

A New Methodology to Screen Water-Splitting Cycles for Hydrogen Production

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Hydrogen Economy

- Currently 11 million tons/year
- In H₂ economy[†]:
 - 200 million tons/year for transportation
 - 450 million tons/year for all non-electric
- H₂ is not a natural resource
 - Must be produced
- Steam reformation of methane
 - CO₂ output
 - Rising fuel prices

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

Alternative H₂ Production

✘ Petroleum

- CO₂, expensive

✘ Electrolysis, high T electrolysis

- Premature, inefficient

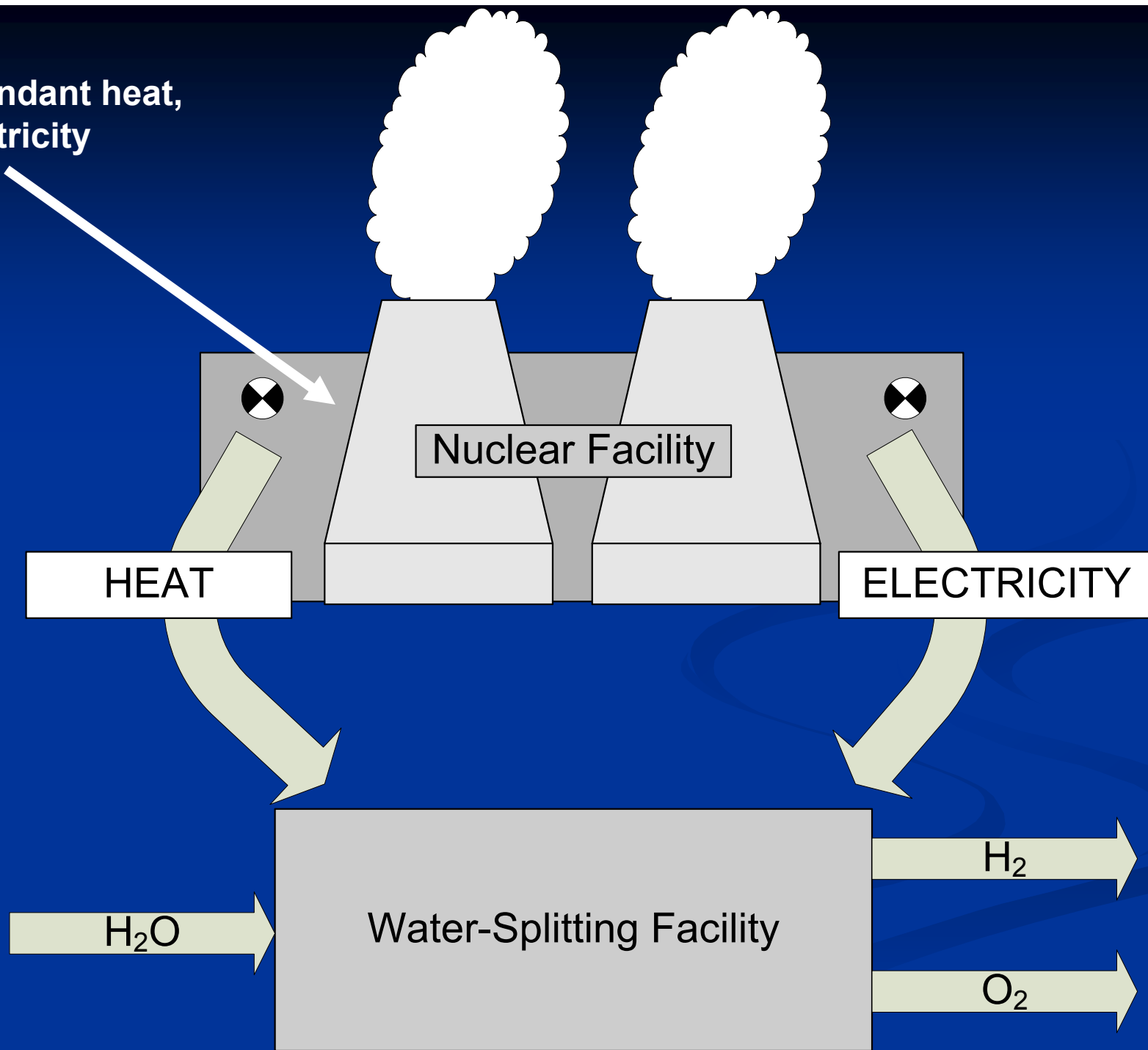
✘ Photocatalytic reactors

- Premature

☑ Thermochemical cycles

- Efficient, established processing techniques

Abundant heat,
electricity



Water-Splitting Cycles

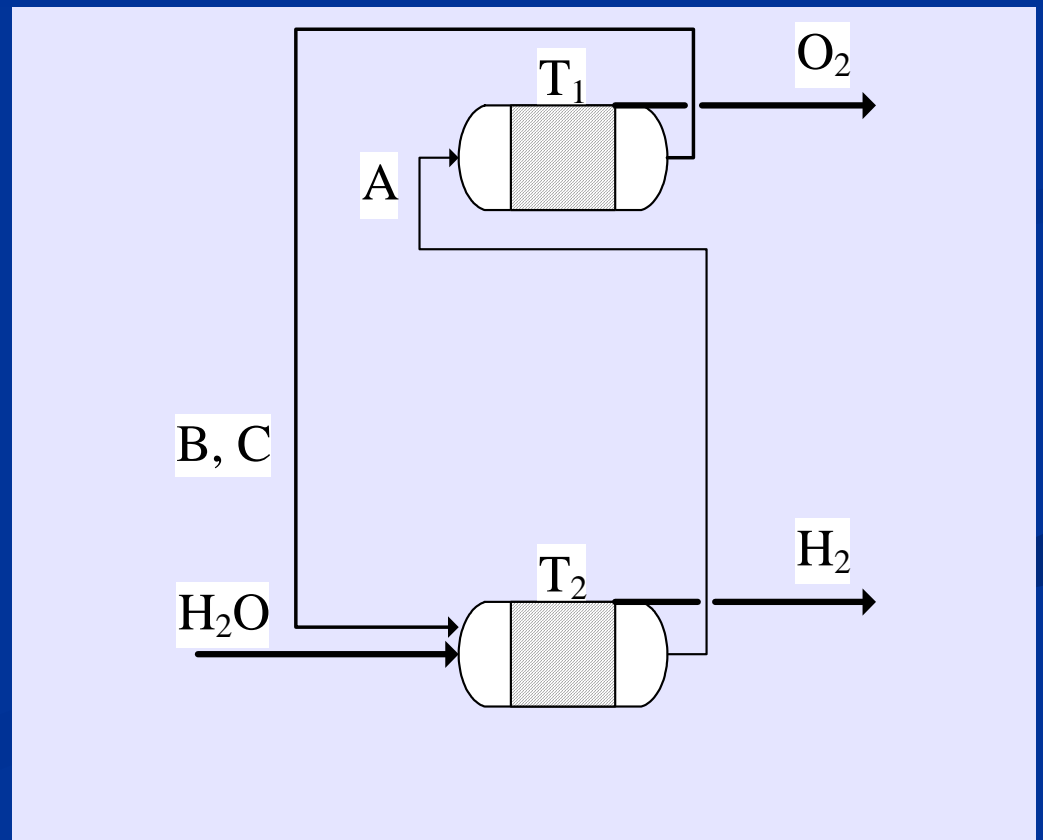
- “New” technology, chosen by DOE’s Nuclear Hydrogen Initiative
- Efficient hydrogen production
 - 50-60% currently, 80-90%+ possible
- Use 950°C or cooler process heat
- 202 cycles known, but few researched
 - Others can be found, through systematic search (Holiastos and Manousiouthakis 1998).

Cycles

- Most are thermochemical, some hybrid electric
- Any number of reactions, species
- Named after institutions or chemicals
- Steady-state operation

Sample 2-step cycle

T_1	$A \longrightarrow B + C + O_2$
T_2	$B + C + H_2O \longrightarrow A + H_2$



Efficiency

- Theoretical, 1 mol basis for cycle comparison
- Minimum reversible energy (heating and work) requirement

$$\eta = \frac{\Delta H_f^\circ(\text{H}_2\text{O})}{Q + W}$$

Q : total heat requirement

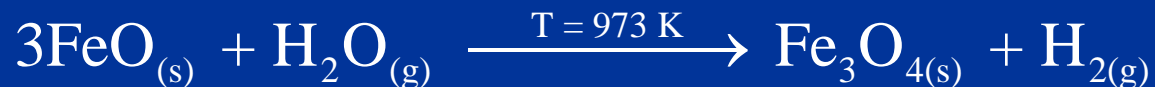
W : separation, electric and shaft work (to move fluids: pumping, compressing).

