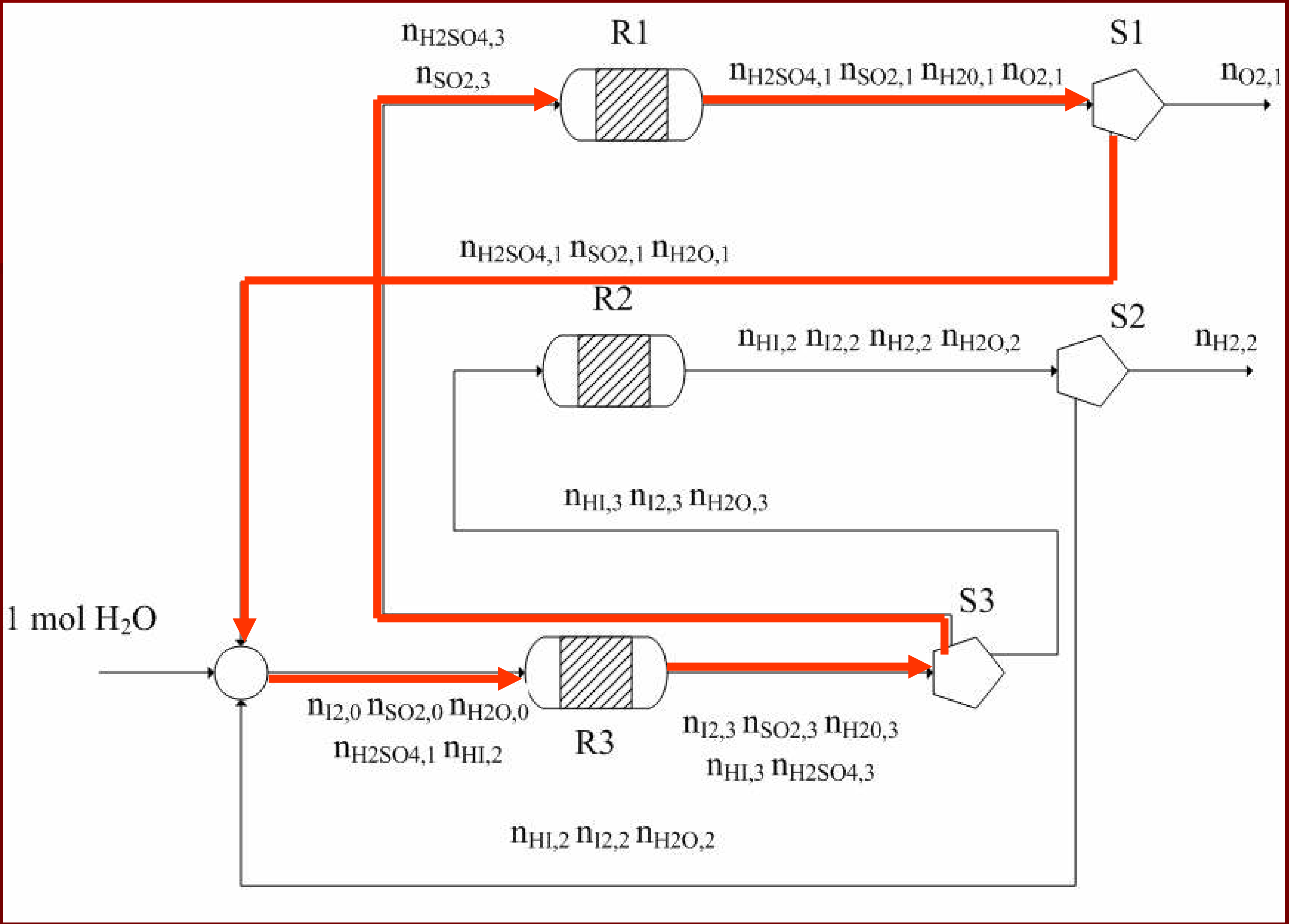
$$I_2 + SO_2 + 2H_2O \xrightarrow{T=393K} 2HI + H_2SO_4$$



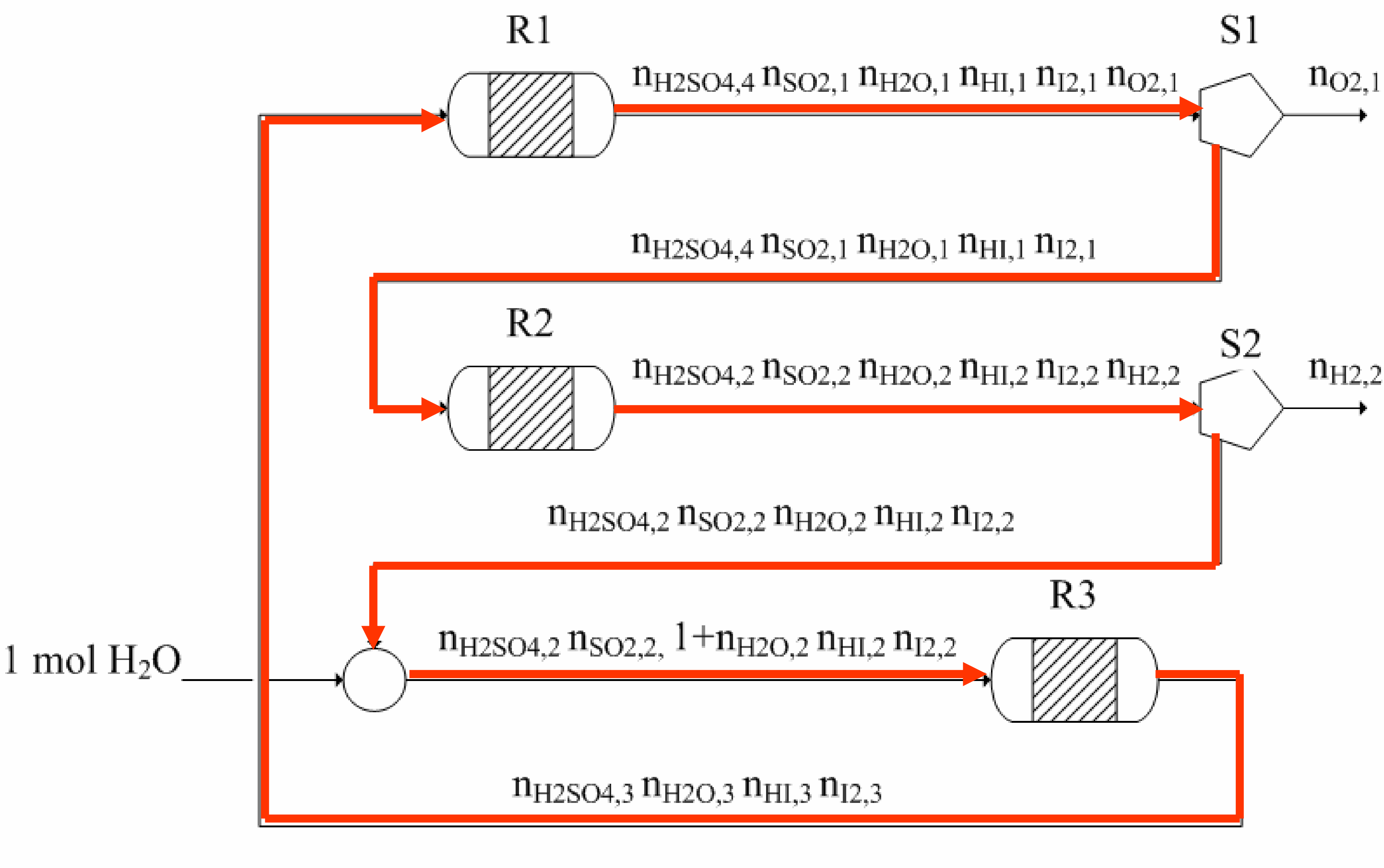
Strategic Separation



Minimum Separation



Strategic Separation

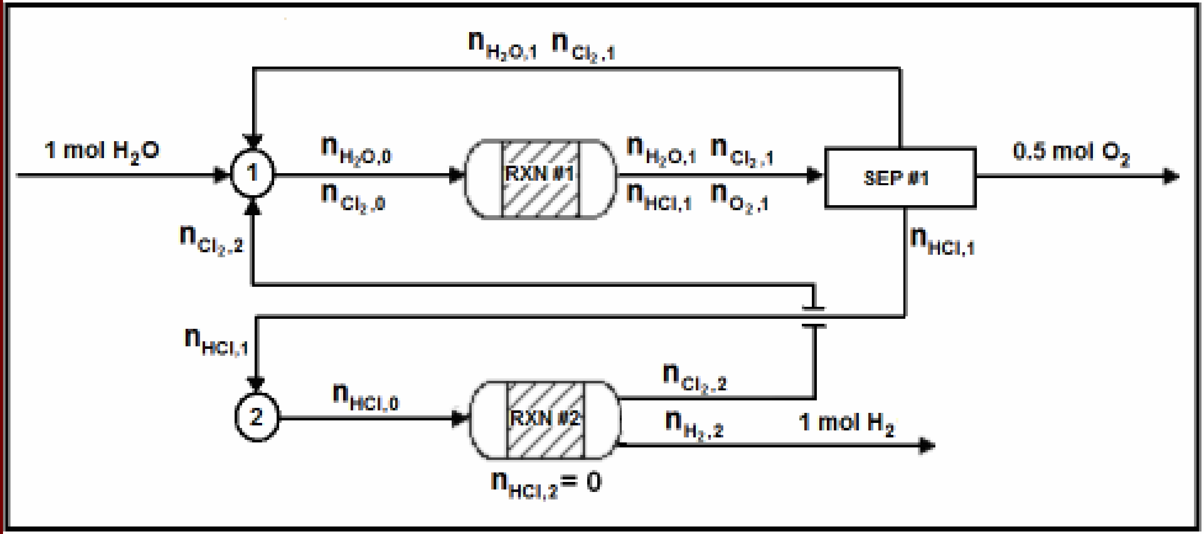


Minimum Separation

Degrees of Freedom

- Caused by linearly dependent equations
- Assume design parameters to define system

