IV.G.3 High-Temperature Thermochemical Processes

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Objectives

- Identify promising thermochemical cycles that have one or more of the following characteristics: high efficiency, high yields and minimal separations, low temperature, low corrosivity
- Evaluate cycles with a scoping flowsheet methodology considering various metrics and identify R&D needs for highest priority cycles
- Select most promising cycles for Nuclear Hydrogen Initiative (NHI) based on updated assessment

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- G. Capital Cost
- H. System Efficiency

Near-term challenges:

- Critical but unknown thermodynamic data and chemistries
- Relatively high costs for experimental verification

Approach

- Identify promising thermochemical cycles from the literature and from current work ongoing at the DOE Office of Energy Efficiency and Renewable Energy, universities, and other institutions
- Evaluate cycles with a scoping flowsheet methodology that includes a consideration of the metrics above and identify R&D needs for highest priority cycles
- Select most promising cycles for NHI based on updated assessment

Accomplishments

- Identified promising thermochemical cycles
  - Hybrid cycles—Cu-Cl, K-Bi, Cu-SO_4, and Zn-SO_4—identified as promising
  - Proprietary cycles are known but are not yet available for discussion
- Collaborated with U.S. and international agencies on the development of a consistent methodology for identifying promising cycles
- Developed NHI scoping flowsheet methodology
- Started evaluation process of promising cycles

Future Directions

- Continue development of methodology to reflect the different levels of maturity for various cycles so that cycles can be compared on an ‘apples-to-apples’ basis
- Quantify go-no go criteria for an objective assessment to obtain an ‘easy’ evaluation of a cycle’s promise
- Continue evaluation of promising alternate cycles and propose/initiate critical R&D activities needed for further evaluation

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Introduction and Approach

This research project is being conducted at Argonne National Laboratory to identify, evaluate, and select the most promising alternate thermochemical cycles for hydrogen production. For the Nuclear Hydrogen Initiative, the heat source for the chemical process is the very high temperature gas reactor (VTGR), which will deliver process heat between 850 and 950°C. Cycles with lower temperature requirements may also be coupled with the VTGR, with the excess heat being used for cogeneration, or alternate heating sources (e.g., solar towers) may be used. Any needed electrical power is obtained from the grid.

A literature search of thermochemical cycles identified in the 1970s and early 1980s has been completed. Two sources that were the most helpful were summary reports by Carty et al. and McQuillan et al. [1, 2]. The Carty et al. report includes the results of in-house experimental work as well as literature surveys on chemical viability. Of the 200 cycles examined, eleven cycles were identified as promising. The McQuillan et al. report has, thus far, considered 202 cycles, but others are awaiting consideration. Fourteen cycles were identified as promising. However, 11 of the 14 required heat in excess of 1000°C, which is outside the range of the VTGR. New cycles will also be considered in the future.

The most frequently used metric for assessing the potential of a thermochemical cycle is efficiency. Efficiency is defined by the following equation:

$$E = \frac{-\Delta H^{\circ}_{25^{\circ}C}(H_2O)}{Q_{hot} + \frac{W}{0.5}} \qquad [3]$$

The numerator is the standard enthalpy of the formation of water at 25°C, which is 68.3 kcal/mol for higher heating value (HHV) or 57.8 kcal/mol for lower heating value (LHV). The denominator includes thermal heat, Q, supplied externally, and different types of work (chemical, electrochemical, mechanical, electrical, separations, etc.) converted to the thermal equivalent (assuming a 50% heat-to-electricity conversion factor). Electrochemical work is defined by the Nernst equation, or $\Delta G = nFE$, where E is the cell potential in volts and F is Faraday’s Constant, 96,493 coulombs [ΔG is in J.]. Work of separation is defined by the equation $\Delta G_{sep} = -RT \, \Sigma_i n_i \ln y_i$, where R is the gas constant, T is the absolute temperature, n is the flow of each component and y is the mole fraction. Chemical work is given by positive free energy for the reaction. Methods for accomplishing the separations or the chemical work are undefined in these early evaluations. Efficiency calculations are not static and will change as more knowledge of the cycle’s chemistry is gained and as processes within the cycle are optimized. In the scoping flowsheet methodology, we define two stages of efficiency calculations.