Previous Surveys

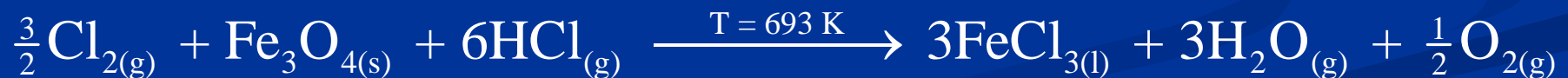
- Brown et al 2000 scored cycles based on known characteristics
 - Good starting point, but not reproducible
 - Arbitrary criteria, no emphasis on efficiency
 - Elemental abundance, “corrosivity”, # elements
 - Rejects cycles with “too positive” free energies
 - Favors well-researched cycles

Sample Thermochemical Cycles

■ Julich

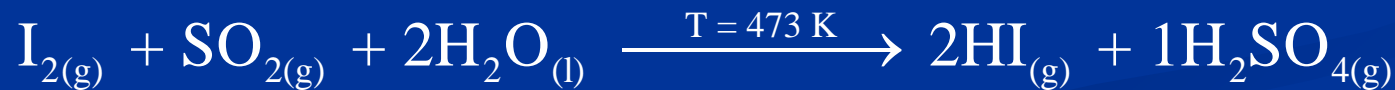


■ Ispra Mark 9

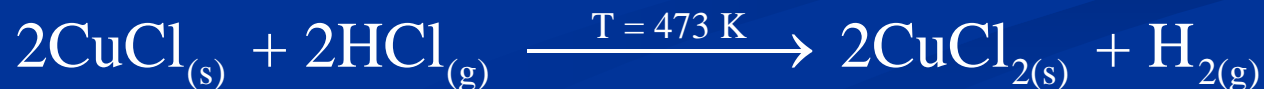
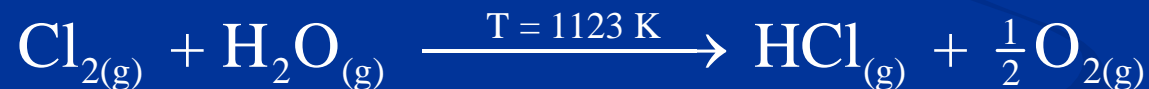


Sample Thermochemical Cycles

■ Sulfur Iodine

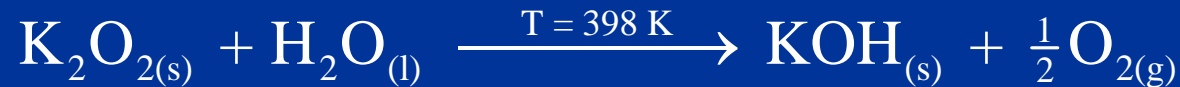
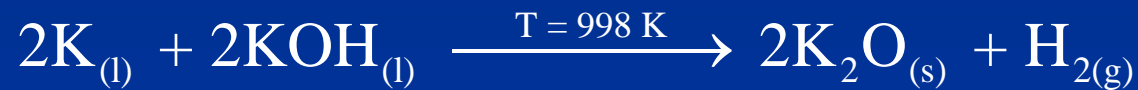