Hallett Air Products



$$Cl_2 + H_2O \xrightarrow{1123K} 2HCl + \frac{1}{2}O_2$$

$$2HCl \xrightarrow{298K} Cl_2 + H_2$$

Degree of Freedom

Reaction #1:

$$K_1(T_1)=\frac{n_{HCl,1}^{2}n_{O_2,1}^{.5}}{n_{Cl_2,1}n_{H_2O,1}[n_{Cl_2,1}+n_{H_2O,1}+n_{HCl,1}+n_{O_2,1}]^{.5}}P^{0.5}$$

$$n_{H_2O,1}=n_{H_2O,0}-\xi_1 \qquad n_{O_2,1}=0.5\xi_1$$

$$n_{Cl_2,1}=n_{Cl_2,0}-\xi_1 \qquad n_{HCl,1}=2\xi_1$$

Reaction #2 (electrolysis):

$$n_{HCl,0}=2\xi_2$$

$$n_{Cl_2,2}=\xi_2 \qquad n_{H_2,2}=\xi_2$$

Mix Point #1:

$$n_{H_2O,0}=1+n_{H_2O,1}$$

$$n_{Cl_2,0}=n_{Cl_2,1}+n_{Cl_2,2}$$

Mix Point #2:

$$n_{HCl,0}=n_{HCl,1}$$

Degree of Freedom

- Example: Hallett Air Products Cycle
  - 10 variables
  - 9 linearly independent equations
  - DOF = 10 – 9 = 1
- After substitutions:
  - Define $n_{Cl2,0}$

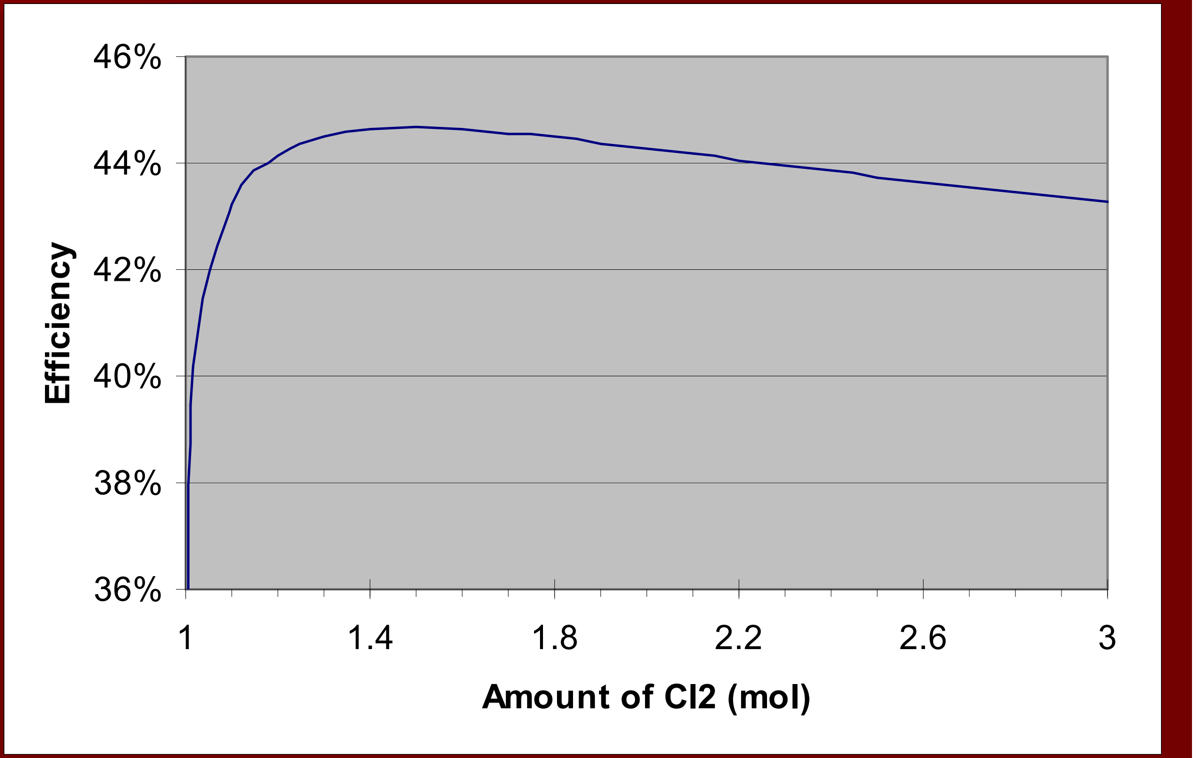
$$n_{Cl_2,0} = n_{Cl_2,1} + 1$$

$$K_1(T_1) = \frac{2^2 0.5^{0.5}}{n_{Cl_2,1} n_{H_2O,1} [n_{Cl_2,1} + n_{H_2O,1} + 2 + 0.5]^{.5}} P^{0.5}$$

$$n_{H_2O,0} = 1 + n_{H_2O,1}$$

Optimizing Excess

- Hallett Air Products Cycle
  - DOF = 1
  - Define $n_{Cl2,0}$

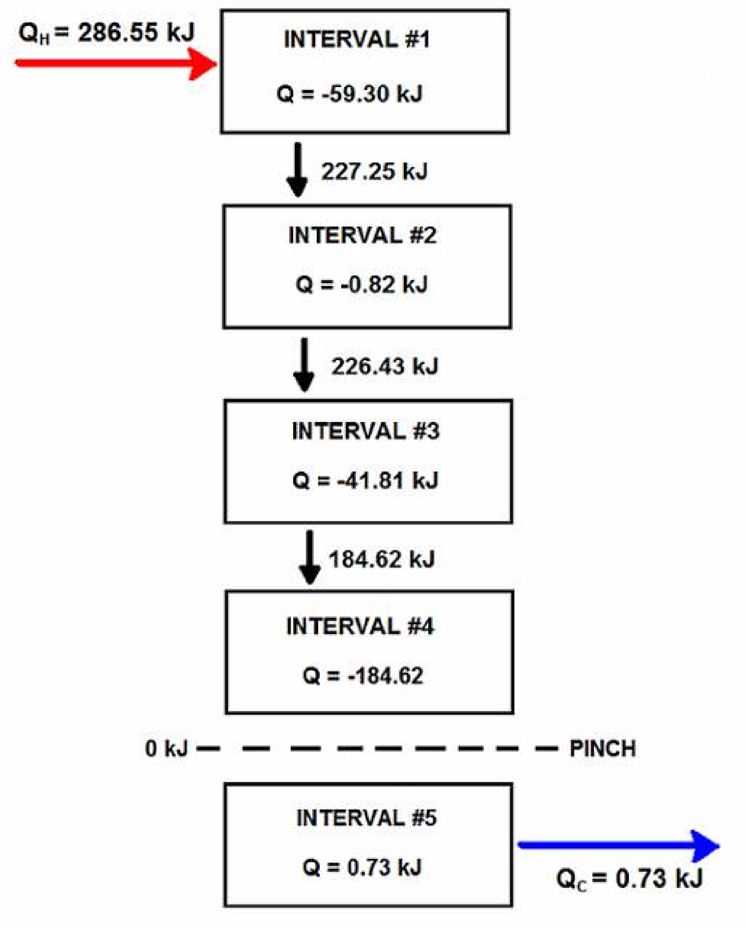


- $n_{Cl2,0} = 1.49\ mol$
- $Efficiency = 44.7\%$

Minimum Utility

- Popular method of finding hot utility
- Heat cascaded from high T → low T
- Pinch occurs at temperature where cumulative system heat is zero
- No heat is transferred across the pinch

