Evaluation and Design of Water-Splitting Cycles

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Overview

- Need for hydrogen
- Water-splitting cycles as solution
- Current evaluation methods
- Efficiency defined
- Our methodology as improvement
- Results of our analysis
- Economics
- Conclusions
Accomplishments

- Novel methodology
  - Rapidly screen cycles without detailed process flowsheets
  - Optimize T, P and excess reactants for non-spontaneous reactions

- Scoping algorithm
  - Calculations refined for best cycles

- Found better cycles than currently favored Sulfur-Iodine and UT-3
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 through 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, as described by Holiastos and Manousiouthakis 1998
Economics

- $1 billion for water-splitting facility
  - $100 million range annual energy costs
- Which cycle is best?
- Few cycles researched in detail
  - Process design too complex
- Efficient cycles desirable
  - Justify increased equipment costs

Bottom line: saving few % efficiency has huge savings over plant lifetime
Cycles

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

Sample 2-step cycle

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>T₁</td>
<td>A → B + C + O₂</td>
</tr>
<tr>
<td>T₂</td>
<td>B + C + H₂O → A + H₂</td>
</tr>
</tbody>
</table>

T₁

T₂

H₂O

B, C

H₂

O₂

T₁

T₂
Efficiency

- Theoretical, 1 mol basis for cycle comparison
- Minimum reversible energy (heating and work) requirement
  - Performance limit
- Thermodynamics: JANAF tables for state functions, pure component averages

\[ \eta = \frac{\Delta H_f^\circ (H_2O)}{Q + W} \]

Q is total heat requirement
W is separation, electric and shaft work†

†Shaft work (pumping, compression) small compared to other terms
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
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

- Cycles are complex, so Lewis et al 2005 developed 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

Our method is truly scoping, based on theoretical requirements
General Methodology

- Cyclic nature couples all calculations
- 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

\[
K_{eq} = K_x \prod_{\text{products}} \left( \frac{n_i}{\sum n_i} \right)^{v_i} \prod_{\text{reactants}} \left( \frac{n_i}{\sum n_i} \right)^{v_i} P \sum \nu
\]
Excess Reactant Handling

Immediate recycle: full separation energy costs

<table>
<thead>
<tr>
<th></th>
<th>T₁</th>
<th>T₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B + C + O₂</td>
<td>B + C + H₂O → A + H₂</td>
</tr>
</tbody>
</table>

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

We optimize T, P, # excess mols and their handling
Cycles cont’d

- Methodology accounts for arbitrarily complex cycles

<table>
<thead>
<tr>
<th></th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
<th>T4</th>
</tr>
</thead>
<tbody>
<tr>
<td>A + B</td>
<td>D + H₂O</td>
<td>C + H₂O</td>
<td>E + F</td>
<td>E + F</td>
</tr>
<tr>
<td>C + O₂</td>
<td>E + F + H₂</td>
<td>B + F</td>
<td>A + D + H₂O</td>
<td></td>
</tr>
</tbody>
</table>
- 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

\( H_{\text{hot}} \) is total enthalpy of cooling streams

\( H_{\text{cold}} \) is total enthalpy of heating streams
Heat is added above the pinch. Heat transfer over the pinch (greater than the minimum heat requirement) goes to cold utility and is wasted. $\Delta T_{\text{min}}$ is closest feasible temperature, since complete heat transfer requires infinite exchanger area.
Heat Integration Method†

- Zonal analysis
  - Approach temperature
- Simplifying algorithm
  - Keep track of total heat usage, advancing to successive zones and reactors
  - Cold utility ignored
    - Leftover heat sometimes useful for electricity generation

† PT&W Plant Design and Economics for Chemical Engineers
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

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

- Phases self-separate
  - We don’t pay for it
- Estimate separation efficiencies

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
    - Newton method to solve for conversion
  - 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 # mols excess
    - Optimize these for each recycle scheme
- Computer crawls through solutions, and maximizes efficiency
Cl₂ (g) + H₂O (g) -> 2HCl (g) + ½O₂ (g), ΔG_{rxn} = -17 kJ / cycle mol
Sample Thermochemical Cycles