■ US-Chlorine

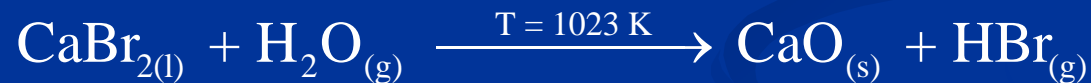


Sample Thermochemical Cycles

■ Gaz de France



■ UT-3 Tokyo

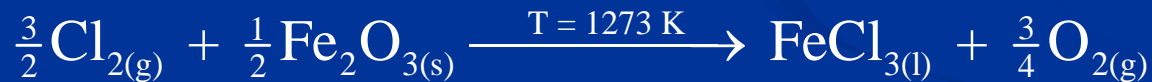


Sample Thermochemical Cycles

■ Ispra Mark 4

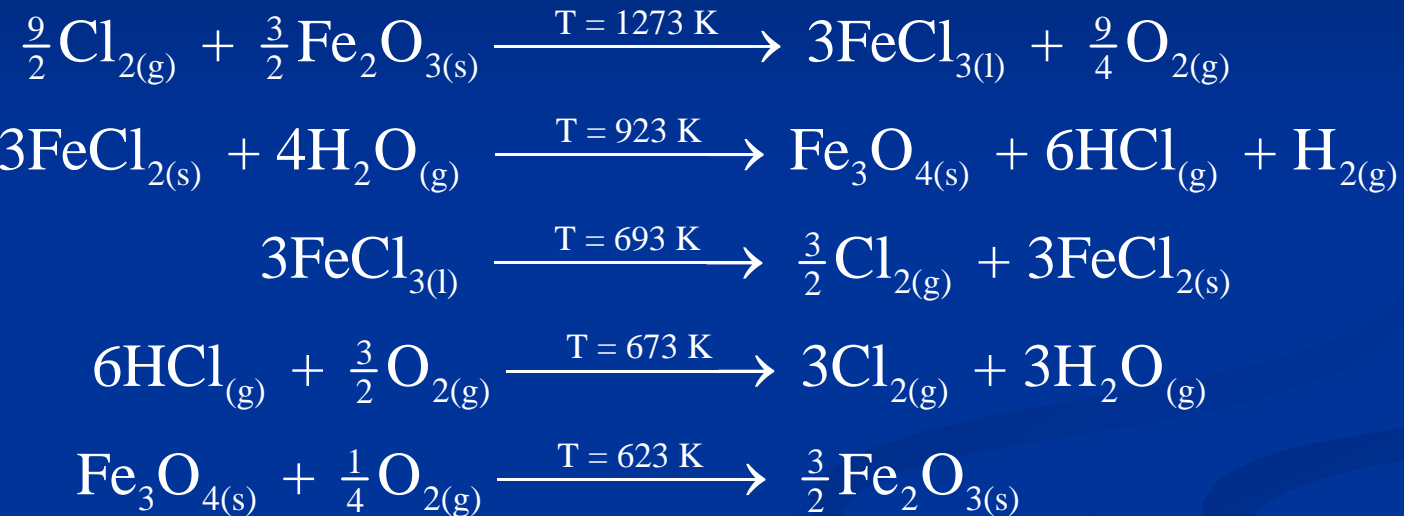


■ Ispra Mark 7A



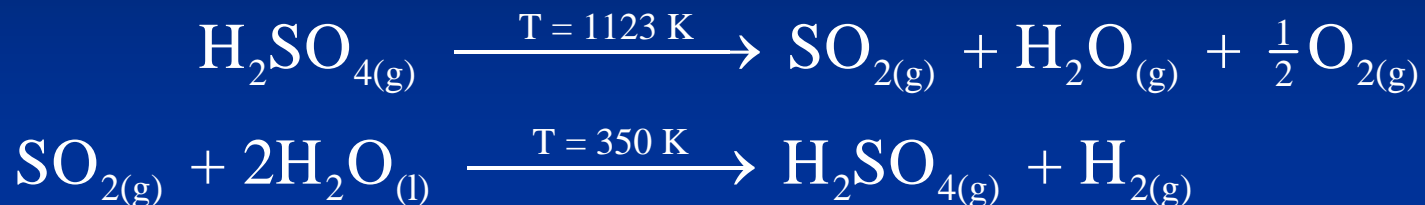
Sample Thermochemical Cycles

■ Ispra Mark 7B

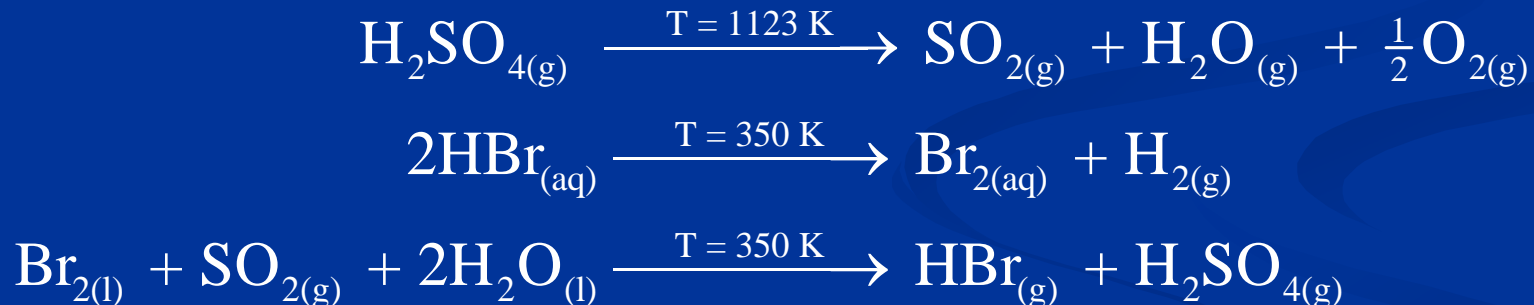


Sample Hybrid Cycles

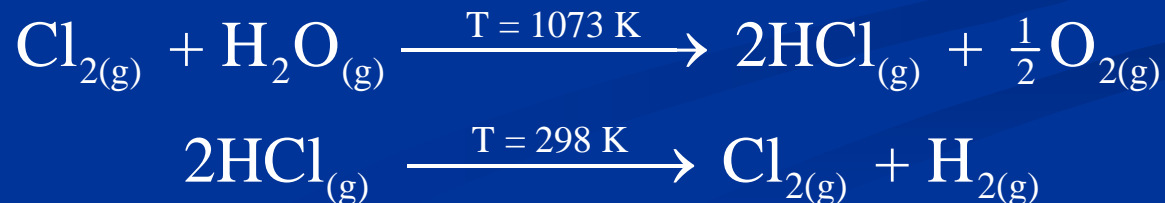
■ Westinghouse



■ Ispra Mark 13



■ Hallett Air Products



	Score†			
	0	1	2	3
# reactions	6	-	-	5
# separations	10	9	8	7
# elements	7	-	6	-
Least abundant element	Ir	Rh, Tc, Os, Ru, Re, Au	Pt, Bi, Pd, Hg, Se	Ag, In, Cd, Sb, Tm, Tl, Lu

Brown's method is good at identifying cycles based on estimated process complexities, but is not quantitative or reproducible. What happens if you change the weights, or add further scoring criteria?

†Adapted from Brown et al 2000

Previous Surveys cont'd

- Lewis et al (2005) developed a systematic approach
 - Scoping method based on efficiency
 - Quantitative, standard basis
 - Oversimplifications
 - Requires detailed flowsheets
 - Not truly scoping
 - Assumes 50% loss of all work energy
 - Does not estimate real separation energy

General Methodology

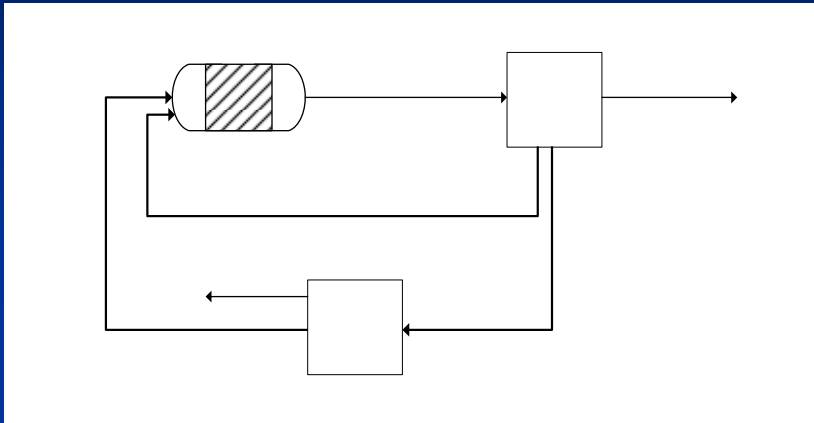
- Decouple the problem
 - Find realistic estimates for Q , W
 - Refine calculations for best cycles
 - Account for additional energy requirements
 - Economic analysis of best cycles
- Apply methodology to all cycles
 - Evaluate the 202 from literature
 - Find unknown cycles

Equilibrium

- Excess reactants added to shift reactions to the right
- How do we handle excess after the reaction?
 - Requires optimization, coupled equations

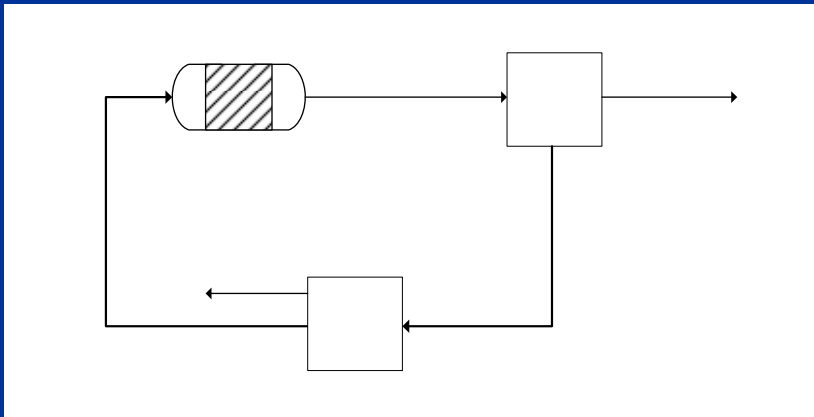
$$K_{eq} = K_x P^{\sum \nu} = \frac{\prod_{\text{products}} \left(\frac{n_i}{\sum n_i} \right)^{\nu_i}}{\prod_{\text{reactants}} \left(\frac{n_i}{\sum n_i} \right)^{\nu_i}} P^{\sum \nu}$$

Excess Reactant Handling



Immediate recycle: full separation energy costs

T_1	$A \longrightarrow B + C + O_2$
T_2	$B + C + H_2O \longrightarrow A + H_2$



No recycle: saves separation energy, but negatively shifts equilibrium in most cases and increases heat cascade requirement

A

T_1

A, B, C, O_2

Sep

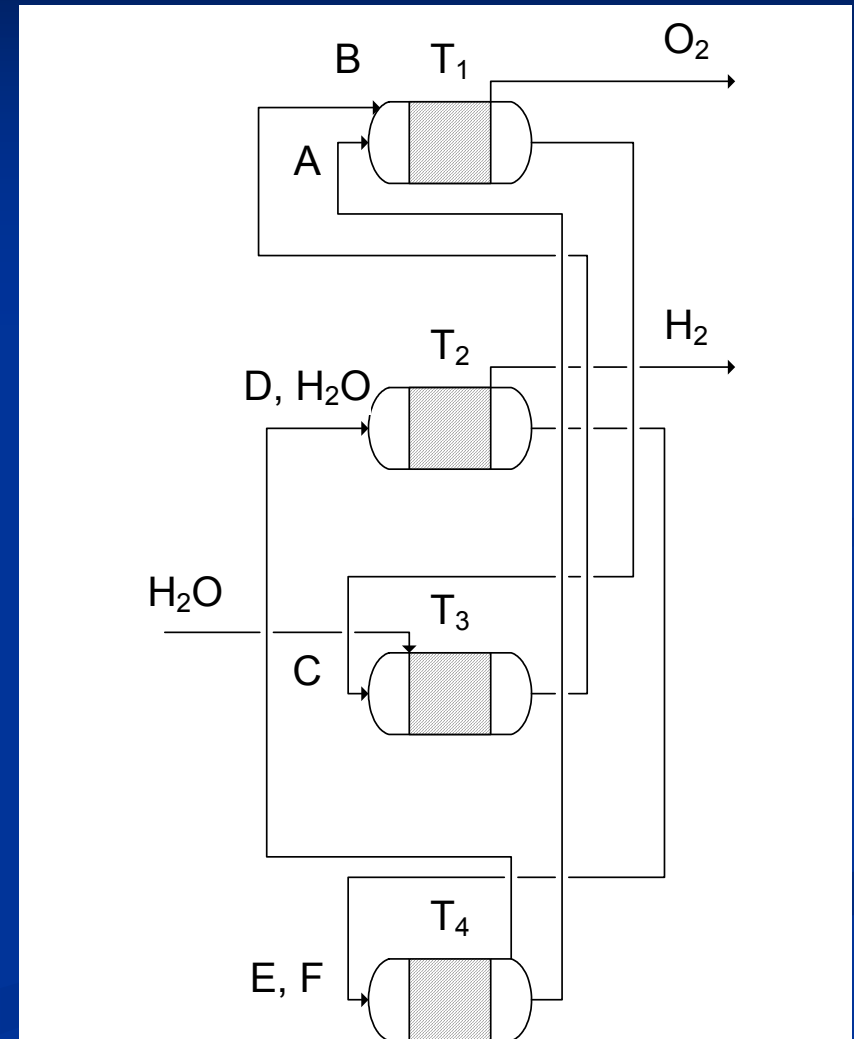
We optimize T, P, # excess moles and their handling