Minimum Utility



Q_H = 286.55 kJ

INTERVAL #1

Q = -59.30 kJ

227.25 kJ

INTERVAL #2

Q = -0.82 kJ

226.43 kJ

INTERVAL #3

Q = -41.81 kJ

184.62 kJ

INTERVAL #4

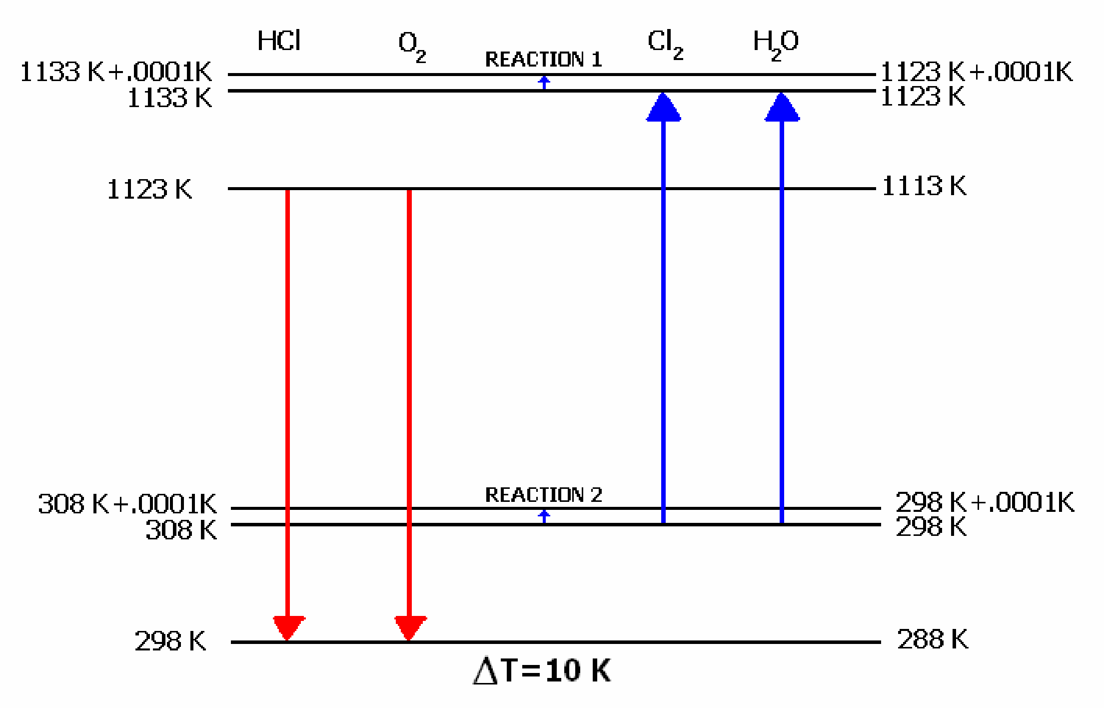
Q = -184.62

0 kJ — — — — — — — — — PINCH

INTERVAL #5

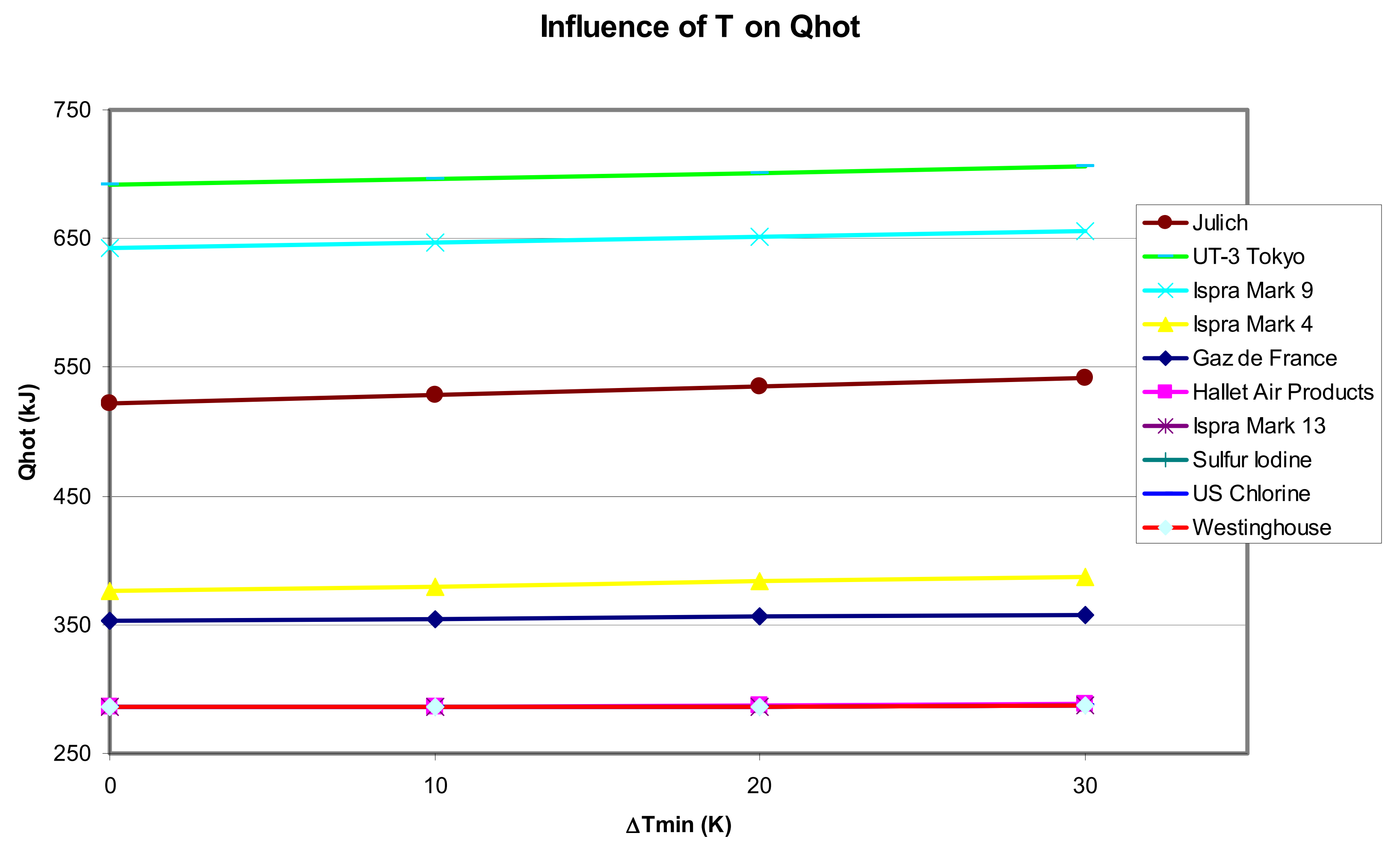
Q = 0.73 kJ

Q_C = 0.73 kJ



- Interval analysis
- Single hot utility & cold utility
- Isothermal reaction
- Heat of reaction

Effect of ΔT_{min} on Q_{hot}



Electrical Work

- Electrical Work
  - – Nernst equation for electrolytic cells
  - – Assume steady-state operation
  - – Assume cell efficiency of 90%†

$$W_{Electric} = -n \cdot F \cdot E^{\circ}$$

† Millikan, Christopher E., DOE 2002

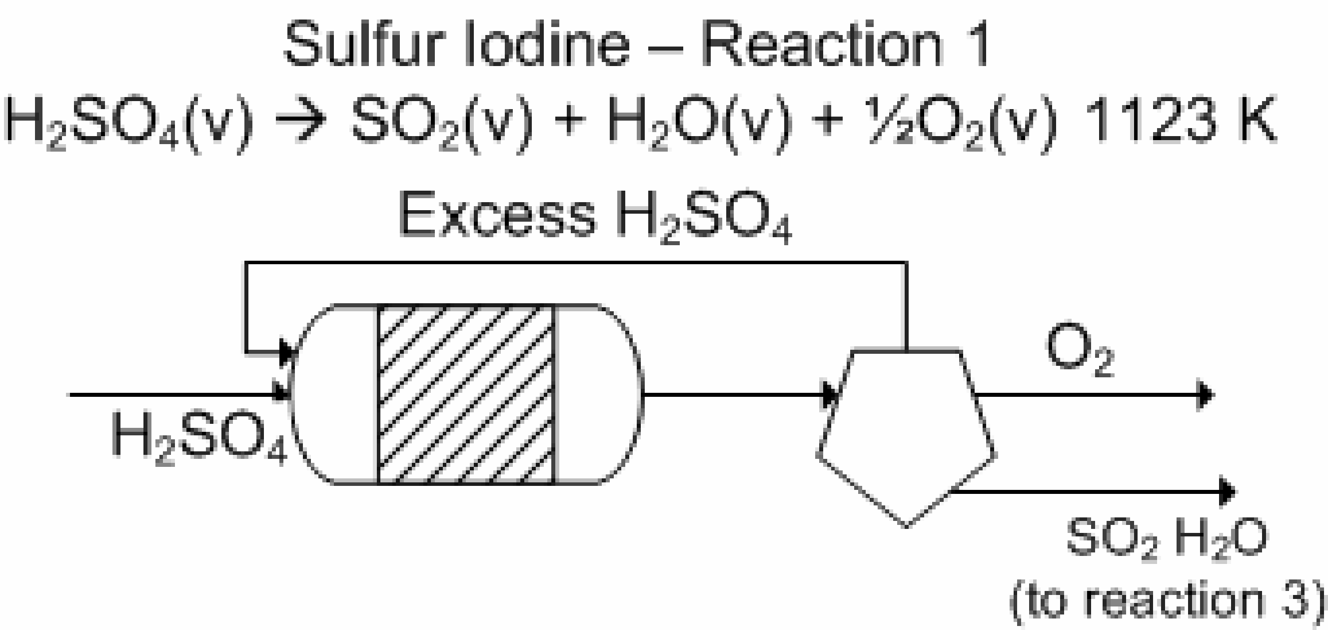
Separations

- Separation Energy
  - Minimum work found
    - Estimate separation efficiencies as 50%[†]
  - Complete separation
  - Phase separation when possible
  - Isothermal Process
  - Real heat & work found

[†] Michele A. Lewis, "FY 2005 Progress Report"

Minimum Separation energy

- Separate species into streams
  - Depends on excess handling configuration
  - Phase separation requires no energy
- Example: Sulfur Iodine RXN#1 Separation