- **Julich**

\[
\begin{align*}
\text{Fe}_3\text{O}_4(s) + 3\text{FeSO}_4(s) & \rightleftharpoons 3\text{Fe}_2\text{O}_3(s) + 3\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \\
3\text{FeO}(s) + \text{H}_2\text{O}(g) & \rightleftharpoons \text{Fe}_3\text{O}_4(s) + \text{H}_2(g) \\
3\text{Fe}_2\text{O}_3(s) + 3\text{SO}_2(g) & \rightleftharpoons 3\text{FeO}(s) + 3\text{FeSO}_4(s)
\end{align*}
\]

- **Ispra Mark 9**

\[
\begin{align*}
3\text{FeCl}_2(s) + 4\text{H}_2\text{O}(g) & \rightleftharpoons \text{Fe}_3\text{O}_4(s) + 6\text{HCl}(g) + \text{H}_2(g) \\
\frac{3}{2}\text{Cl}_2(g) + \text{Fe}_3\text{O}_4(s) + 6\text{HCl}(g) & \rightleftharpoons 3\text{FeCl}_3(l) + 3\text{H}_2\text{O}(g) + \frac{1}{2}\text{O}_2(g) \\
3\text{FeCl}_3(s) & \rightleftharpoons \frac{3}{2}\text{Cl}_2(g) + 3\text{FeCl}_2(s)
\end{align*}
\]
Sample Thermochemical Cycles

**Sulfur Iodine**

\[
\begin{align*}
H_2SO_4(g) & \xrightarrow{T = 1123 K} SO_2(g) + H_2O(g) + \frac{1}{2}O_2(g) \\
2HI(g) & \xrightarrow{T = 573 K} I_2(g) + H_2(g) \\
I_2(g) + SO_2(g) + 2H_2O(l) & \xrightarrow{T = 473 K} 2HI(g) + 1H_2SO_4(g)
\end{align*}
\]

**US-Chlorine**

\[
\begin{align*}
Cl_2(g) + H_2O(g) & \xrightarrow{T = 1123 K} HCl(g) + \frac{1}{2}O_2(g) \\
2CuCl_2(s) & \xrightarrow{T = 773 K} 2CuCl(l) + Cl_2(g) \\
2CuCl(l) + 2HCl(g) & \xrightarrow{T = 473 K} 2CuCl_2(s) + H_2(g)
\end{align*}
\]
Sample Thermochemical Cycles

- **Gaz de France**

\[
2K_2O(s) \xrightarrow{T = 1098 \text{ K}} K(g) + K_2O_2(s)
\]

\[
2K(l) + 2\text{KOH}(l) \xrightarrow{T = 998 \text{ K}} 2K_2O(s) + \text{H}_2(g)
\]

\[
K_2O_2(s) + \text{H}_2\text{O}(l) \xrightarrow{T = 398 \text{ K}} \text{KOH}(s) + \frac{1}{2}\text{O}_2(g)
\]

- **UT-3 Tokyo**

\[
\text{CaBr}_2(l) + \text{H}_2\text{O}(g) \xrightarrow{T = 1023 \text{ K}} \text{CaO}(s) + \text{HBr}(g)
\]

\[
4\text{H}_2\text{O}(g) + 3\text{FeBr}_2(s) + \text{Br}_2(g) + \text{CaO}(s) \xrightarrow{T = 873 \text{ K}}
\]

\[
\text{CaBr}_2(s) + \frac{1}{2}\text{O}_2(g) + \text{Fe}_3\text{O}_4(s) + \text{HBr}(g) + \text{H}_2(g)
\]

\[
\text{Fe}_3\text{O}_4(s) + 8\text{HBr}(g) \xrightarrow{T = 573 \text{ K}} \text{Br}_2(g) + 3\text{FeBr}_2(s) + 4\text{H}_2\text{O}(g)
\]
Sample Thermochemical Cycles