Cycles cont'd

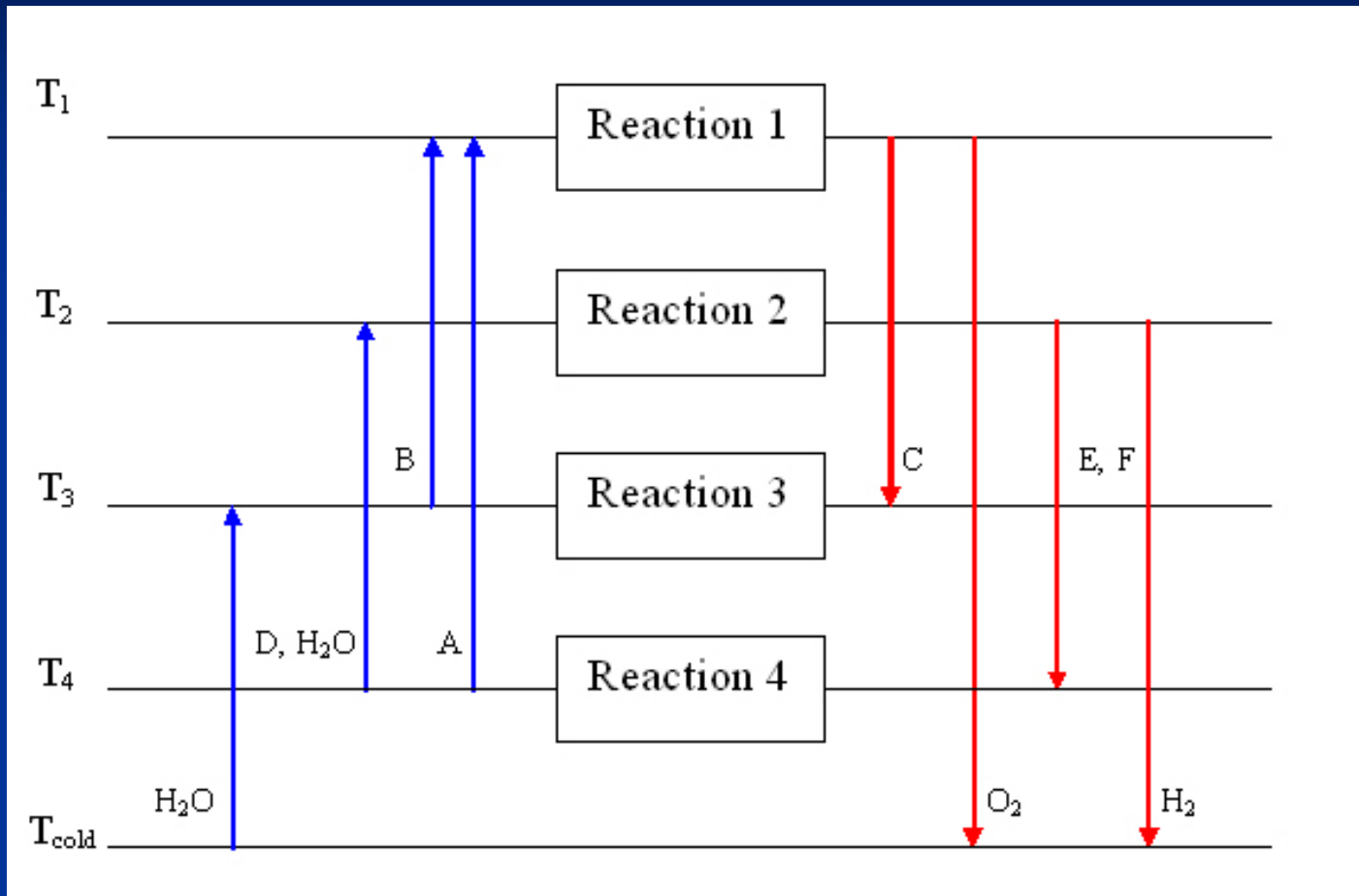
- Methodology accounts for arbitrarily complex cycles

T_1	$A + B \longrightarrow C + O_2$
T_2	$D + H_2O \longrightarrow E + F + H_2$
T_3	$C + H_2O \longrightarrow B + F$
T_4	$E + F \longrightarrow A + D + H_2O$

Conditions optimized for each reactor

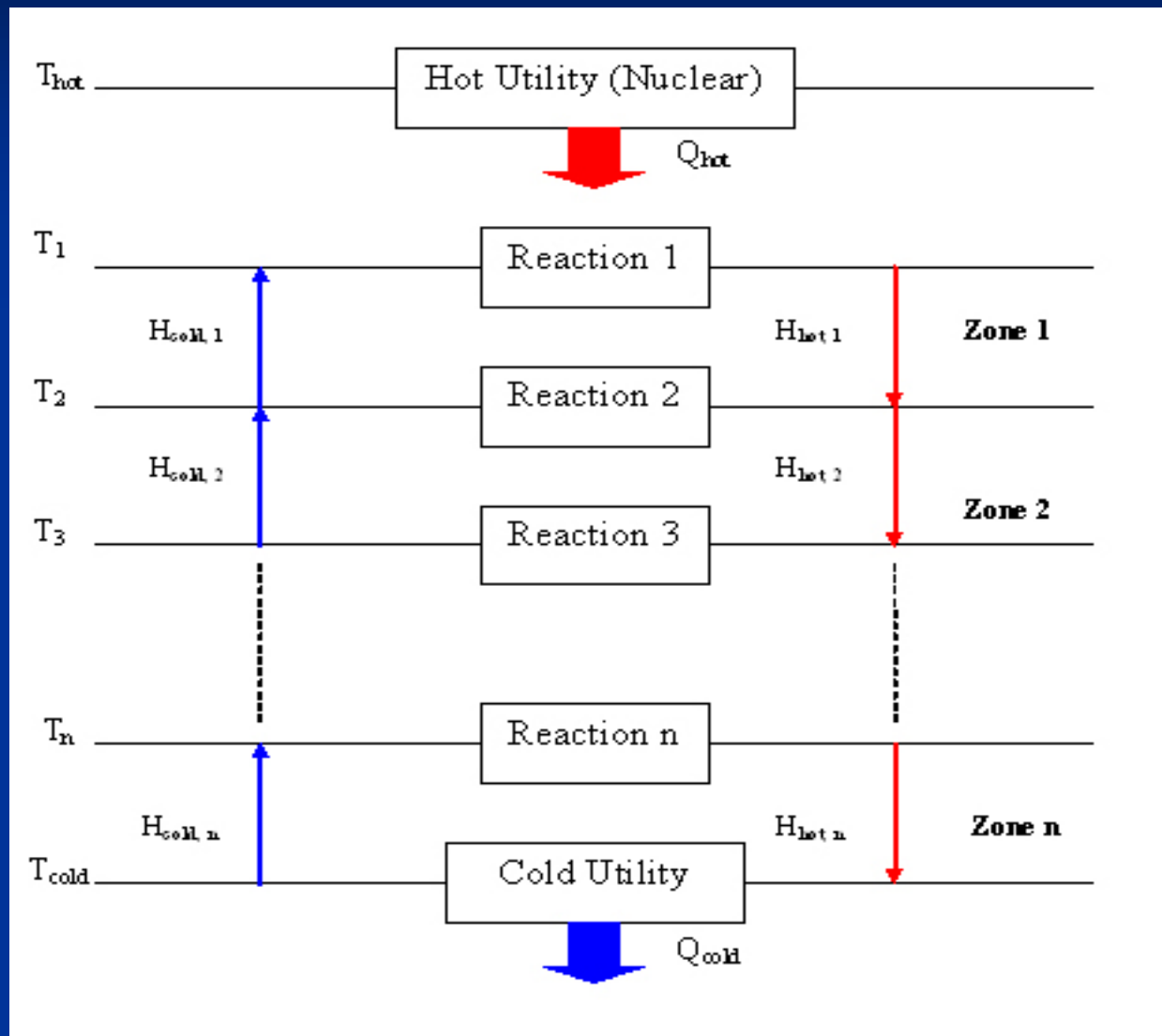


Heat Requirements



- Maximize heat recovery from exothermic reactions and cooling streams
- Pinch occurs when there is not enough heat to power reactions or heat streams, requiring input from the hot utility