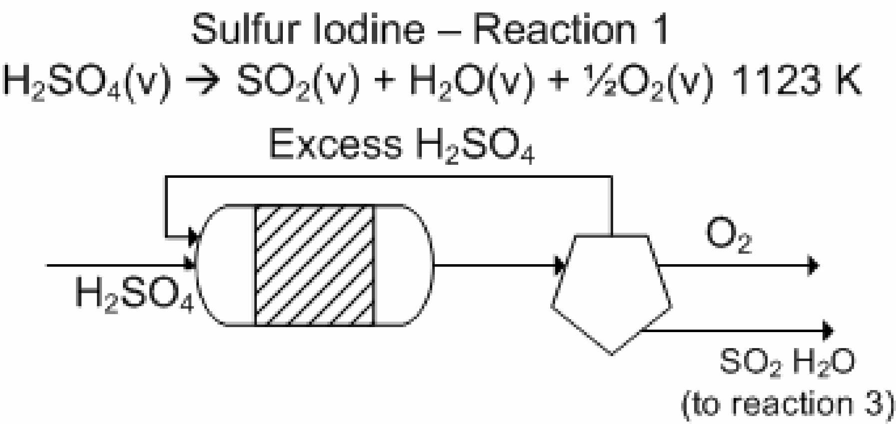


Minimum Separation Work

$$W_{SEP,Minimum} = \Delta G_{Mixing} = R \cdot T \sum_i n_i \cdot \ln(x_i)$$

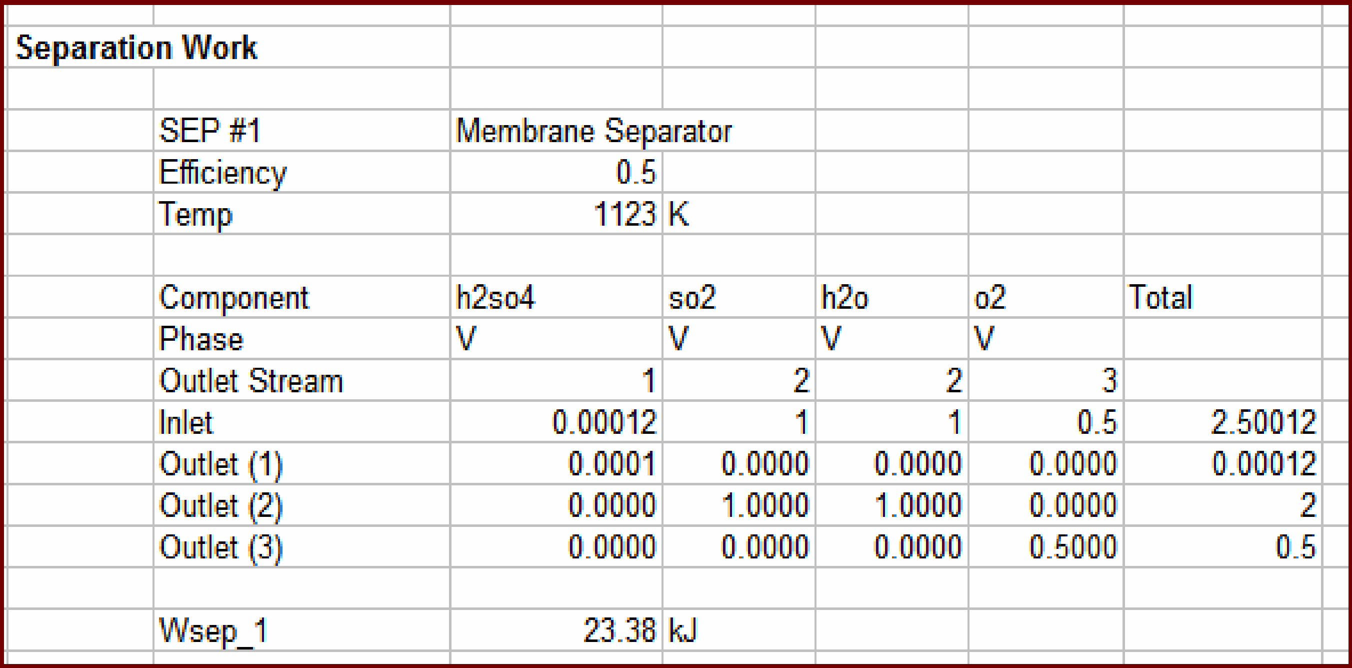
$$W_{SEP,Minimum} = R \cdot T \left[\left(\sum_i n_i \cdot \ln(x_i) \right)_{OUT} - \left(\sum_i n_i \cdot \ln(x_i) \right)_{IN} \right]$$

Minimum Separation Work



Sulfur Iodine – Reaction 1

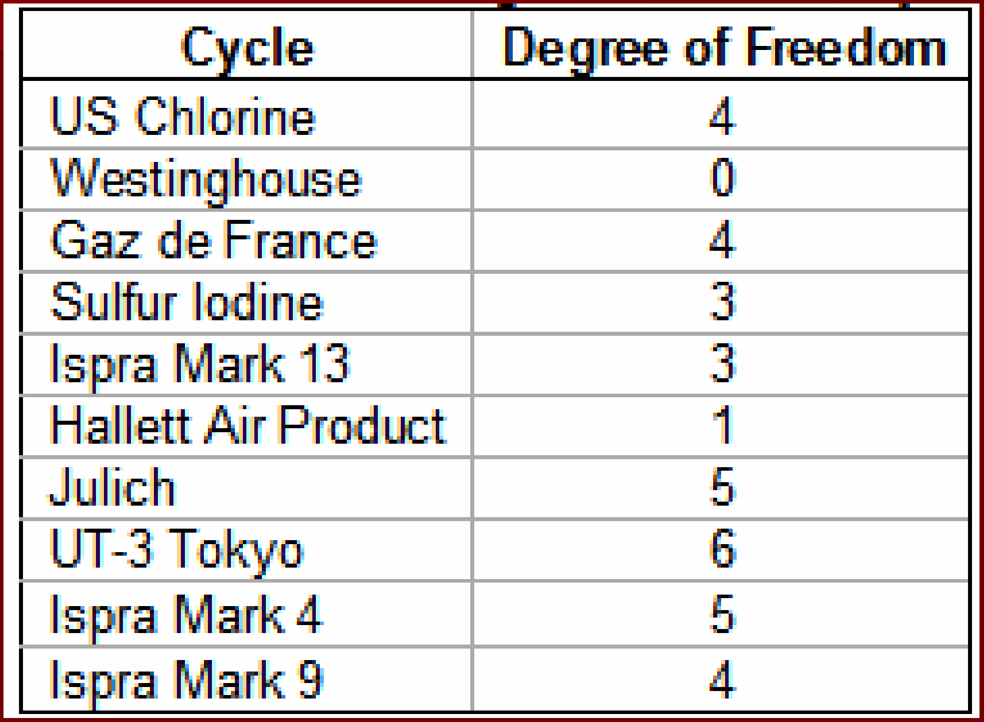
$H_2SO_4(v) \rightarrow SO_2(v) + H_2O(v) + \frac{1}{2}O_2(v)$ 1123 K



Separation Work						
	SEP #1	Membrane Separator				
	Efficiency	0.5				
	Temp	1123	K			
	Component	h2so4	so2	h2o	o2	Total
	Phase	V	V	V	V	
	Outlet Stream	1	2	2	3	
	Inlet	0.00012	1	1	0.5	2.50012
	Outlet (1)	0.0001	0.0000	0.0000	0.0000	0.00012
	Outlet (2)	0.0000	1.0000	1.0000	0.0000	2
	Outlet (3)	0.0000	0.0000	0.0000	0.5000	0.5
	Wsep_1	23.38	kJ			

Results

Degree of Freedom

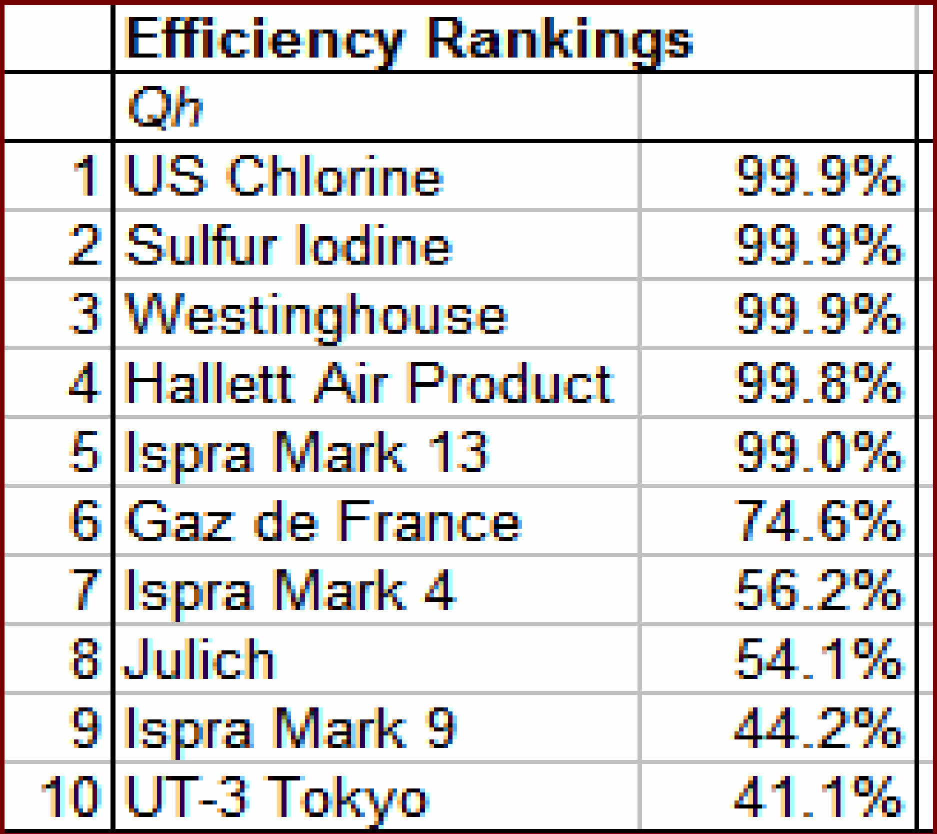


Cycle	Degree of Freedom
US Chlorine	4
Westinghouse	0
Gaz de France	4
Sulfur Iodine	3
Ispra Mark 13	3
Hallett Air Product	1
Julich	5
UT-3 Tokyo	6
Ispra Mark 4	5
Ispra Mark 9	4

- Constant for all configurations investigated
  - Does not include reaction temperatures

Minimum Utility Criterion

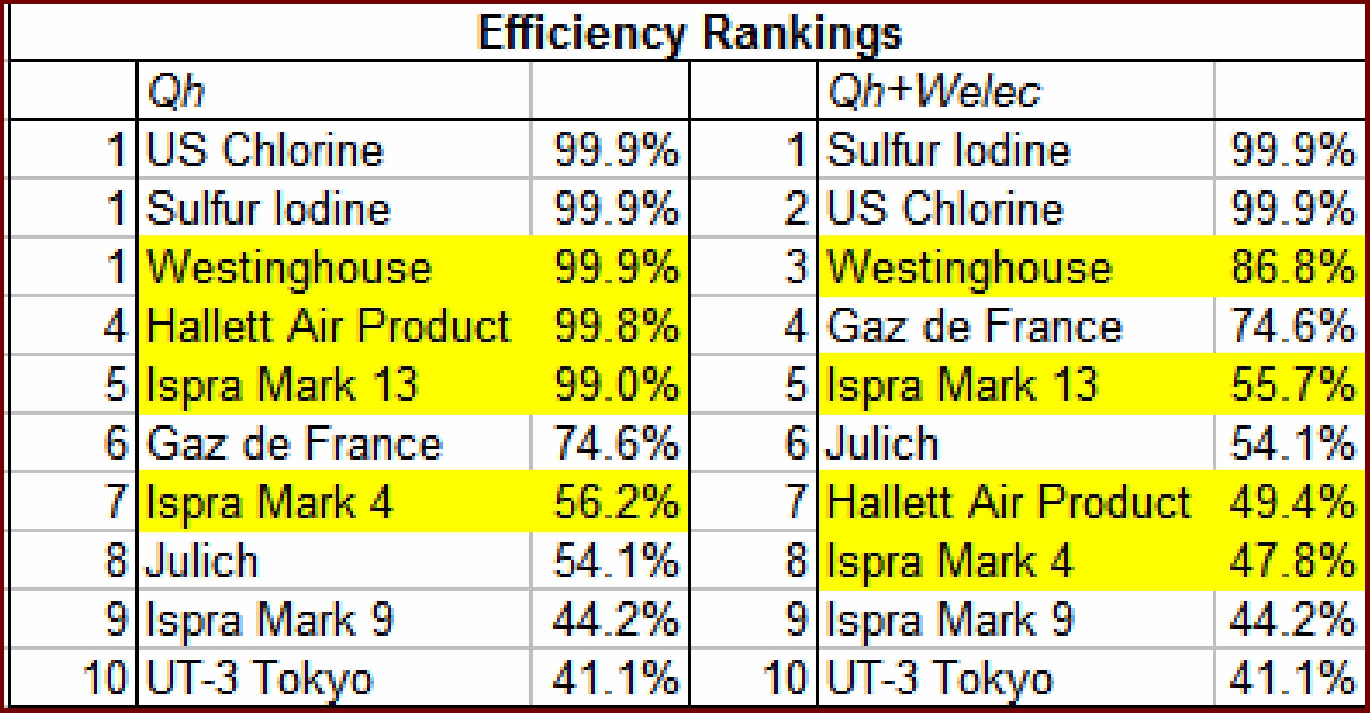
- Cycle rankings based on Q_{hot} (ΔT_{min}=10K)
  - Optimized feeds, equilibrium considered, reactants recycled



