

Evaluation and Design of Thermochemical and Hybrid Water-Splitting Cycles

Scott Mullin, Uchenna Odi, and Jacob Tarver

Department of Chemical Engineering, The University of Oklahoma

Professor Miguel Bagajewicz, instructor

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Abstract

We developed a methodology for evaluating and screening water-splitting cycles. Screening is effective without need for advanced flowsheets. We first define the thermodynamic efficiency of each cycle using the minimum reversible energy (heating and work) requirement. We base this calculation on a new algorithm that uses excess reactants for reactions that are not spontaneous (high negative ΔG) as well as minimum utility calculations using the pinch method. We also include the separation work, when needed. We then assess the real efficiency of the cycle by estimating real minimum heating utility as well as separation energy. We finally optimize T, P and excess reactants for each cycle, and provide examples.

I Introduction

Water-splitting cycles are actively pursued as hydrogen production methods, and the US Department of Energy plans to implement water-splitting facilities using heat and electricity from nuclear power plants [1]. Other hydrogen production technologies – electrolysis, photolysis, and petroleum reforming – are not efficient and cannot meet projected demands [2]. Schultz 2003 estimates 200 million tons of hydrogen will be required annually to meet transportation needs in a complete hydrogen economy. The current method, steam reformation of methane, is becoming expensive with rising fuel costs, and most of the hydrogen produced by this method is consumed locally. Furthermore, carbon dioxide emissions are undesirable due to concerns about global warming. Water-splitting cycles are efficient and produce no harmful emissions. Thermal energy from a nuclear power plant is sufficient to produce large amounts of hydrogen while maintaining electricity production. A Gas Turbine Modular Helium Reactor (GT-MHR) will supply 950°C process heat to a water-splitting facility [3] – enough to meet peak temperature requirements.

Water-splitting cycles use a series of chemical reactions to convert water into hydrogen and oxygen. The oxygen produced is not marketable, but could be used at nearby chemical facilities if the demand exists. Interest in water-splitting cycles evolved during the oil crisis in the 1970s, and over 202 such cycles were investigated and reported in literature. Research lapsed as oil became cheap, but hydrogen production technology is pursued with renewed vigor as oil prices climb. Products from each reactor are separated and cycled to other reactors, and ultimately make a complete circuit and begin as reactant. Most cycles operate continuously, and reactions are thermally driven with exception to hybrid cycles, which contain one or more electrolytic processes. Finding the most efficient cycles is of interest because of the large energy requirements needed for adequate production. Water-splitting facilities must be co-designed with nuclear reactors, and will not be implemented for at least 10 to 20 years. Construction will be capital intensive, but there is time to search for better cycles than the currently favored University of Tokyo (UT-3) and Sulfur Iodine cycles, each of which are reported to operate near 50% efficiency. Heat and electricity used for hydrogen generation reduce the electricity available for sale as utility. Energy wasted by the water-splitting facility limits profit through electricity sales, and increasing efficiency by a few percent justifies increased equipment costs over the lifetime of the facility.

Estimating capital costs is difficult, and design complexities for each cycle are numerous. Few cycles have been researched in detail, and only the Sulfur Iodine and UT-3 cycles have been operated on bench-scale. Development costs will vary greatly among each cycle, depending on operating conditions (T, P, pH), and energy requirements for process equipment. Further complications include unstable energy prices, which propagate error into total economic analyses. Equipment and control costs are also very high, and are sensitive to price changes as technologies improve, etc. Behaviors of the UT-3 and SI cycles are well understood, but research of other cycles remains immature. Finding the economically best process requires detailed flowsheeting, optimization and costing for each cycle – an infeasible approach for screening large numbers of cycles. A standard methodology is needed to determine the best process.

Brown et. al 2000 compiled known cycles from literature and evaluated their potential for development and implementation [4]. Cycles were scored and ranked according to various criteria affecting process economics, such as presence of corrosive chemicals, number of reactions and separation steps, etc. The approach is useful for identifying cycles with positive economic attributes (less equipment at lower costs) but is not quantitative. Changing the number of criteria or the weight of each evaluation metric results in different cycle rankings, and does not reliably estimate economic profitability. Furthermore, Brown’s method favors cycles with extensive research. Well-researched cycles are favorable because they are nearer implementation, but they are not necessarily the most efficient. Brown’s report remains a useful guide, but more recent studies have attempted to improve the cycle evaluation method.

Lewis et. al 2005 describe a scoping methodology for evaluating cycles, using efficiency as a basis [5]. The report determines efficiency using heat of formation as basis, and accounts for heat requirement using the heat integration technique, electrolysis work with the Nernst equation, and ideal separation energies. The method has shortcomings, since work terms (including separation work) were assumed 50% efficient. Efficiency of real work compared to ideal work varies with separation equipment and process design, and can be higher or lower than 50%. Furthermore, the method requires flowsheet development – a time-consuming process.