For Stage 1 evaluation, we calculate an idealized efficiency where the reactions are assumed to go to 100% completion. We use the reaction temperatures given in the cycle’s definition and pinch analysis for optimizing energy usage. In pinch analysis, the exothermic heat is recovered and used for endothermic processes only when temperatures can be matched. These calculations are normalized to one mole of water. For cycles that appear promising after the Stage 1 analysis, we calculate a more detailed Stage 2 efficiency that is based on equilibrium data. The effect of less than 100% yield is explicitly considered. Reaction temperatures may be adjusted to increase yields. For promising cycles, a process flow diagram (PFD) is designed and energy usage is usually optimized with a heat exchange network, but we are currently using pinch analysis. Stage 2 evaluations allow consideration of more realistic separations and recycle streams. Mechanical work may be estimated from the unit operations in the PFD. Shaft work is usually a relatively small component of the work load and can be ignored unless gas compressors are used in the PFD. In Stage 2 evaluations, reaction temperatures may be adjusted again when kinetic data are taken into account. For instance, reactions that have high yields at low temperatures may be kinetically hindered and only proceed to a measurable extent at higher temperatures. Reaction temperatures are then readjusted to realize reasonable reaction rates.

Results

We identified several cycles—Cu-Cl, Cu-SO_4, Zn-SO_4, and K-Bi—as promising. These are hybrid cycles, i.e., they contain an electrochemical reaction. Three of these (Cu-SO_4, Zn-SO_4 and the K-Bi) were not evaluated in the McQuillan et al. report [2]. They are nevertheless considered promising because their reported idealized efficiencies are high, e.g., 57-62% (LHV) for Cu-SO_4, 46% (LHV) for Zn-SO_4 [1], 48% (LHV) for K-Bi [4] and 51% (LHV) for Cu-Cl. These cycles are being reexamined with our scoping flowsheet methodology to provide a consistent evaluation since the original calculations were done at different times by different people. We illustrate our methodology with the hybrid Cu-SO_4 cycle.

We used HSC (database name derived from the letters for enthalpy, entropy and heat capacity) as the thermodynamic database [5]. The two major reactions in this cycle and their temperatures are the following:

$$CuO + SO_2(g) + H_2O \rightarrow CuSO_4 + H_2(g) \qquad (25^oC) \qquad (1)$$

$$CuSO_4 \rightarrow CuO + SO_2(g) + \tfrac{1}{2}O_2(g) \qquad (850^oC) \qquad (2)$$

We assumed the above temperatures from the Carty et al. report. At these temperatures, the free energies of the reactions are slightly positive: 1.08 and 1.73 kcal/mole, respectively. We assume that they will be driven to the right by the evolution of the gaseous products. Table 1 lists the Stage 1 enthalpy balance (heats of reaction and sensible and latent heats for phase changes) for both the endothermic and the exothermic reactions. Figure 1 shows the heating, cooling, and pinch curves. In pinch analysis, cumulative heating and cooling loads are plotted vs. temperature level, and the pinch curve is obtained by offsetting the cooling curve (exothermic heat) so that the pinch curve lies below the heating curve (endothermic heat) at all points. The offset is determined by the desired driving force, in this case 10°C, at the pinch.

The total enthalpy, Q, requirement is the sum of the offset (determined from the pinch analysis) and

Table 1. Summary of the Heats

	Tin[a], °C	Tout[b], °C	Heat, kcal
Heat			
$CuSO_4$ Rx	850	850	71.95
$CuSO_4$	25	850	20
Cool			
CuO Rx	25	25	-7.54
CuO	850	25	-9.90
SO_2(g)	850	25	-9.08
1/2 O_2(g)	850	25	-3.30