	Efficiency Rankings	
	Qh	
1	US Chlorine	99.9%
2	Sulfur Iodine	99.9%
3	Westinghouse	99.9%
4	Hallett Air Product	99.8%
5	Ispra Mark 13	99.0%
6	Gaz de France	74.6%
7	Ispra Mark 4	56.2%
8	Julich	54.1%
9	Ispra Mark 9	44.2%
10	UT-3 Tokyo	41.1%

Minimum Utility and Electrolysis Work Criterion

- Cycle rankings based on Q_{hot} (ΔT_{min}=10K) and W_{elec} only
  - Optimized feeds, equilibrium considered

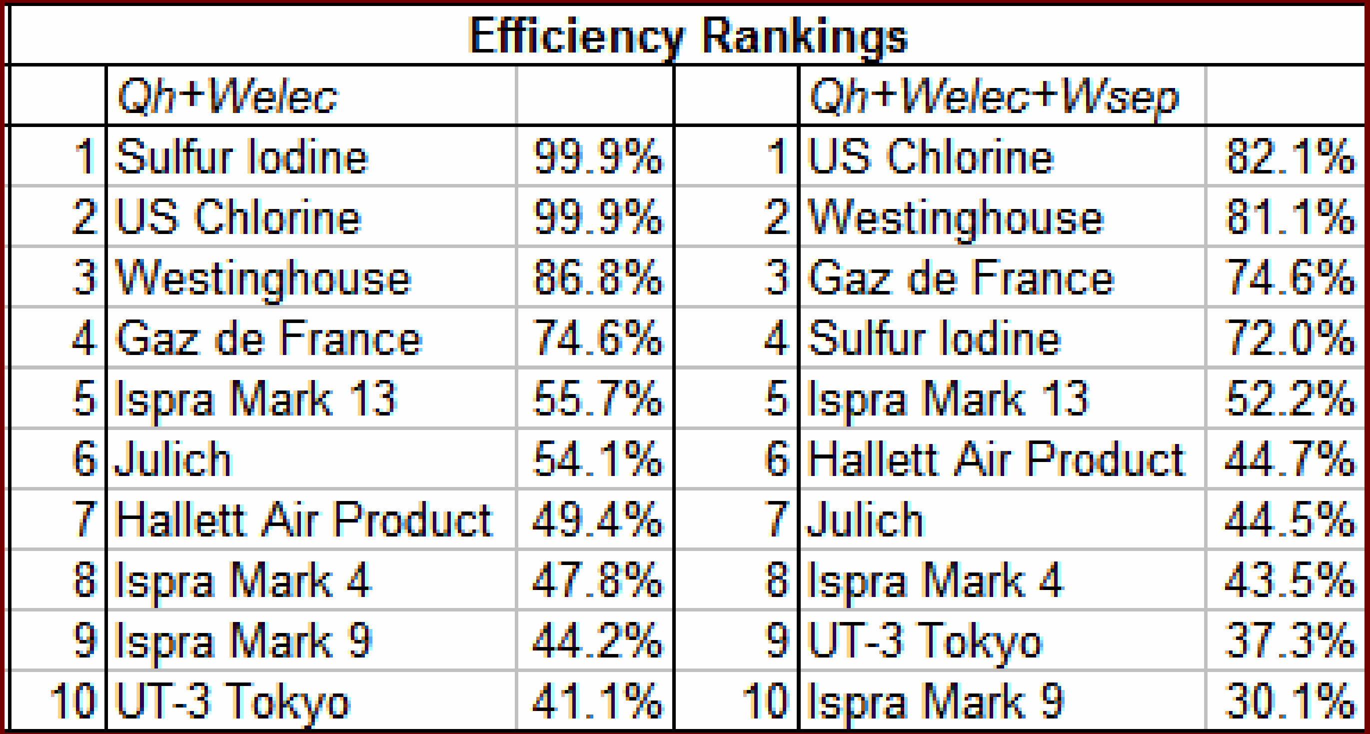


Efficiency Rankings

	Qh			*Qh+Welec*	
1	US Chlorine	99.9%	1	Sulfur Iodine	99.9%
1	Sulfur Iodine	99.9%	2	US Chlorine	99.9%
1	Westinghouse	99.9%	3	Westinghouse	86.8%
4	Hallett Air Product	99.8%	4	Gaz de France	74.6%
5	Ispra Mark 13	99.0%	5	Ispra Mark 13	55.7%
6	Gaz de France	74.6%	6	Julich	54.1%
7	Ispra Mark 4	56.2%	7	Hallett Air Product	49.4%
8	Julich	54.1%	8	Ispra Mark 4	47.8%
9	Ispra Mark 9	44.2%	9	Ispra Mark 9	44.2%
10	UT-3 Tokyo	41.1%	10	UT-3 Tokyo	41.1%

Minimum Utility, Electrolysis Work and (ideal) Separation Work ($\eta=0.5$) Criterion

- Cycle rankings based on Q_{hot} ($\Delta T_{min}=10K$), W_{elec}, and W_{sep}
  - Optimized feeds, equilibrium considered

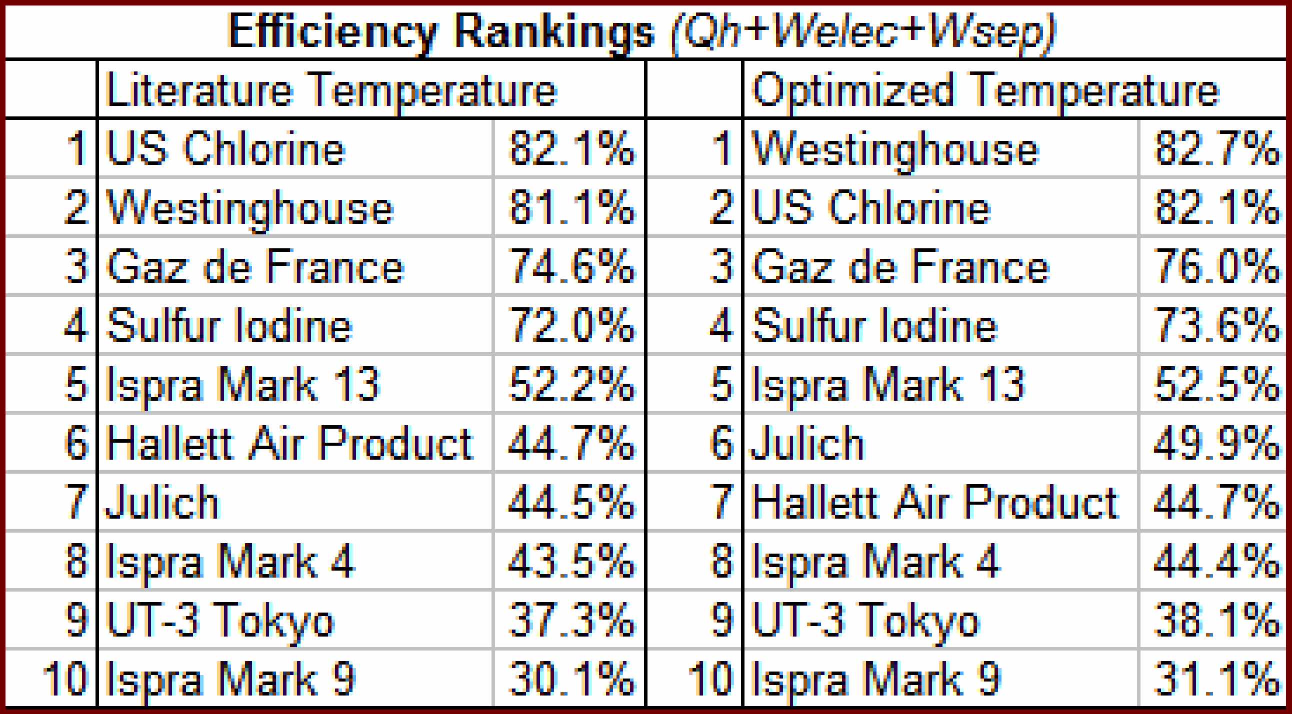


Efficiency Rankings

	Qh+Welec			*Qh+Welec+Wsep*	
1	Sulfur Iodine	99.9%	1	US Chlorine	82.1%
2	US Chlorine	99.9%	2	Westinghouse	81.1%
3	Westinghouse	86.8%	3	Gaz de France	74.6%
4	Gaz de France	74.6%	4	Sulfur Iodine	72.0%
5	Ispra Mark 13	55.7%	5	Ispra Mark 13	52.2%
6	Julich	54.1%	6	Hallett Air Product	44.7%
7	Hallett Air Product	49.4%	7	Julich	44.5%
8	Ispra Mark 4	47.8%	8	Ispra Mark 4	43.5%
9	Ispra Mark 9	44.2%	9	UT-3 Tokyo	37.3%
10	UT-3 Tokyo	41.1%	10	Ispra Mark 9	30.1%

