A Scoping Flowsheet Methodology for Evaluating Alternative Thermochemical Cycles

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Outline

• Introduction

• Description of scoping flowsheet methodology for calculating efficiencies for thermochemical cycles

• Illustration of methodology with the hybrid CuSO4 cycle

• Summary
Definitions

- **Alternative cycles**: Cycles other than the U.S. DOE baseline cycles sulfur-iodine, the hybrid sulfur, and the calcium-bromine
- **Possible alternative cycles**:
  - Cycles suggested in the literature that were either not developed or contained a barrier that current technology may overcome
  - New cycles
- **Characteristics of promising alternative cycles**
  - High efficiencies, chemically viable, feasible with respect to engineering
Phase I Evaluation

General screening criteria for evaluating alternative cycles
High natural abundance

Logarithmic Crustal Abundances: $\log(\text{Si}) = 6.0$

Atomic Number

Logarithmic Abundance by Number
Acceptable toxicity

- U.S. Environmental Protection Agency has very low allowable release rates for Hg, Se, and Cd and cycles with these elements would not be easily commercialized
Phase II Evaluation

Scoping flowsheet methodology to calculate efficiency of alternative cycles in a consistent manner
Efficiency changes with effort

From Pascal Anzieu at CEA
Thermochemical cycle assessment levels

• Level 1
  - Stoichiometric reactions presumed to go to 100% completion
  - *No competing product formation*
  - Heat and work inputs
    - *Heat*: reaction, sensible, and latent (*no non-idealities, no partial yields*)
    - *Work*: electrochemical, chemical potential, and separation (*no pumps or compressors*)
  - Reaction temperatures as proposed in the literature
Thermochemical cycle assessment levels

• Level 2
  - Equilibrium compositions with less than 100% yields and competing products allowed
  - Heat and work inputs as before
  - Reaction temperatures adjusted to increase desired yields
Consistent assumptions in the methodology

- \( \text{H}_2\text{O} \) enters as a liquid at 25° C; 
  \( \text{H}_2 \) and \( \text{O}_2 \) are released at atmospheric pressure at 25 °C
  - One mole of water is used in Level 1
  - Number of moles to be determined in Level 2

- Work terms calculated through standard equations, not measured

- Solvation effects ignored for Level 1 and 2 efficiency calculations

- 10°C delta T needed as a driving force for heat exchange

- Energy usage optimized with pinch analysis
Definitions in the methodology, Cont.

- Efficiency (LHV) calculated with equation

\[
E = \frac{-\Delta H_{25^\circ C}^{\circ} (H_2O(g))}{Q_{hot} + \frac{W}{0.5}}
\]

- Efficiency of converting heat to work is assumed to be 50%.
Promising alternative cycles that passed Phase I general screening

- Cu-SO$_4$
- Zn-SO$_4$
- Cu-Cl
- Mg-Cl
- Other cycles may be identified in the future

These cycles had high reported efficiencies in the literature
Cu-SO₄ cycle: a promising alternative cycle

• Reactions:
  - CuO + SO₂(g) + H₂O → CuSO₄ + H₂  25°C (Thermally? Electrochemically?)
  - CuSO₄ → CuO + ½O₂ + SO₂(g)  850°C

• Why promising?
  - High maximum theoretical efficiency
    - 57 to 62% (LHV) reported in 1980
  - Less corrosive than other sulfur cycles
    - No water in the high-temperature reaction
  - Possible to leverage R&D for other sulfur cycles for this cycle
  - Demonstrated
    - All reactions proved in the laboratory (Gas Technology Institute)
## Energy balance for the Level 1 analysis

<table>
<thead>
<tr>
<th>Reaction #</th>
<th>Heat Type</th>
<th>Mole</th>
<th>( \text{Tin}^a ) (°C)</th>
<th>( \text{Tout}^b ) (°C)</th>
<th>( \Delta H ), kcal</th>
<th>( \Delta G ), kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>Reaction 1</td>
<td>1</td>
<td>25</td>
<td>25</td>
<td>-7.54</td>
<td>1.08</td>
</tr>
<tr>
<td>CuSO(_4)</td>
<td>Reaction 2</td>
<td>1</td>
<td>850</td>
<td>850</td>
<td>71.95</td>
<td>1.73</td>
</tr>
<tr>
<td>CuSO(_4)</td>
<td>Sensible 1</td>
<td>1</td>
<td>25</td>
<td>850</td>
<td>27.26</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>Sensible 1</td>
<td>1</td>
<td>850</td>
<td>25</td>
<td>-10.15</td>
<td></td>
</tr>
<tr>
<td>SO(_2)(g)</td>
<td>Sensible 1</td>
<td>1</td>
<td>850</td>
<td>25</td>
<td>-9.98</td>
<td></td>
</tr>
<tr>
<td>O(_2)(g)</td>
<td>Sensible 0.5</td>
<td>1</td>
<td>850</td>
<td>25</td>
<td>-3.23</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>68.31</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)\(\text{Tin} = \text{Initial temperature}\)