[a] Tin = Initial temperature
[b] Tout = Final temperature

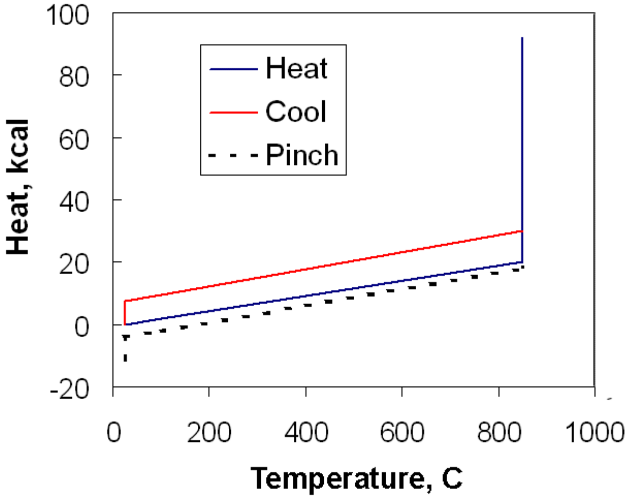

Figure 1. Pinch Analysis for the Cu-SO_4 Cycle

the endothermic external heat load. Work terms are converted to their heat equivalent and are included in the efficiency calculation. Table 2 shows the details of the efficiency calculation. The resulting efficiency is 69.2% (LHV). The Carty et al. report specifies that reaction 1 can not be thermally driven even though the free energy of the reaction is only slightly positive. Their experimental work indicates a minimum cell potential of 0.45 V [1]. The corresponding efficiency with electrochemical work is 46.2% (LHV), as shown in Table 2.

Table 2. Summary of Efficiency Calculations for Two Cycles

Energy, kcal	$CuSO_4$ Stage 1	$CuSO_4$[a] Stage 1	$CuSO_4$ Stage 2	CuCl Stage 2
H_2, LHV	57.8	57.8	24.6[b]	57.8
Enthalpy (Q)	62.1	62.1	28.9	66.8
Pinch (Q)	11.6	11.6	11.8	28.2
Chemical Work[c]	5.6	5.6	0.0	0.0
Electrochemical Work[a]	0.0	41.5	17.6	37.0
Separation Work[c]	4.2	4.3	5.2	0.0
Ideal Efficiency (LHV)	**69.2%**	**46.2%**	**38.7%**	**43.8%**

[a] With electrochemical work

[b] After normalization to the amount of hydrogen produced at equilibrium

[c] Work terms corrected to heat equivalent at 50%

For the Stage 2 analysis, we used the equilibrium module of HSC to obtain equilibrium compositions for the two reactions [5]. Figure 2 shows the equilibrium composition for reaction 1. Note that one mole of water is converted to 0.42 moles of hydrogen at 25°C, and the amount decreases at higher temperatures. The equilibrium composition for reaction 2 (not shown) indicates that the reaction goes nearly to completion at 1100°C. For this analysis, we chose to use 1100°C to eliminate recycle of the high-temperature streams. We have rewritten reactions 1 and 2 as reactions 3 and 4 to show the new material balance. Note that in Stage 2, less than 1 mole of H_2 may be produced from 1 mole of water feed, resulting in unreacted or excess water.

$$0.43CuO + 0.43SO_2(g) + 0.92H_2O \rightarrow 0.39Cu\ SO_4{*}H_2O + 0.035Cu\ SO_4{*}3H_2O + 0.43H_2(g) \quad (3)$$

$$0.39Cu\ SO_4{*}H_2O + 0.035Cu\ SO_4{*}3H_2O \rightarrow 0.43CuO + 0.43SO_2(g) + 0.50H_2O(g) + 0.21O_2(g) \quad (4)$$

The Stage 2 efficiency is 38.7% (LHV), as shown in Table 2. A preliminary process flow diagram is shown in Figure 3. The Stage 2 process now has a difficult SO_2/O_2 separation, a very high temperature reaction step, substantial recycle quantities whose energy costs are presently ignored, and lower efficiency. This decrease in efficiency is expected. In this Stage 2 analysis, we have not explicitly considered any species other than cupric sulfate and its hydrates. This is justified because