- **Ispra Mark 4**

\[
\begin{align*}
\text{Cl}_2(g) + \text{H}_2\text{O}_2(g) & \xrightarrow{T = 1123 \text{ K}} 2\text{HCl}_2(g) + \frac{1}{2} \text{O}_2(s) \\
\text{H}_2\text{S}_2(g) & \xrightarrow{T = 1073 \text{ K}} \text{S}_2(g) + \text{H}_2(g) \\
2\text{FeCl}_3(l) & \xrightarrow{T = 693 \text{ K}} \text{Cl}_2(g) + 2\text{FeCl}_2(s) \\
2\text{FeCl}_2(s) + 2\text{HCl}_2(g) + \text{S}_2(l) & \xrightarrow{T = 473 \text{ K}} 2\text{FeCl}_3(s) + \text{H}_2\text{S}_2(g)
\end{align*}
\]

- **Ispra Mark 7A**

\[
\begin{align*}
\frac{3}{2} \text{Cl}_2(g) + \frac{1}{2} \text{Fe}_2\text{O}_3(s) & \xrightarrow{T = 1273 \text{ K}} \text{FeCl}_3(l) + \frac{3}{4} \text{O}_2(g) \\
3\text{FeCl}_2(s) + 4\text{H}_2\text{O}_2(g) & \xrightarrow{T = 923 \text{ K}} \text{Fe}_3\text{O}_4(s) + 6\text{HCl}_2(g) + \text{H}_2(g) \\
3\text{FeCl}_3(l) & \xrightarrow{T = 693 \text{ K}} \frac{3}{2} \text{Cl}_2(g) + 3\text{FeCl}_2(s) \\
\text{Fe}_3\text{O}_4(s) + \frac{1}{4} \text{O}_2(g) & \xrightarrow{T = 623 \text{ K}} \frac{3}{2} \text{Fe}_2\text{O}_3(s) \\
\text{Fe}_2\text{O}_3(s) + \text{HCl}_2(g) & \xrightarrow{T = 393 \text{ K}} 2\text{FeCl}_3(l) + 3\text{H}_2\text{O}_2(l)
\end{align*}
\]
Sample Thermochemical Cycles

- Ispra Mark 7B

\[
\begin{align*}
\frac{9}{2} \text{Cl}_2(g) + \frac{3}{2} \text{Fe}_2\text{O}_3(s) & \xrightarrow{T = 1273 \text{ K}} 3\text{FeCl}_3(l) + \frac{9}{4} \text{O}_2(g) \\
3\text{FeCl}_2(s) + 4\text{H}_2\text{O}(g) & \xrightarrow{T = 923 \text{ K}} \text{Fe}_3\text{O}_4(s) + 6\text{HCl}(g) + \text{H}_2(g) \\
3\text{FeCl}_3(l) & \xrightarrow{T = 693 \text{ K}} \frac{3}{2} \text{Cl}_2(g) + 3\text{FeCl}_2(s) \\
6\text{HCl}(g) + \frac{3}{2} \text{O}_2(g) & \xrightarrow{T = 673 \text{ K}} 3\text{Cl}_2(g) + 3\text{H}_2\text{O}(g) \\
\text{Fe}_3\text{O}_4(s) + \frac{1}{4} \text{O}_2(g) & \xrightarrow{T = 623 \text{ K}} \frac{3}{2} \text{Fe}_2\text{O}_3(s)
\end{align*}
\]
Sample Hybrid Cycles

- **Westinghouse**

  \[
  \begin{align*}
  H_2SO_4(g) & \xrightarrow{T = 1123 \text{ K}} SO_2(g) + H_2O(g) + \frac{1}{2}O_2(g) \\
  SO_2(g) + 2H_2O(l) & \xrightarrow{T = 350 \text{ K}} H_2SO_4(g) + H_2(g)
  \end{align*}
  \]

- **Ispra Mark 13**

  \[
  \begin{align*}
  H_2SO_4(g) & \xrightarrow{T = 1123 \text{ K}} SO_2(g) + H_2O(g) + \frac{1}{2}O_2(g) \\
  2HBr(aq) & \xrightarrow{T = 350 \text{ K}} Br_2(aq) + H_2(g) \\
  Br_2(l) + SO_2(g) + 2H_2O(l) & \xrightarrow{T = 350 \text{ K}} HBr(g) + H_2SO_4(g)
  \end{align*}
  \]