Temperature Optimization

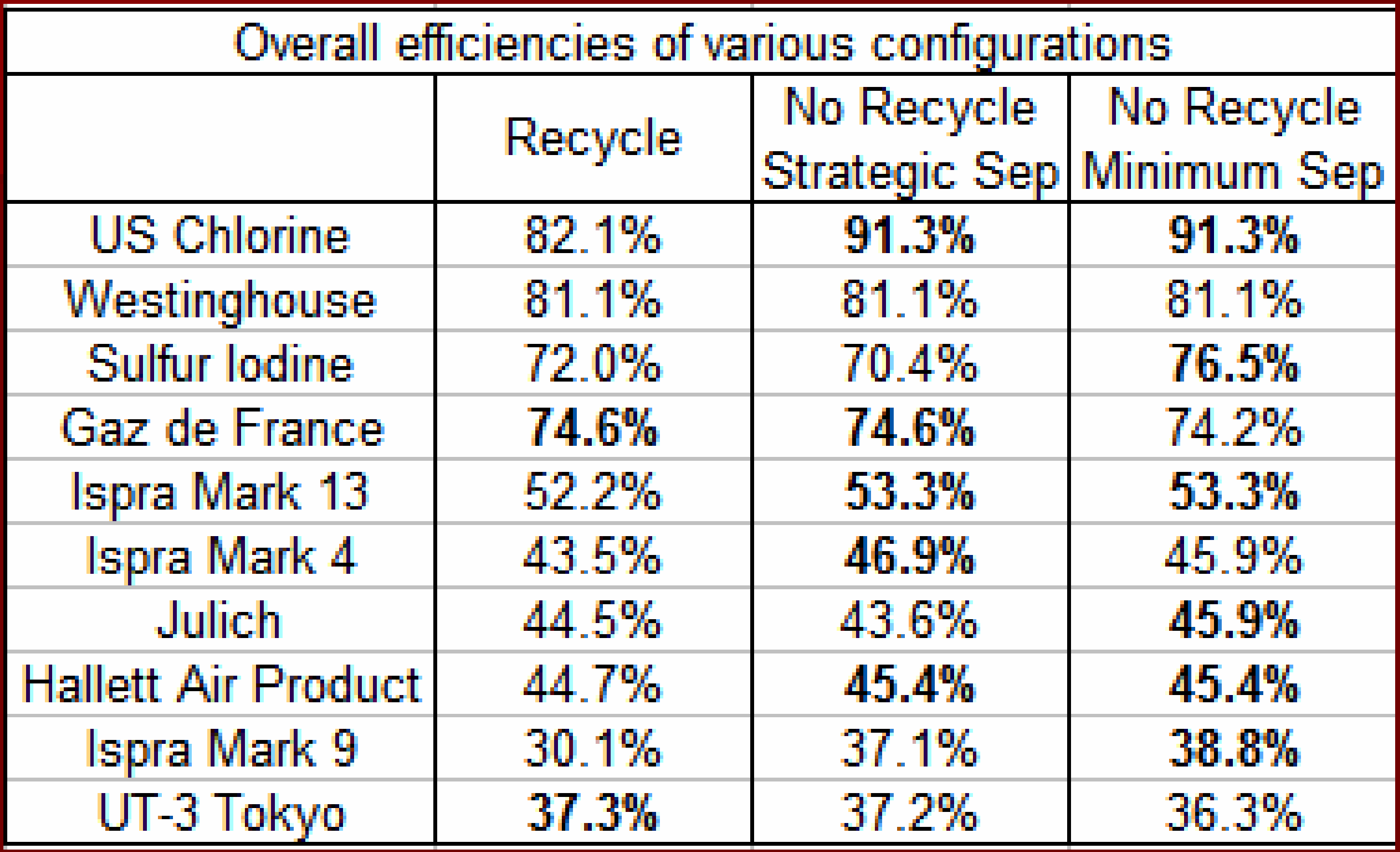
- Limited by phase changes
  - – Optimized feeds, equilibrium considered



Efficiency Rankings *(Qh+Welec+Wsep)*

	Literature Temperature			Optimized Temperature	
1	US Chlorine	82.1%	1	Westinghouse	82.7%
2	Westinghouse	81.1%	2	US Chlorine	82.1%
3	Gaz de France	74.6%	3	Gaz de France	76.0%
4	Sulfur Iodine	72.0%	4	Sulfur Iodine	73.6%
5	Ispra Mark 13	52.2%	5	Ispra Mark 13	52.5%
6	Hallett Air Product	44.7%	6	Julich	49.9%
7	Julich	44.5%	7	Hallett Air Product	44.7%
8	Ispra Mark 4	43.5%	8	Ispra Mark 4	44.4%
9	UT-3 Tokyo	37.3%	9	UT-3 Tokyo	38.1%
10	Ispra Mark 9	30.1%	10	Ispra Mark 9	31.1%

Comparison of Results

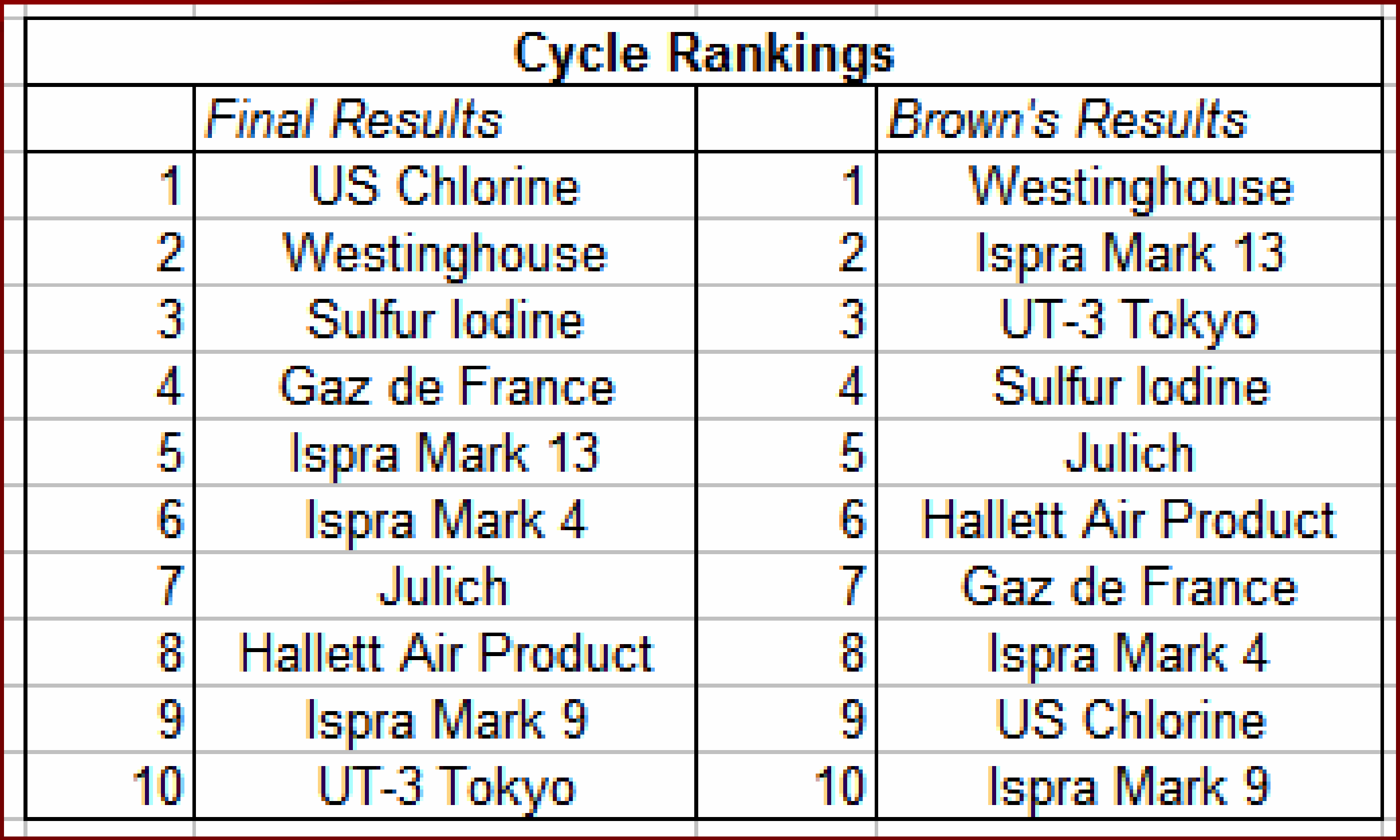


Overall efficiencies of various configurations

	Recycle	No Recycle Strategic Sep	No Recycle Minimum Sep
US Chlorine	82.1%	**91.3%**	**91.3%**
Westinghouse	81.1%	81.1%	81.1%
Sulfur Iodine	72.0%	70.4%	**76.5%**
Gaz de France	**74.6%**	**74.6%**	74.2%
Ispra Mark 13	52.2%	**53.3%**	**53.3%**
Ispra Mark 4	43.5%	**46.9%**	45.9%
Julich	44.5%	43.6%	**45.9%**
Hallett Air Product	44.7%	**45.4%**	**45.4%**
Ispra Mark 9	30.1%	37.1%	**38.8%**
UT-3 Tokyo	**37.3%**	37.2%	36.3%

- W is ideal/0.5
- All energy terms have been included
- Different option is best depending on cycle