\(^b\)\(\text{Tout} = \text{Final temperature}\)
**Pinch Analysis — Matching exothermic and endothermic reactions**

- Heat curve represents endothermic process
- Cool curve represents exothermic process
- Pinch is the amount of heat needed to drive the cool curve below the heat curve at every point
- For Cu-SO₄ level-1 analysis: 8.2 kcal are needed for pinch
## Level 1 Efficiency Calculation

<table>
<thead>
<tr>
<th></th>
<th>Energy, kcal/mol H₂</th>
<th>Heat Equivalent(^a), kcal/mol H₂</th>
<th>Energy, kcal/mol H₂</th>
<th>Heat Equivalent(^a), kcal/mol H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total heat-in</td>
<td>68.3</td>
<td>68.3</td>
<td>68.3</td>
<td>68.3</td>
</tr>
<tr>
<td>Pinch heat</td>
<td>8.2</td>
<td>8.2</td>
<td>8.2</td>
<td>8.2</td>
</tr>
<tr>
<td>Chemical potential work (ΔG)</td>
<td>2.81(^b)</td>
<td>5.62</td>
<td>1.73</td>
<td>3.46</td>
</tr>
<tr>
<td>Separation work</td>
<td>2.15</td>
<td>4.3</td>
<td>2.15</td>
<td>4.3</td>
</tr>
<tr>
<td>Electrochemical work</td>
<td>0</td>
<td>0</td>
<td>20.75</td>
<td>41.5</td>
</tr>
<tr>
<td>Sum of heat and work inputs</td>
<td></td>
<td>86.42</td>
<td></td>
<td>125.76</td>
</tr>
<tr>
<td>Enthalpy of formation, H₂ (LHV)</td>
<td>57.8</td>
<td></td>
<td>57.8</td>
<td></td>
</tr>
<tr>
<td>Efficiency (LHV)</td>
<td>66.9%</td>
<td></td>
<td>46.0%</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Assumes 50% conversion factor for heat to work  
\(^b\) Includes the contribution of the free energy change for reaction 1
Level 2 efficiency calculations based on equilibrium data

- Important criteria for Level 2 calculations of efficiency
  - Yields close to 100%
  - Competing product formation to be minimized

- If available, experimental data may make the selection of reaction conditions more realistic
  - Temperature, pressure, composition
**Rxn. 1 CuO + SO$_2$(g) $\rightarrow$ CuSO$_4$ + H$_2$ (g)**

- Only 43% of the water is split at 25°C
**Rxn. 2: 0.43 CuSO₄ \rightarrow 0.43 CuO + 0.43 SO₂ + 0.21 O₂**

- Complete conversion of SO₃ at 1100°C
- Difficult SO₂ and O₂ separation
- Efficiency (LHV) = 38.1%
- Large recycle stream of unreacted chemicals not accounted for in energy balance
Experimental data: product of electrochemical reaction is CuSO₄*5H₂O (not pure CuSO₄)

- Significant excess water is needed for a high yield of H₂
- Experimental results agree with thermodynamic analysis with excess water:
  - Pentahydrate is the major product with 9 extra moles of water
- Pentahydrate requires extra dehydration step (800°C?)
Level 2 efficiency with the pentahydrate

- Pinch heat = 135 kcal (vs. 8 kcal in level-1 analysis)

- Level 2 efficiency is now 30.7% (LHV) primarily because of the large amount of heat needed for removing free and hydrated water

- Most critical need (dealing with excess water) is thus identified for optimization
Summary

- The methodology shows the ability to rapidly screen processes with reasonable realism at Level 1.

- More accurate Level 2 simulations can find problem areas.

- For the Cu-SO₄ cycle, efficiency estimates change from 66.9 to 30.7% as we learn more about the chemistry.

- Process design optimization could provide improvement.