- **Hallett Air Products**

  \[
  \begin{align*}
  Cl_2(g) + H_2O(g) & \xrightarrow{T = 1073 \text{ K}} 2HCl(g) + \frac{1}{2}O_2(g) \\
  2HCl(g) & \xrightarrow{T = 298 \text{ K}} Cl_2(g) + H_2(g)
  \end{align*}
  \]
Results

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

<table>
<thead>
<tr>
<th>Rank</th>
<th>Facility</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Hallett Air Products</td>
</tr>
<tr>
<td>1.</td>
<td>US-Chlorine</td>
</tr>
<tr>
<td>1.</td>
<td>Sulfur Iodine</td>
</tr>
<tr>
<td>1.</td>
<td>Ispra Mark 13</td>
</tr>
<tr>
<td>1.</td>
<td>Westinghouse</td>
</tr>
<tr>
<td>2.</td>
<td>Ispra Mark 9</td>
</tr>
<tr>
<td>3.</td>
<td>Ispra Mark 4</td>
</tr>
<tr>
<td>4.</td>
<td>Gaz de France</td>
</tr>
<tr>
<td>5.</td>
<td>UT-3 Tokyo</td>
</tr>
<tr>
<td>6.</td>
<td>Julich</td>
</tr>
<tr>
<td>7.</td>
<td>Ispra Mark 7B</td>
</tr>
<tr>
<td>8.</td>
<td>Ispra Mark 7A</td>
</tr>
</tbody>
</table>
$Q_H$ analysis with $\Delta T_{min}=0$

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

- **Hallett Air Products**: 100.0%
- **US-Chlorine**: 100.0%
- **Sulfur Iodine**: 100.0%
- **Ispra Mark 13**: 100.0%
- **Westinghouse**: 100.0%
- **Ispra Mark 9**: 85.7%
- **Ispra Mark 4**: 78.2%
- **Gaz de France**: 75.0%
- **UT3 Tokyo**: 54.9%
- **Julich**: 54.8%
- **Ispra Mark 7B**: 52.4%
- **Ispra Mark 7A**: 52.3%

The diagram above illustrates the cycle efficiencies for various cycles using $Q_h$ for $\Delta T_{min}=0$. Each cycle is represented by a horizontal bar, with the efficiency percentage indicated.
Now we consider $W_{\text{sep, stoich}}$ and $W_{\text{elec}}$ as well.

<table>
<thead>
<tr>
<th>$Q_H$ only</th>
<th>$Q_H$, $W_{\text{sep, stoich}}$, and $W_{\text{elec}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Hallett Air Products</td>
<td>1. US-Chlorine</td>
</tr>
<tr>
<td>1. US-Chlorine</td>
<td>2. Sulfur Iodine</td>
</tr>
<tr>
<td>1. Sulfur Iodine</td>
<td>3. Westinghouse</td>
</tr>
<tr>
<td>1. Ispra Mark 13</td>
<td>4. Ispra Mark 9</td>
</tr>
<tr>
<td>1. Westinghouse</td>
<td>5. Gaz de France</td>
</tr>
<tr>
<td>2. Ispra Mark 9</td>
<td>6. Ispra Mark 4</td>
</tr>
<tr>
<td>3. Ispra Mark 4</td>
<td>7. Ispra Mark 13</td>
</tr>
<tr>
<td>5. UT-3 Tokyo</td>
<td>9. Hallett Air Products</td>
</tr>
<tr>
<td>6. Julich</td>
<td>10. UT-3 Tokyo</td>
</tr>
<tr>
<td>7. Ispra Mark 7B</td>
<td>11. Ispra Mark 7A</td>
</tr>
<tr>
<td>8. Ispra Mark 7A</td>
<td>12. Ispra Mark 7B</td>
</tr>
</tbody>
</table>