Comparison with Brown’s Results



Cycle Rankings

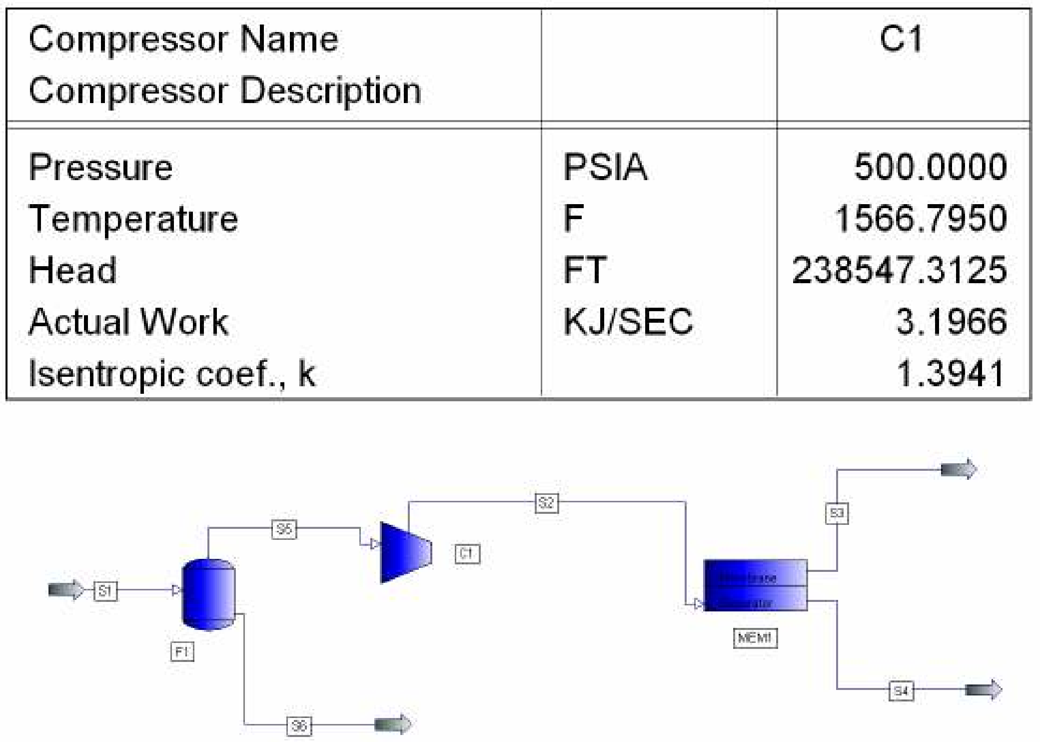
	Final Results		*Brown's Results*
1	US Chlorine	1	Westinghouse
2	Westinghouse	2	Ispra Mark 13
3	Sulfur Iodine	3	UT-3 Tokyo
4	Gaz de France	4	Sulfur Iodine
5	Ispra Mark 13	5	Julich
6	Ispra Mark 4	6	Hallett Air Product
7	Julich	7	Gaz de France
8	Hallett Air Product	8	Ispra Mark 4
9	Ispra Mark 9	9	US Chlorine
10	UT-3 Tokyo	10	Ispra Mark 9

Real Separation Energy

- Numerous recycle configurations
- Numerous separation techniques
- Difficult to achieve 100% separation
- Used membrane separators to estimate separation work for gas phase separations
- Membrane separators cannot operate at high temperatures

Real Separation Energy

- Real Separation work estimated for top 4 cycles
- Estimated as compressor work for membrane separator



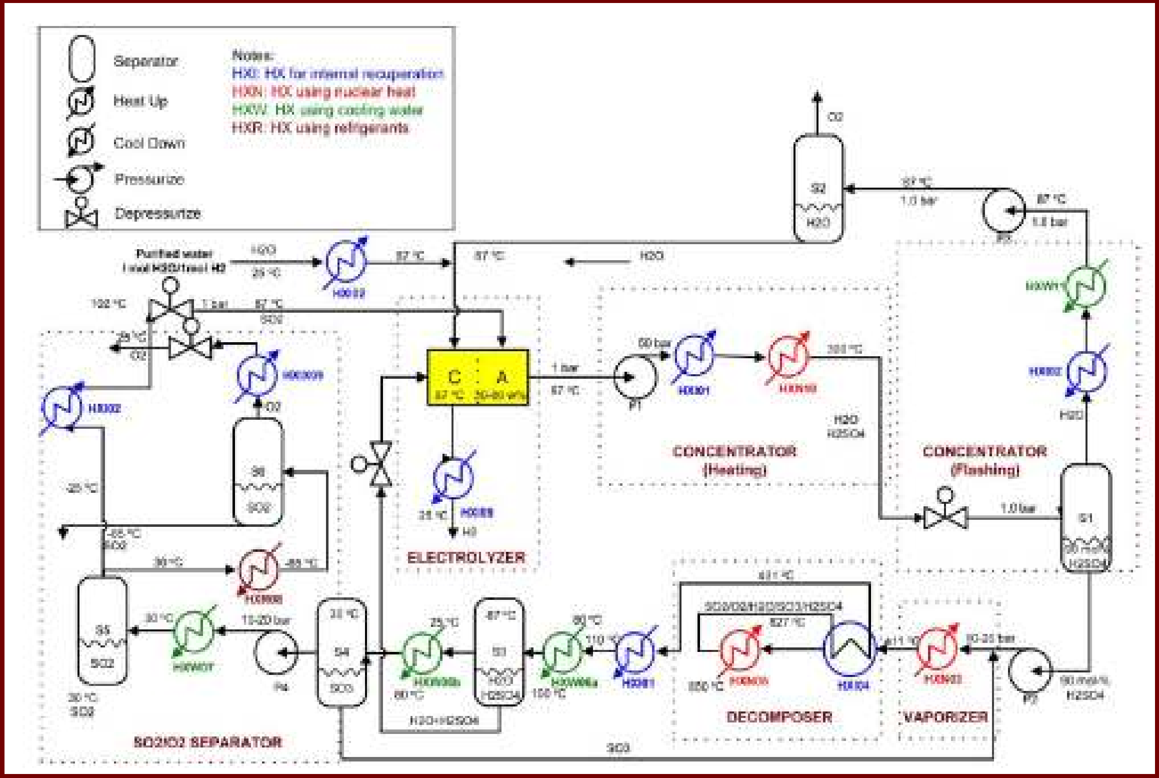
Compressor Name Compressor Description		C1
Pressure	PSIA	500.0000
Temperature	F	1566.7950
Head	FT	238547.3125
Actual Work	KJ/SEC	3.1966
Isentropic coef., k		1.3941

Real Separation Work (Membranes Only)

Cycle	Reaction 1	Reaction 2	Reaction 3	Wsep Ideal (kJ)	Wsep Real (kJ)	Efficiency w/ Wsep Real
US Chlorine	Membrane $HCl,O_2 \rightarrow HCl/O_2$	Phase $CuCl_2,H_2 \rightarrow CuCl_2/H_2$	Phase $CuCl,Cl_2 \rightarrow CuCl/Cl_2$	61.75	83.28	77.4%
Sulfur Iodine	Membrane $H_2O,SO_2,O_2 \rightarrow H_2O,SO_2/O_2$	Phase $HI,H_2SO_4 \rightarrow HI/H_2SO_4$	Phase $I_2,H_2 \rightarrow I_2/H_2$	110.68	119.80	70.4%
Westinghouse	Membrane $H_2O,SO_2,O_2 \rightarrow H_2O,SO_2/O_2$	Phase $H_2SO_4,H_2 \rightarrow H_2SO_4/O_2$	N/A	23.36	32.5	79.0%
Gaz de France	Phase $K_2O,H_2 \rightarrow K_2O/H_2$	Phase $K,K_2O_2 \rightarrow K/K_2O_2$	Phase $KOH,O_2 \rightarrow KOH/O_2$	0	0	74.6%

Real Separation Energy

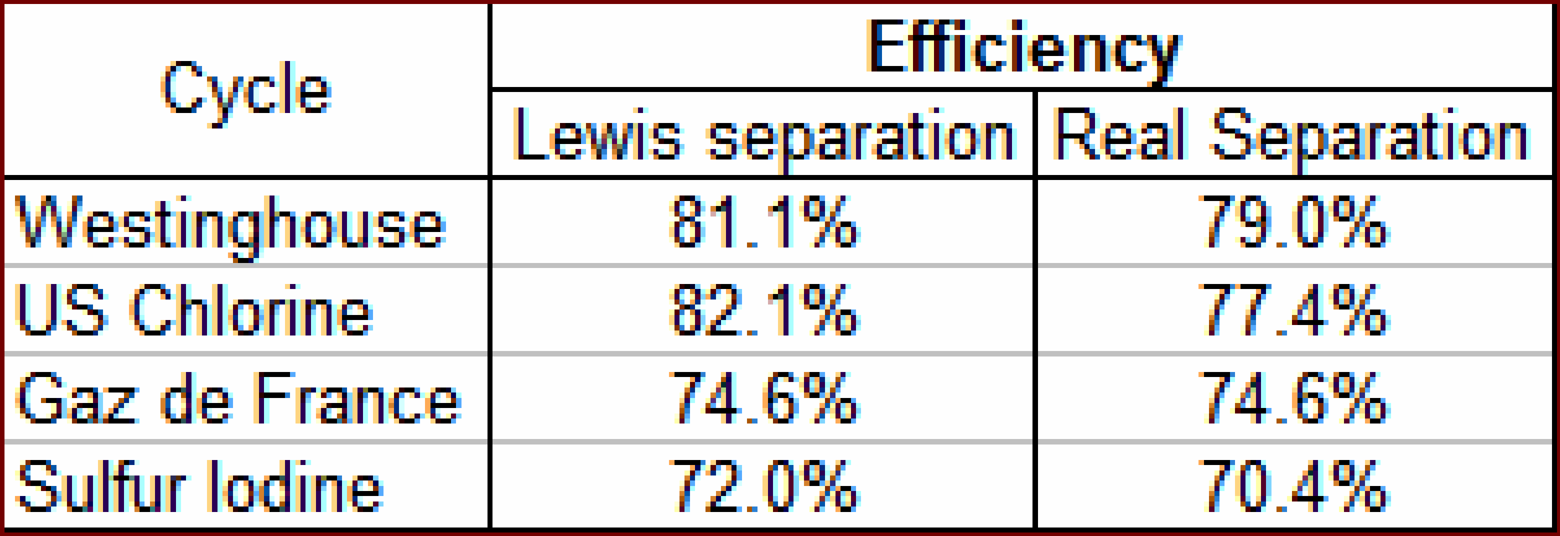
- Actual work for a given system can only be determined with a detailed flow sheet