Generic Heat Integration



H_{hot} is total enthalpy of cooling streams

H_{cold} is total enthalpy of heating streams

Electrical Work

- Nernst equation for electrolytic cells
- Assume steady-state operation of electrolytic cells
 - New electrolysis methods efficient compared to batch process[†]
- Hybrid cycles treated same in heat integration

$$W_{\text{elec}} = -nFE^{\circ}$$

$$E^{\circ} = E^{\circ}_{(298)} + \int_{298}^T \frac{d(E^{\circ}(T))}{dT}$$

[†]Motupally et al 1998

Separation Work

- Minimum separation estimate

$$W_{sep} = -\Delta G = -\Delta \sum_{i=0} n_i \mu_i = -RT \Delta \sum_{i=0} n_i \ln x_i$$

Assuming isothermal separation

$$W_{sep} = RT \left[\left(\sum_{i=0} n_i \ln x_i \right)_{out} - \left(\sum_{i=0} n_i \ln x_i \right)_{in} \right]$$

- Phases self-separate

- We don't pay for it

- Estimate separation efficiencies

$$W = \frac{W_{sep,ideal}}{\eta_{separation}}$$

This provides us with a minimum requirement. Chemical mixing and individual processes will increase W . Assign efficiencies to each process: e.g. assume distillation columns 50% efficient

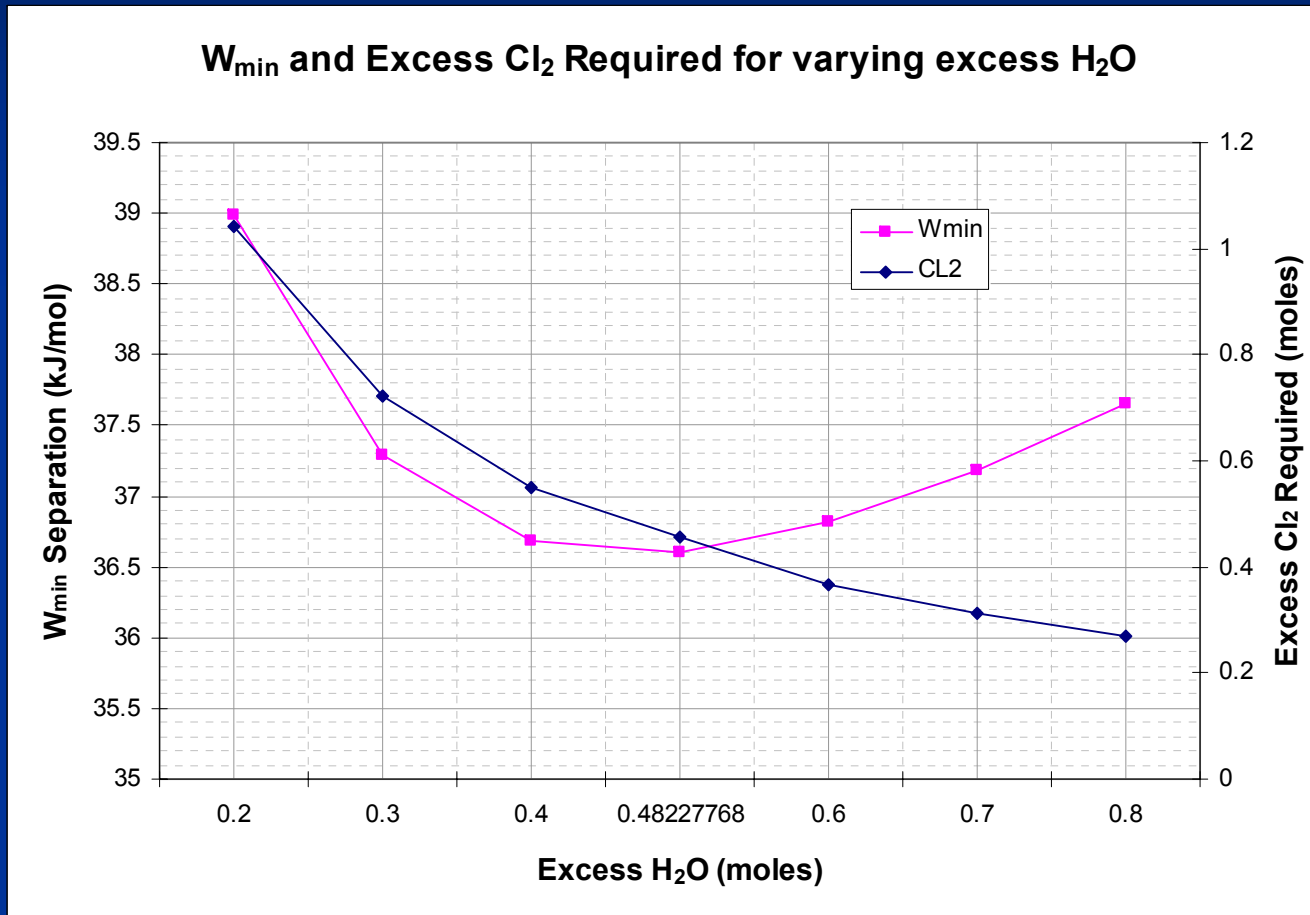
Solution Procedure

- Most reactions go to completion
 - No excess reactants to handle
 - Optimize reactors individually
- For other reactions
 - Find equilibrium concentrations
 - Know how much product we need from connectivity

Solution Procedure cont'd

- Computer algorithm finds optimum efficiency for each T
 - P easy to find
 - Finds Q and W for each # moles excess
 - Optimize these for each recycle scheme
- Computer crawls through solutions, and maximizes efficiency