We ameliorate the shortcomings of the Lewis method by developing a process that can rapidly screen cycles without requiring flowsheet development, providing an ideal basis for efficiency comparison. Ideal requirements are found first, and then real effects such as incomplete reactions and real separation energies are calculated as more is known about the cycle. The method allows for additional energy terms – accounting for pressurization of hydrogen for distribution, heat recovery through co-generation of electricity, etc. We applied the methodology to nine thermochemical and three hybrid water-splitting cycles, and rank the best cycles **Table 1**.

Table 1 Ranks and efficiencies of best cycles.

Westinghouse	85%
Gaz de France	75%
US Chlorine	61%
Sulfur Iodine	55%
Ispra Mark 13	53%
Ispra Mark 9	52%

The Westinghouse and Gaz de France cycles are highly efficient and deserve future consideration. The methodology is designed to process all known cycles, and eventually integrate with further methodology to find and evaluate novel cycles using thermodynamic databases. Holiastos and Manousiouthakis 1998 describe a method for finding thermodynamically feasible reaction clusters [6] and can be modified to find water-splitting cycles. Process flow diagrams should be developed for the most efficient cycles in order to determine which is most economically viable, as shown in **Appendix A**.

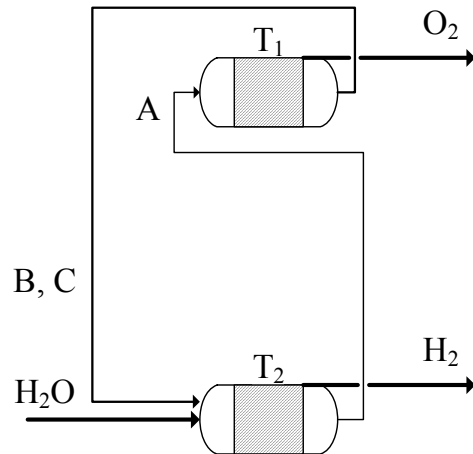
II Water-Splitting Cycles

Water decomposes into hydrogen and oxygen spontaneously at 2500°C, but the process cannot feasibly be used for hydrogen generation. Materials that withstand such high temperatures are prohibitively expensive, and separating the two gases is difficult. Without separation, the gases recombine during cooling. Furthermore, temperatures of 2500°C are not attainable for large scale processes. Nuclear power is the only feasible source for such high temperatures, but transporting high temperature gases is inefficient and highly capital intensive.

Water-splitting cycles include two or more chemical reactions with the net result of water decomposition. Most reactions are driven thermally, though “hybrid” cycles include one or more electrolytic steps. As products leave one reactor, they are heated (or cooled) and separated as necessary, and sent to other reactors. Hydrogen and oxygen gases are produced and separated in different reactions – avoiding problems experienced in simple water decomposition. All other species are eventually regenerated. The result is the same as simple water decomposition, so cycles essentially catalyze the decomposition via a series of steps. Peak temperatures for most cycles range from 800 to 950°C: avoiding need for exotic materials. By our convention, reactions are sorted according to temperature, with the hottest reaction numbered as 1 in each cycle.

T₁	$A \longrightarrow B + C + O_2$
T₂	$B + C + H_2O \longrightarrow A + H_2$

Cycle 1 Example two-step cycle. Note that cycles may have different generic reactions.



A decomposes into B, C and oxygen. Oxygen is separated, and B and C are sent to the next reactor where water is added as feed. B and C are oxidized into A and hydrogen is produced. Hydrogen is separated and A is sent to the first reactor, completing the cycle. If T₂ is above room temperature, H₂O feed must be heated. B and C are cooled as they flow towards reaction 2, and their heat value is recovered to heat water and A as it transfers to reaction 1. Reaction heats must also be considered when assessing recoverable heat values. The heat

integration method is used to find minimum heat usage, as detailed in **Heat Requirement**.