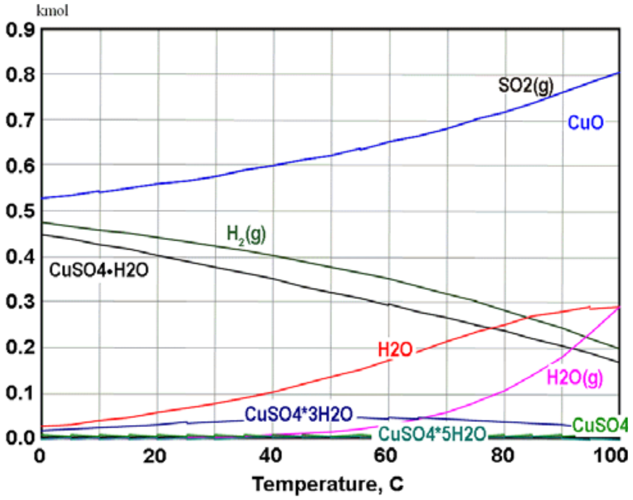

Figure 2. Equilibrium Composition for a System with Equimolar Amounts of CuO, SO_2(g) and H_2O

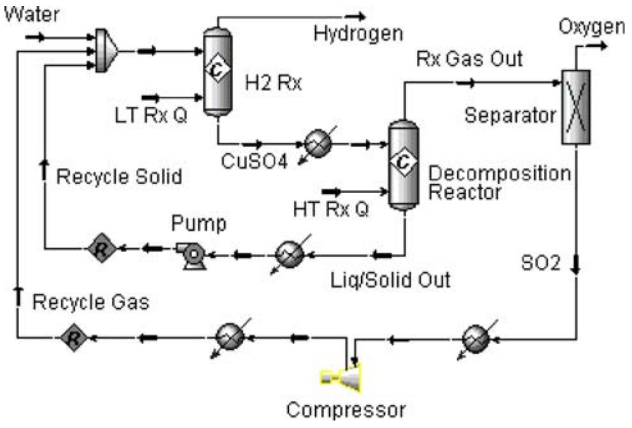

Figure 3. Process Flow Diagram for $CuSO_4$ Process

only hydrated species are reported in the literature [1,6]. Carty et al. did not report any species being formed other than $CuSO_4*5H_2O$. According to the equilibrium module, $CuSO_4*5H_2O$ is the primary product when reaction 1 is run in an excess of water [6]. We will discuss the energy costs of running reaction 1 in an excess of water and the energy costs of recycle in a later report. No relevant kinetic data were found in the literature to justify changing the reaction temperature.

If the decision is made to proceed with further development, the most critical needs are designing and optimizing the electrochemical cell (such as a fluidized electrolyte system and/or electrocatalysts); determining the extent of side-product formation, if any; determining energy-efficient methods for removing the waters of hydration; and dealing with the recycle streams in the Cu-SO_4 high-temperature decomposition if the maximum temperature is limited to 850°C or so. The primary advantages of this cycle are its relatively low corrosivity and a common reaction with the sulfur cycles. In the Cu-SO_4 cycle, water is removed from the hydrated forms of $CuSO_4$ rather than from sulfuric acid, as it is in the sulfur-iodine cycle. Also, anhydrous SO_3 is decomposed to SO_2 and oxygen in the absence of water vapor. Hence, the high-temperature reactions are less corrosive. The membrane currently under development for the sulfur cycles could also be used to advantage in this cycle. The membrane, if successfully developed, will lower the maximum temperature and facilitate SO_3 decomposition and separations. Whether these advantages are sufficiently compelling to support further development of this cycle remains to be determined.

Work is ongoing with the other cycles. A preliminary value for the Stage 2 efficiency for the Cu-Cl cycle, shown in Table 2, is a promising 43.8% (LHV) [7]. Work on two other cycles has just started.

Conclusions

We initially selected four cycles as promising. We have illustrated our scoping flowsheet methodology with the hybrid Cu-SO_4 cycle in this report. Evaluations of both the hybrid Cu-SO_4 and the Cu-Cl cycles are in progress. Our methodology shows the ability to rapidly screen processes at Stage 1 with reasonable realism. More accurate simulations are done in Stage 2 to find problem areas (unexpected by-products, unrealistic process conditions, problematic separations, etc.) so that process development efforts can be focused. We are in the process of evaluating the other two cycles with this methodology. When all analyses are complete, we will provide updated assessments to rationalize further selection.

FY 2005 Publications/Presentations

1. Presentation at the 2005 DOE Hydrogen Program Review, May 23-26, 2005, Washington D.C.

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