Example Optimization



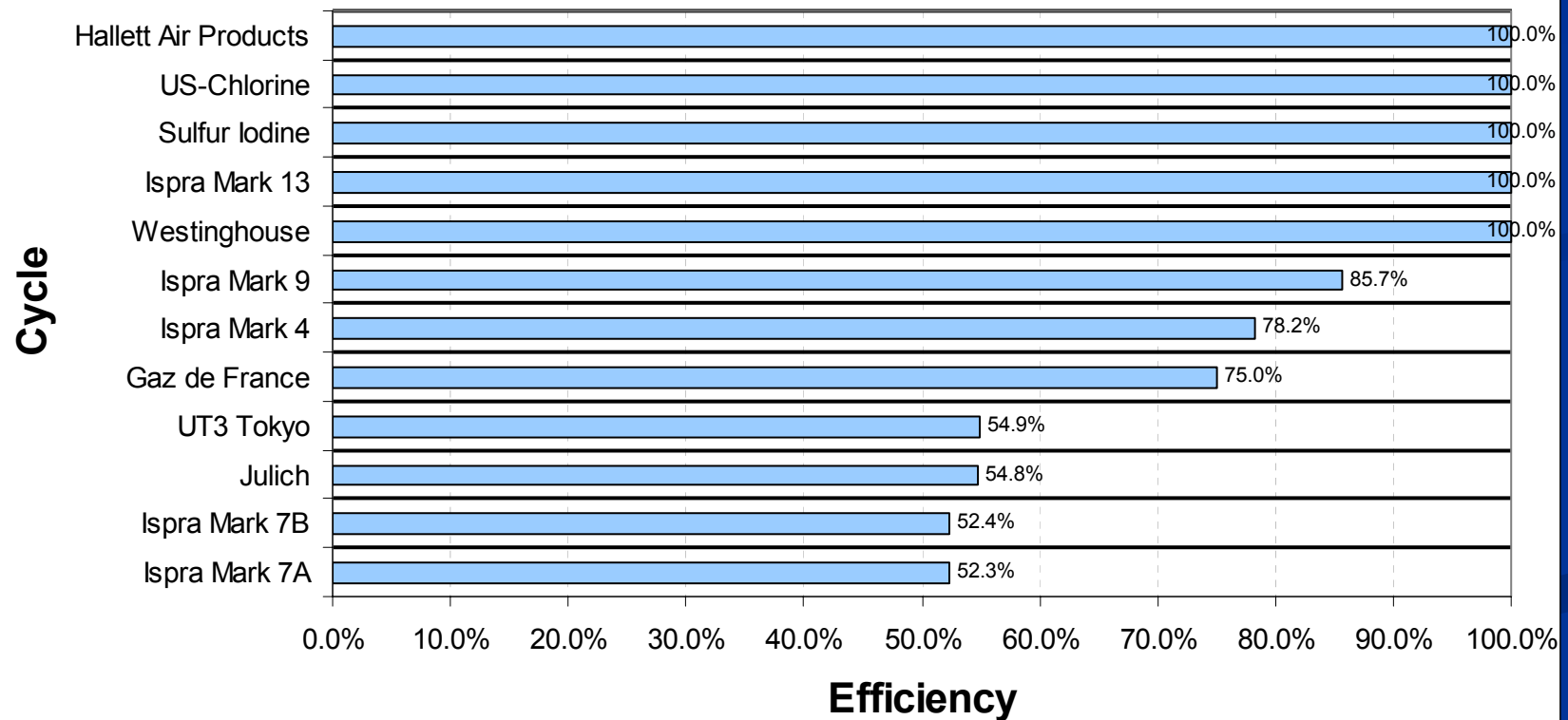
Results

- Cycle rankings based on Q_H analysis with $\Delta T_{\min}=0$

1. Hallett Air Products
1. US-Chlorine
1. Sulfur Iodine
1. Ispra Mark 13
1. Westinghouse
2. Ispra Mark 9
3. Ispra Mark 4
4. Gaz de France
5. UT-3 Tokyo
6. Julich
7. Ispra Mark 7B
8. Ispra Mark 7A

Q_H analysis with $\Delta T_{\min}=0$

Cycle Efficiencies using Q_h for $\Delta T_{\min}=0$



Results cont.

- Now we consider $W_{\text{sep, stoich}}$ and W_{elec} as well

Q_H only

1. Hallett Air Products
1. US-Chlorine
1. Sulfur Iodine
1. Ispra Mark 13
1. Westinghouse
2. Ispra Mark 9
3. Ispra Mark 4
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5. UT-3 Tokyo
6. Julich
7. Ispra Mark 7B
8. Ispra Mark 7A

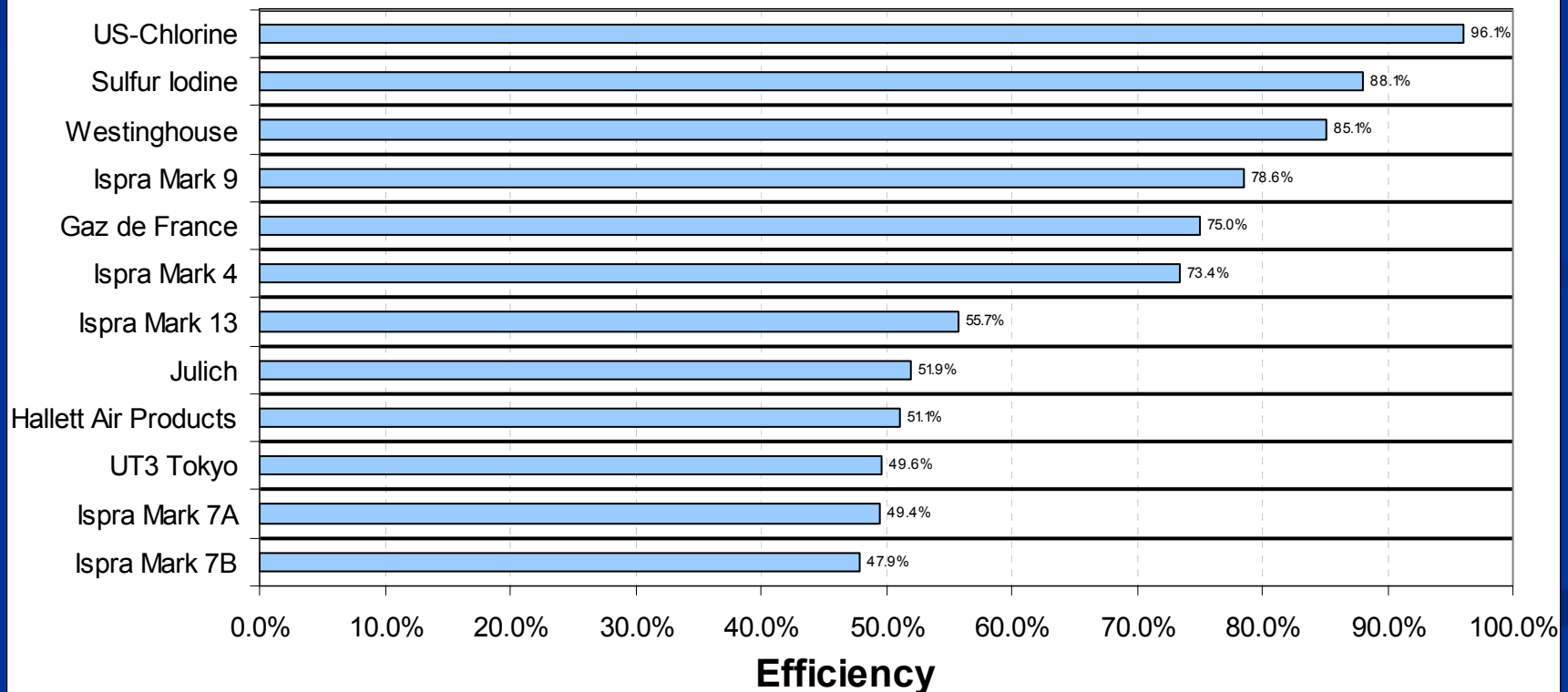
Q_H , $W_{\text{sep, stoich}}$, and W_{elec}

1. US-Chlorine
2. Sulfur Iodine
3. Westinghouse
4. Ispra Mark 9
5. Gaz de France
6. Ispra Mark 4
7. Ispra Mark 13
8. Julich
9. Hallett Air Products
10. UT-3 Tokyo
11. Ispra Mark 7A
12. Ispra Mark 7B

Note: arrows indicate only cycles that change 3+ positions

Q_H , W_{elec} , and stoichiometric separation analysis with $\Delta T_{min}=0$

Cycle Efficiencies using Q_H , W_{elec} , and $W_{sep, stoich}$ for $\Delta T_{min}=0$



Results cont'd

- Now we substitute $W_{\text{sep, stoich}}$ with $W_{\text{sep, excess}}$

Q_H , $W_{\text{sep, stoich}}$, and W_{elec}

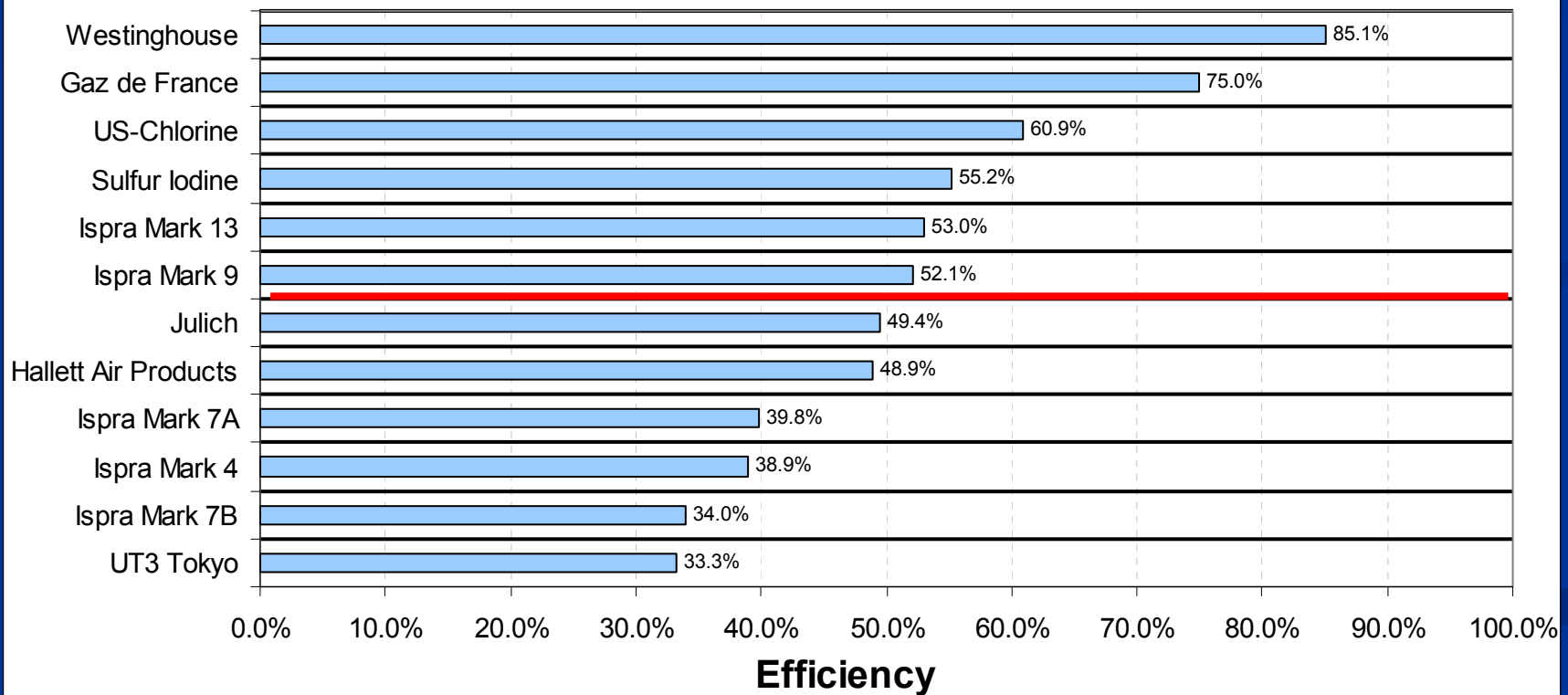
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Q_H , $W_{\text{sep, excess}}$, and W_{elec}