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 $\Delta T_{min}=0$

<table>
<thead>
<tr>
<th>Company/Country</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>US-Chlorine</td>
<td>96.1%</td>
</tr>
<tr>
<td>Sulfur Iodine</td>
<td>88.1%</td>
</tr>
<tr>
<td>Westinghouse</td>
<td>85.1%</td>
</tr>
<tr>
<td>Ispra Mark 9</td>
<td>78.6%</td>
</tr>
<tr>
<td>Gaz de France</td>
<td>75.0%</td>
</tr>
<tr>
<td>Ispra Mark 13</td>
<td>73.4%</td>
</tr>
<tr>
<td>Julich</td>
<td>55.7%</td>
</tr>
<tr>
<td>Hallett Air Products</td>
<td>51.9%</td>
</tr>
<tr>
<td>UT3 Tokyo</td>
<td>51.1%</td>
</tr>
<tr>
<td>Ispra Mark 7A</td>
<td>49.4%</td>
</tr>
<tr>
<td>Ispra Mark 7B</td>
<td>47.9%</td>
</tr>
</tbody>
</table>

Efficiency distribution for various companies.
Results cont’d

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

<table>
<thead>
<tr>
<th>$Q_H$, $W_{\text{sep, stoich}}$, and $W_{\text{elec}}$</th>
<th>$Q_H$, $W_{\text{sep, excess}}$, and $W_{\text{elec}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. US-Chlorine</td>
<td>1. Westinghouse</td>
</tr>
<tr>
<td>2. Sulfur Iodine</td>
<td>2. Gaz de France</td>
</tr>
<tr>
<td>4. Ispra Mark 9</td>
<td>4. Sulfur Iodine</td>
</tr>
<tr>
<td>5. Gaz de France</td>
<td>5. Ispra Mark 13</td>
</tr>
<tr>
<td>6. Ispra Mark 4</td>
<td>6. Ispra Mark 9</td>
</tr>
<tr>
<td>7. Ispra Mark 13</td>
<td>7. Julich</td>
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<td>9. Hallett Air Products</td>
<td>9. Ispra Mark 7A</td>
</tr>
<tr>
<td>10. UT-3 Tokyo</td>
<td>10. Ispra Mark 4</td>
</tr>
<tr>
<td>11. Ispra Mark 7A</td>
<td>11. Ispra Mark 7B</td>
</tr>
<tr>
<td>12. Ispra Mark 7B</td>
<td>12. UT-3 Tokyo</td>
</tr>
</tbody>
</table>
$Q_H$, $W_{\text{elec}}$, and excess separation analysis with $\Delta T_{min}=0$
Top 6 Thermochemical Cycles

- Based upon full analysis at $\Delta T_{\text{min}} = 0$
  
  1. Westinghouse
  2. Gaz de France
  3. US-Chlorine
  4. Sulfur Iodine
  5. Ispra Mark 13
  6. Ispra Mark 9

- What about $\Delta T_{\text{min}} > 0$?
  - Some cycles more sensitive
Effect of $\Delta T_{\text{min}}$ on $Q_H$

$Q_h$ vs $\Delta T_{\text{min}}$ for Top 6 Cycles

- Ispra Mark 9
- Ispra Mark 13
- Sulfur Iodine
- US-Chlorine
- Gaz de France
- Westinghouse
Corresponding Efficiency

Cycle Efficiencies using $Q_h$ vs $\Delta T_{\text{min}}$ for Top 6 Cycles

- Ispra Mark 9
- Ispra Mark 13
- Sulfur Iodine
- US-Chlorine
- Gaz de France
- Westinghouse
Effect of $\Delta T_{\text{min}}$ on $Q_h + W_{\text{elec}} + W_{\text{sep, stoich}}$

$Q_h + W_{\text{elec}} + W_{\text{sep, stoich}}$ vs $\Delta T_{\text{min}}$ for Top 6 Cycles

- Ispra Mark 9
- Ispra Mark 13
- Sulfur Iodine
- US-Chlorine
- Gaz de France
- Westinghouse
Corresponding Efficiency

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

- Julich
- US-Chlorine
- Ispra Mark 4
- Sulfur Iodine
- Ispra Mark 7a
- Gaz de France
Comparison of $W_{\text{sep, stoich}}$ and $W_{\text{sep, excess}}$ for Top 6 Cycles