Taken from **Y.H. Jeong, M.S. Kazimi, K.J. Hohnholt, and B. Yildiz** resource

Real Separation Work

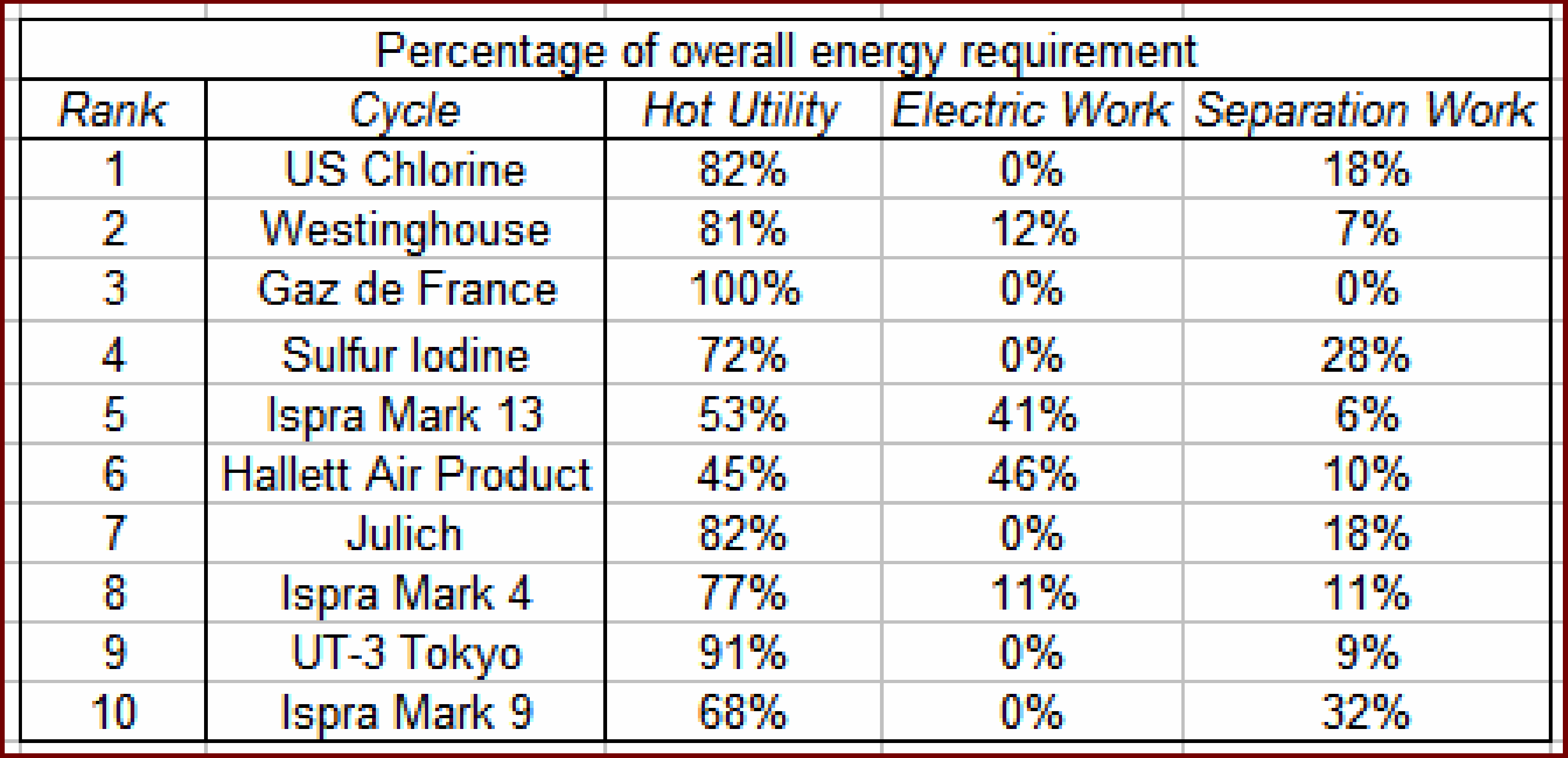
- Comparison of efficiency for Lewis separation and real separation for top 4 cycles



Cycle	Efficiency	
	Lewis separation	Real Separation
Westinghouse	81.1%	79.0%
US Chlorine	82.1%	77.4%
Gaz de France	74.6%	74.6%
Sulfur Iodine	72.0%	70.4%

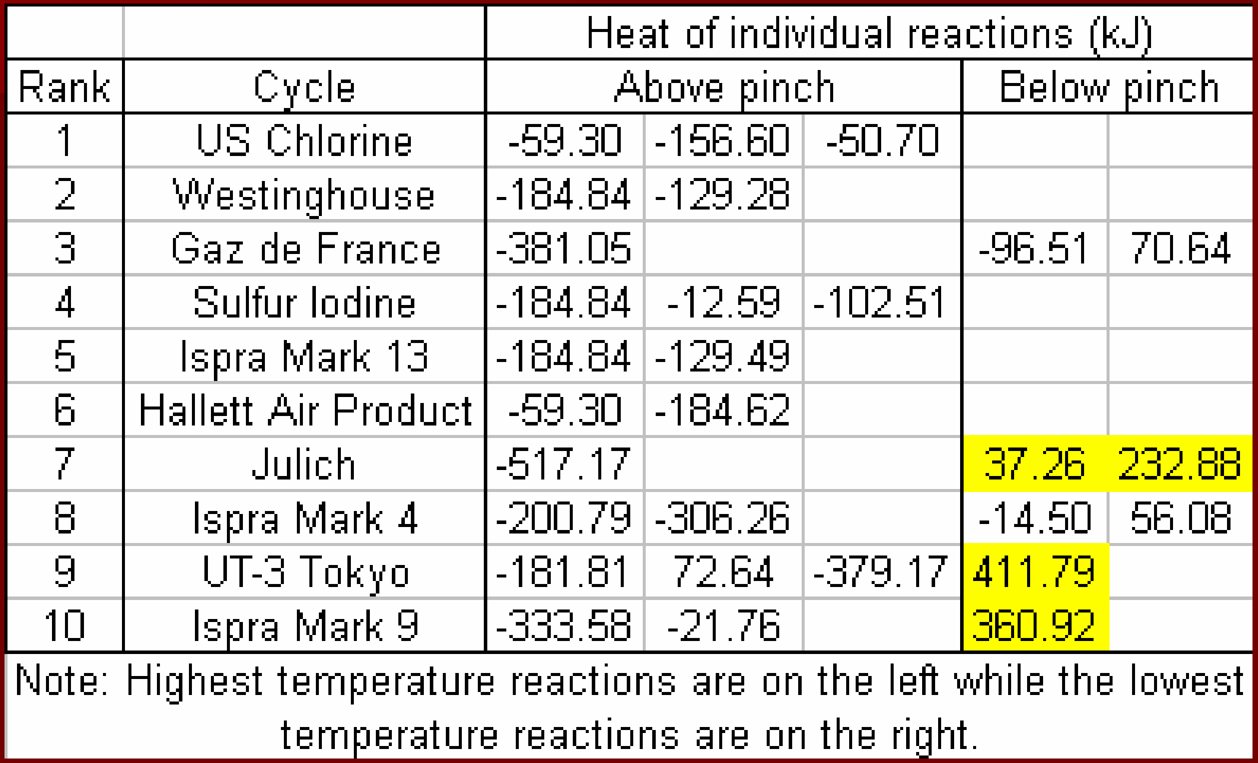
Screening Process

- Over 200 documented cycles
- Find a quick method of finding efficiency



Percentage of overall energy requirement				
Rank	*Cycle*	*Hot Utility*	*Electric Work*	*Separation Work*
1	US Chlorine	82%	0%	18%
2	Westinghouse	81%	12%	7%
3	Gaz de France	100%	0%	0%
4	Sulfur Iodine	72%	0%	28%
5	Ispra Mark 13	53%	41%	6%
6	Hallett Air Product	45%	46%	10%
7	Julich	82%	0%	18%
8	Ispra Mark 4	77%	11%	11%
9	UT-3 Tokyo	91%	0%	9%
10	Ispra Mark 9	68%	0%	32%

Screening Process



		Heat of individual reactions (kJ)				
Rank	Cycle	Above pinch			Below pinch	
1	US Chlorine	-59.30	-156.60	-50.70		
2	Westinghouse	-184.84	-129.28			
3	Gaz de France	-381.05			-96.51	70.64
4	Sulfur Iodine	-184.84	-12.59	-102.51		
5	Ispra Mark 13	-184.84	-129.49			
6	Hallett Air Product	-59.30	-184.62			
7	Julich	-517.17			37.26	232.88
8	Ispra Mark 4	-200.79	-306.26		-14.50	56.08
9	UT-3 Tokyo	-181.81	72.64	-379.17	411.79	
10	Ispra Mark 9	-333.58	-21.76		360.92	

Note: Highest temperature reactions are on the left while the lowest temperature reactions are on the right.

- Exclude process with high exothermic reaction(s) at low temperature

Conclusions

- Efficiency based method can quickly rank hydrogen producing cycles
- Best configuration of excess handling depends on cycle being considered
- Phase separation and good cascade properties benefit efficiency

Questions

References

Aqueous Standard Reduction Potentials”. Physical Sciences Information Gateway. 9 March 2006 < http://www.psigate.ac.uk >.

Bagajewicz, M. *“Pinch and Minimum Utility Usage”.* 11 March 2007 <http://www.ou.edu/class/che-design/a-design/Minimum%20Utility.pdf>.

Brown, L.C., S.K. Showalter, and J.F. Funk. *Nuclear Production of Hydrogen Using Thermochemical Water-Splitting Cycles,* 2000.

JANAF Data. National Institute of Standards and Technology. 9 March 2006 <http://webbook.nist.gov>.

Jeong Y.H., M. S. Kazimi, K.J. Hohnholt, and B. Yildiz. *Optimization of the Hybrid Sulfur Cycle for Hydrogen Generation.* MIT-NES-TR-004, 2005.

Lewis, M. A.; *High-Temperature Thermochemical Processes.* DOE Hydrogen Program, FY 2005 Progress Report, September 2005.

Perry, Robert H. *Perry’s Chemical Engineers’ Handbook, 7th ed.* McGraw-Hill, 1997.

Winnick, Jack. *Chemical Engineering Thermodynamics.* John Wiley & Sons, Inc, 1997.