1. Westinghouse
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8. Hallett Air Products
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10. Ispra Mark 4
11. Ispra Mark 7B
12. UT-3 Tokyo

Q_H , W_{elec} , and excess separation analysis with $\Delta T_{min}=0$

Cycle Efficiencies using Q_h , W_{elec} , and $W_{sep, excess}$ for $\Delta T_{min}=0$



Top 6 Thermochemical Cycles

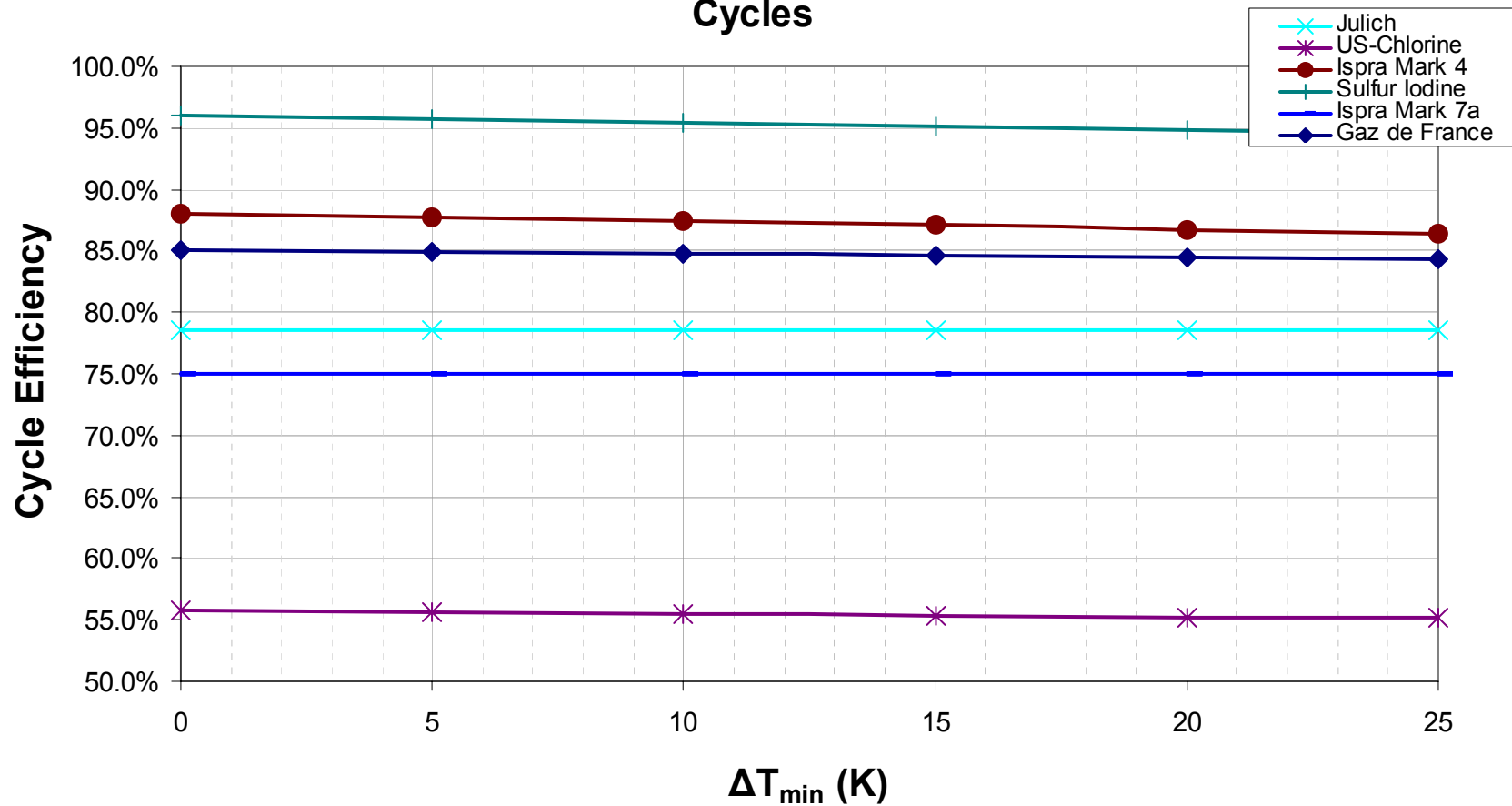
- Based upon full analysis at $\Delta T_{\min} = 0$