<table>
<thead>
<tr>
<th>Cycle</th>
<th>$W_{\text{sep, stoich}}$</th>
<th>$W_{\text{sep, excess}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ispra Mark 9</td>
<td>215.2</td>
<td>30.3</td>
</tr>
<tr>
<td>Ispra Mark 13</td>
<td>43.3</td>
<td>17.2</td>
</tr>
<tr>
<td>Sulfur Iodine</td>
<td>232.0</td>
<td>38.7</td>
</tr>
<tr>
<td>US-Chlorine</td>
<td>183.7</td>
<td>11.7</td>
</tr>
<tr>
<td>Gaz de France</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Westinghouse</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Effect of $\Delta T_{\text{min}}$ on $Q_h + W_{\text{elec}} + W_{\text{sep, excess}}$

$Q_h + W_{\text{elec}} + W_{\text{sep, excess}}$ vs $\Delta T_{\text{min}}$ for Top 6 Cycles

- Ispra Mark 9
- Ispra Mark 13
- Sulfur Iodine
- US-Chlorine
- Gaz de France
- Westinghouse
Corresponding Efficiency

Cycle Efficiencies using $Q_h + W_{\text{elec}} + W_{\text{sep, excess}}$ vs $\Delta T_{\text{min}}$ for Top 6 Cycles

- Ispra Mark 9
- Ispra Mark 13
- Sulfur Iodine
- US-Chlorine
- Gaz de France
- Westinghouse
<table>
<thead>
<tr>
<th></th>
<th>Reported (thermal)</th>
<th>Theoretical (thermal)</th>
<th>Theoretical (heat/work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur-Iodine</td>
<td>52%†</td>
<td>100%</td>
<td>55%</td>
</tr>
<tr>
<td>Tokyo UT-3</td>
<td>49%†</td>
<td>55%</td>
<td>33%</td>
</tr>
<tr>
<td>Westinghouse</td>
<td>50%</td>
<td>100%</td>
<td>85%</td>
</tr>
</tbody>
</table>

†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
Westinghouse Cycle - Heat Profile

1073 K

$\Delta H_{\text{xn1}}$

$\text{H}_2\text{SO}_4(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$

+$0.5\text{O}_2(\text{g})$

350 K

$\Delta H_{\text{xn2}}$

$\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{g}) + \text{H}_2(\text{g})$

Zone 1

$\text{SO}_2$, $\text{H}_2\text{O}$

$\text{O}_2$

Zone 2

$\text{H}_2\text{O}$

298 K

$\text{H}_2$
Westinghouse Cycle - Heat Profile

\[ \Delta H_{rxn1} = 184.8 \text{ kJ} \]

\[ \text{H}_2\text{SO}_4(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) + 0.5 \text{O}_2(\text{g}) \]

\[ \text{H}_2\text{SO}_4 = 94.3 \text{ kJ} \]

Zone 1 = -28.8 kJ

\[ \Delta H_{rxn2} = 129.5 \text{ kJ} \]

\[ \text{SO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{g}) + \text{H}_2(\text{g}) \]

\[ \text{O}_2,a = -12.7 \text{ kJ} \]

\[ \text{SO}_2, \text{H}_2\text{O} = -110.3 \text{ kJ} \]

Zone 2 = 2.4 kJ

\[ \text{H}_2\text{O} = 4.7 \text{ kJ} \]

\[ \text{O}_2,b = -0.8 \text{ kJ} \]

\[ \text{H}_2 = -1.5 \text{ kJ} \]

298 K
Westinghouse - Heat Cascade

\[
\begin{align*}
Q_H & \quad -288.0 \text{ kJ} \\
\Delta H_{\text{rxn}1} & \quad 184.8 \text{ kJ} \\
\Delta H_{\text{rxn}2} & \quad 129.5 \text{ kJ} \\
\text{H}_2\text{O} + \text{SO}_2 & \quad -110.3 \text{ kJ} \\
\text{O}_2 & \quad -13.5 \text{ kJ} \\
\text{H}_2\text{SO}_4 & \quad 94.3 \text{ kJ} \\
\text{H}_2 & \quad -1.5 \text{ kJ} \\
\text{H}_2\text{O} & \quad 4.7 \text{ kJ} \\
\end{align*}
\]

7 exchangers
Westinghouse - Heat Exchanger Network

\[ \Delta H_{\text{rxn} \ 1} = 184.8 \text{ kJ} \]
\[ \text{H}_2\text{SO}_4(g) \rightarrow \text{SO}_2(g) + \text{H}_2\text{O}(g) + 0.5 \text{O}_2(g) \]

\[ \Delta H_{\text{rxn} \ 2} = 129.5 \text{ kJ} \]
\[ \text{SO}_2(g) + 2 \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_4(g) + \text{H}_2(g) \]

Zone 1 = -28.8 kJ

Zone 2 = 2.4 kJ
Westinghouse - Heat Exchanger Network

\[ \Delta H_{\text{rxn1}} \]

\[ \Delta H_{\text{rxn2}} \]
Handling Solids

- Physical transport of solids difficult
  - Grinders necessary
- Slow heat transfer between solids
  - Use sweep gas as intermediate heat carrier
- Solid separations
  - Usually oxides and halide salts – solvent separation
• Solids do not move – reactors run in parallel batch
  • Preserves efficiency, but increases capital costs and instability
• Reported thermal efficiency 49%, compared to 55% theoretical

†Adapted from Brown et al 2000
US Chlorine – Heat Cascade

1123 K

\[ \text{Cl}_2(v) + \text{H}_2\text{O}(v) \rightarrow 2\text{HCl}(v) + \frac{1}{2}\text{O}_2(v) \]

HCl \quad O_2

773 K \quad \text{Cl}_2

2\text{CuCl}_2(s) \rightarrow 2\text{CuCl}(l) + \text{Cl}_2(v)

HCl \quad \text{CuCl}

473 K \quad \text{CuCl}_2

2\text{CuCl}(s) + 2\text{HCl}(aq) \rightarrow 2\text{CuCl}_2(s) + \text{H}_2(v)

HCl \quad \text{CuCl}

298 K \quad \text{H}_2\text{O}

2\text{CuCl}_2(s) \rightarrow 2\text{CuCl}(l) + \text{Cl}_2(v)
US Chlorine – Process Flow Diagram
Gaz de France - Heat Exchange Network

\[ \Delta H_{rxn\ 3} \]

\[ H_2O \]

\[ K_2O \]

\[ K_2O_2 \]

\[ H_2 \]

\[ O_2 \]

\[ \Delta H_{rxn\ 2} \]

\[ \Delta H_{rxn\ 1} \]

\[ HX-1 \]

\[ HX-2 \]

\[ HX-3 \]

\[ HX-4 \]

\[ HX-5 \]

\[ HX-6 \]

\[ HX-7 \]

\[ HX-8 \]
Capital Cost

- New technology
- Processes involve highly corrosive materials and high temperatures†
  - Resistance to degradation involved within the cycles
  - High temperature quality material required
  - Research involved for design
- Some kinetics are currently unknown
- Contract work involved

†Perret et al 2004
500 tons/day hydrogen production

Equilibrium (complete reaction)

Maximum heat exchange area possible

Highly corrosive materials

Scale up has never been done
## Capital Cost Results

<table>
<thead>
<tr>
<th></th>
<th>Westinghouse</th>
<th>Gaz de France</th>
<th>US-Chlorine</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Efficiency</strong></td>
<td>85%</td>
<td>75%</td>
<td>60%</td>
</tr>
<tr>
<td><strong>FCI</strong></td>
<td>$3,100,000,000</td>
<td>$6,200,000,000</td>
<td>$3,100,000,000</td>
</tr>
<tr>
<td><strong>Energy Cost</strong></td>
<td>$27,000,000</td>
<td>$39,000,000</td>
<td>$38,000,000</td>
</tr>
<tr>
<td><strong>Process Cost, $/lb H₂ produced</strong></td>
<td>$0.07</td>
<td>$0.11</td>
<td>$0.11</td>
</tr>
</tbody>
</table>
Conclusions

- Scoping methodology can screen large number of cycles with reasonable accuracy
- Sulfur-Iodine and other popular cycles are not necessarily best
- Find cycles with phase separations and good heat cascade
Questions?
References