1. Westinghouse
2. Gaz de France
3. US-Chlorine
4. Sulfur Iodine
5. Ispra Mark 13
6. Ispra Mark 9

- What about $\Delta T_{\min} > 0$?
 - Some cycles more sensitive

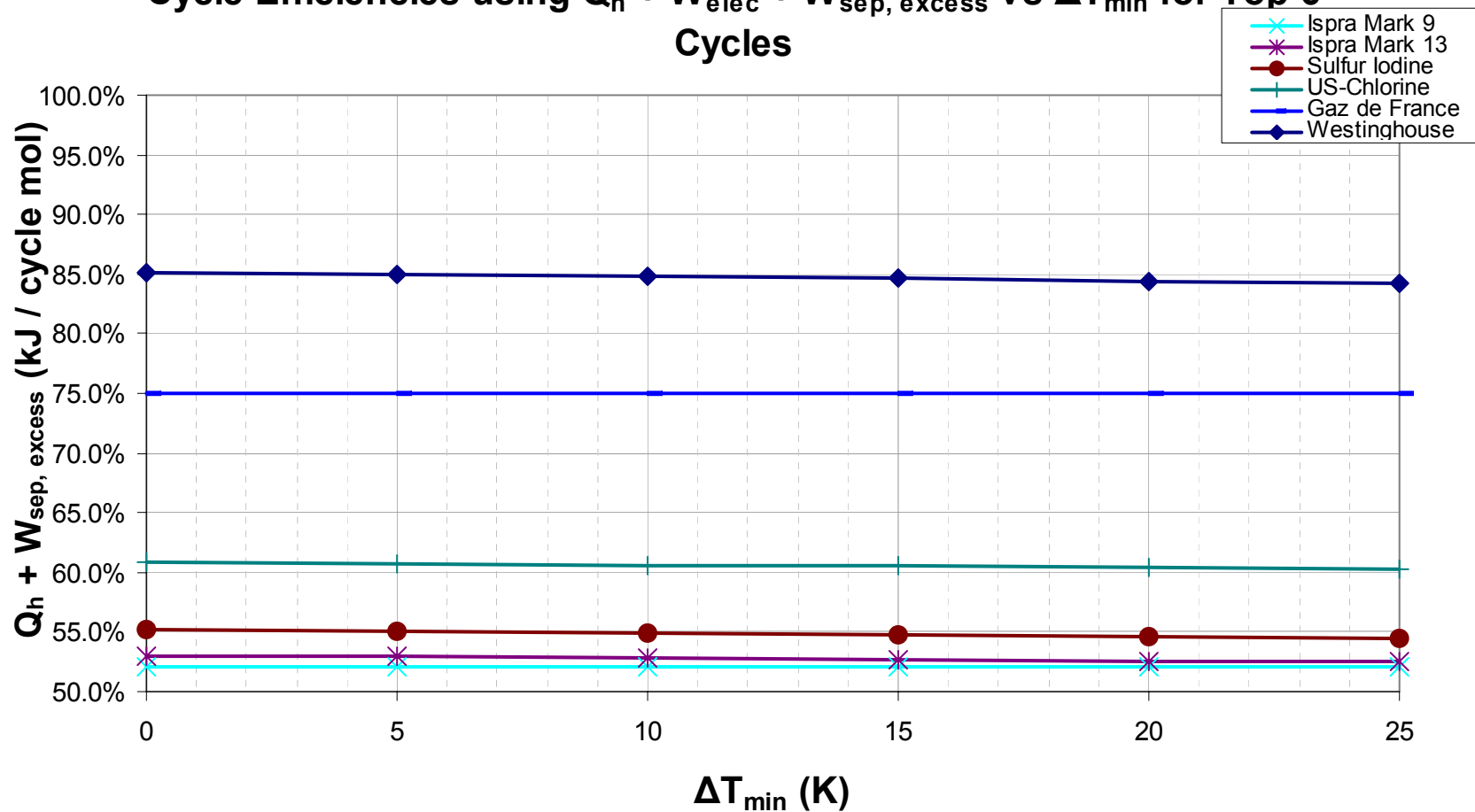
Corresponding Efficiency

Cycle Efficiencies using $Q_h + W_{elec} + W_{sep, stoich}$ vs ΔT_{min} for Top 6 Cycles



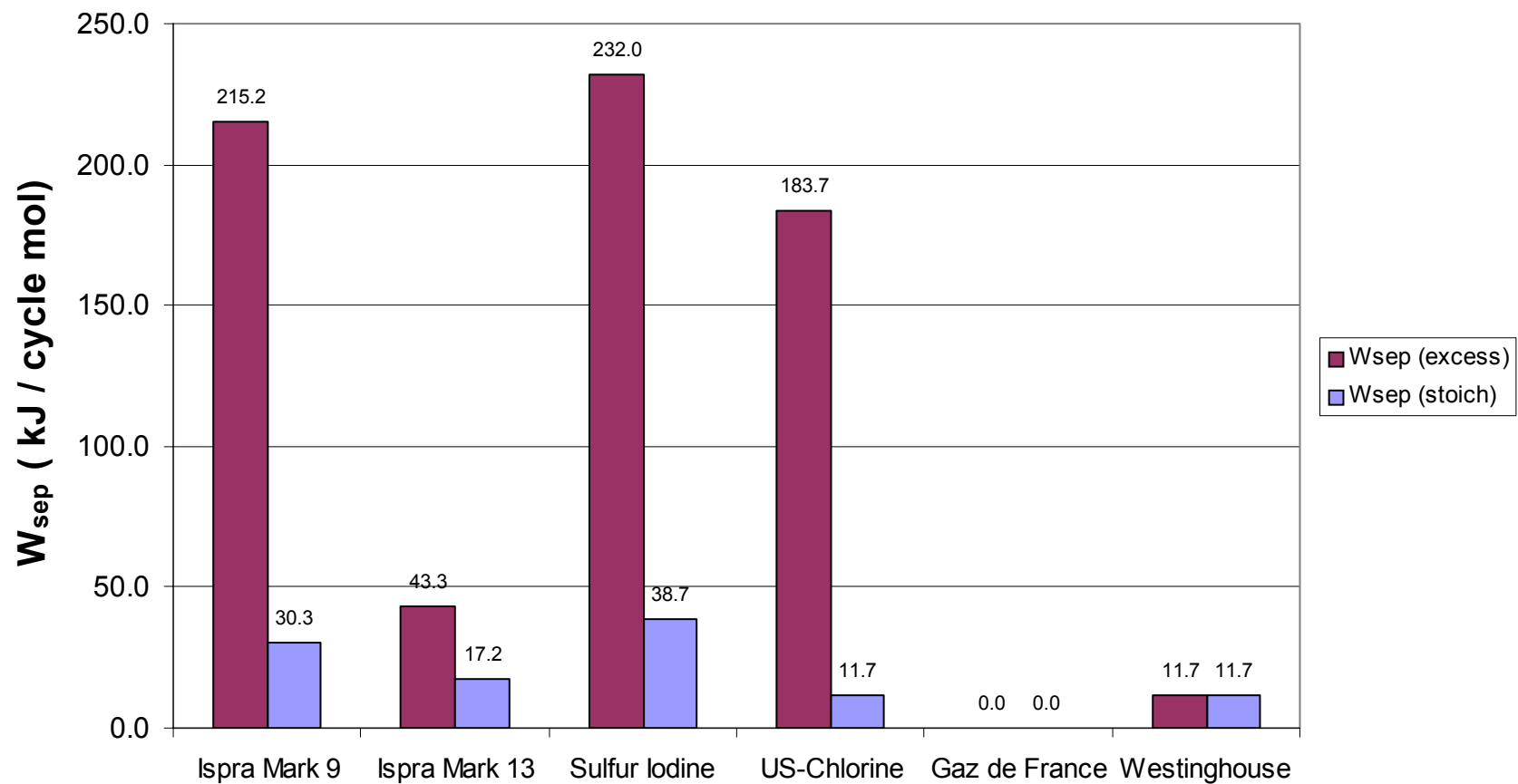
Corresponding Efficiency

Cycle Efficiencies using $Q_h + W_{elec} + W_{sep, excess}$ vs ΔT_{min} for Top 6 Cycles



$W_{\text{sep, stoich}}$ vs. $W_{\text{sep, excess}}$

Comparison of $W_{\text{sep, stoich}}$ and $W_{\text{sep, excess}}$ for Top 6 Cycles



Efficiency: Literature Comparison[†]

	Reported (thermal)	Theoretical (thermal)	Theoretical (heat/work)
Sulfur-Iodine	52% [‡]	100%	55%
Tokyo UT-3	49% [‡]	55%	33%
Westinghouse	50%	100%	85%

[†]Brown et al 2000

[‡]10% additional efficiency projected with electricity co-generation

Good Cycle Characteristics

- Hottest reaction exothermic, cascades heat to power rest of the cycle
 - Minimizes Q
- Products phase separate from each other, and from reactants
 - Minimizes W
- No high T , P , corrosivity, etc. as described by Brown et al 2000

Economic Methodology

- 500 ton/day production target
 - Enough for 0.95 million cars, according to Schultz
- Heat Integration
 - Temperature intervals
 - Cascades
 - Heat exchanger network
- Process Flow Diagrams
 - Assumptions
 - Solids handling
 - Capital cost

Capital Cost Results

	Westinghouse	Gaz de France	US-Chlorine
Efficiency	85%	75%	60%
FCI	\$3,100,000,000	\$6,200,000,000	\$3,100,000,000
Energy Cost	\$27,000,000	\$39,000,000	\$38,000,000
Process Cost, \$/lb H ₂ produced	\$0.07	\$0.11	\$0.11

Conclusions

- Scoping methodology can screen large number of cycles with reasonable accuracy, optimizing P, T and excess reactants
- Sulfur-Iodine and other popular cycles are not necessarily best.
- Find cycles with phase separations and good heat cascade

Questions?

References

Brown, L.C.; Showalter, S.K.; Funk, J.F.; *Nuclear Production of Hydrogen Using Thermochemical Water-Splitting Cycles*. 2000. US DOE project under NERI grant DE-FG03-99SF21888

Holiastos, K.; Manousiouthakis, V.; *Automatic Synthesis of Thermodynamically Feasible Reaction Clusters* AIChE Journal, Vol. 44, No. 1, January 1998 pp. 164-173

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

Motupally, S.; Mah, D.T; Freire, F.J.; Weidner, J.W.; *Recycling Chlorine from Hydrogen Chloride - A new and economical electrolytic process*. The Electrochemical Society Interface, 1998

Peters, M.; Timmerhaus, K. D.; West, R. E.; *Optimization Application: Pinch Technology Analysis* Plant Design and Economics for Chemical Engineers. pp. 414-433. McGraw-Hill, NYC, 2003

Schultz, K. R. *Use of the Modular Helium Reactor for Hydrogen Production*. General Atomics Report. September 2003 US DOE Grant No. DE-FG03-99SF21888