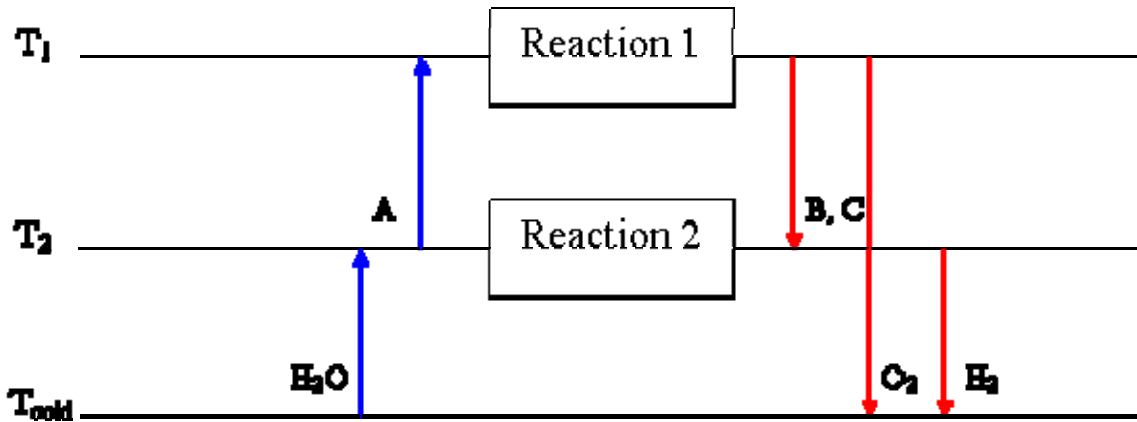
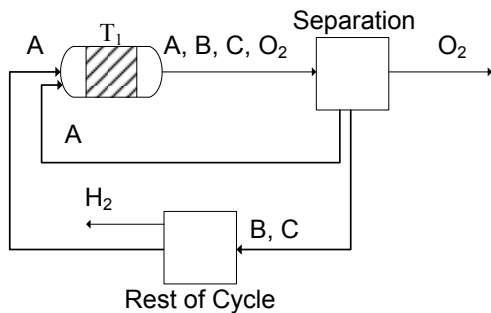


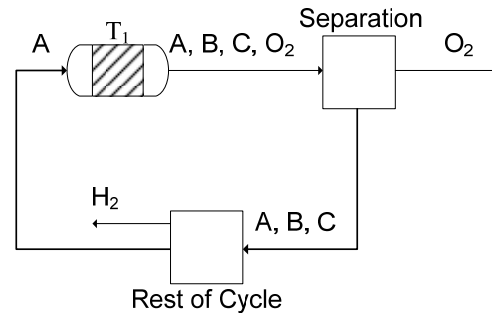
Figure 1 Cycle 1 heat cascade.

If the free energy for a reaction is too positive, excess reactants must be handled. There are two major options:

1. Separate excess reactants and recycle directly to the reactor
2. Send excess reactants to subsequent reactors



Option 1 Complete recycle of A.



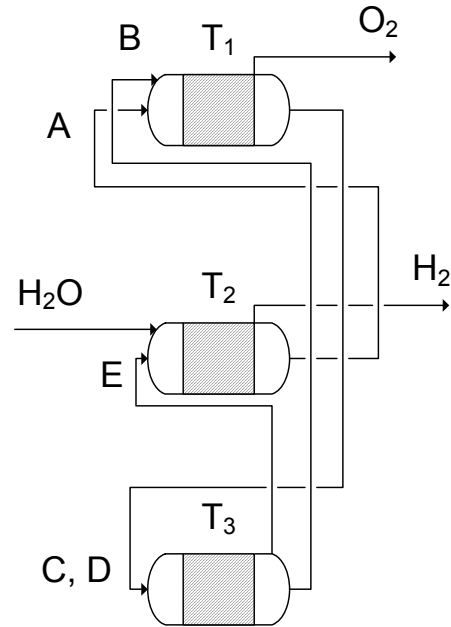
Option 2 No recycle of A.

Partial separation results in a third option, with some A immediately recycled, and the rest sent to other reactors. This analysis must be considered for each reaction. Option 1 is favored in most cases because spontaneous reactions reach full conversion at equilibrium and do not require excess reactants. Sending the excess reactants to the rest of the cycle saves separation work in some cases, though chemical compatibility must be considered to prevent unwanted reactions. Option 2 shifts equilibria of subsequent reactions in many cases, and though it can have positive or neutral effects, the result usually shifts reactions negatively. In **Cycle 1**, for example, sending excess A to reaction 2 will shift equilibrium to the left by decreasing reactant concentrations. Sending excess B and/or C to reaction 1 will shift equilibrium to the left

in that reaction as well. Furthermore, increasing the total amount of material circulating in the cycle will increase heat requirements. If A can be sent to the rest of the cycle without requiring separation, energy requirements will be decreased. Pressure, temperature and handling of excess reactants are optimized for each system. As explained in **Equilibrium Effects**, the algorithm accounts for heat, separation, and shaft work requirements. Electrochemical and thermochemical reactors are optimized in the same way, with the exception that electrolytic reactors require additional electrical work.

T₁	$A + B \longrightarrow C + D + O_2$
T₂	$E + H_2O \longrightarrow A + H_2$
T₃	$C + D \longrightarrow B + E$

Cycle 2 Example three-step cycle.
Note that cycles may have different generic reactions.



T, P and excess products are optimized for the additional reactor. Even in simple cases, there is considerable coupling between energy requirements for separation and heating. We are looking for the minimum energy requirements assuming perfect process control. Control systems will be expensive for any cycle, and must be considered during economic analysis, which is decoupled from efficiency estimates.

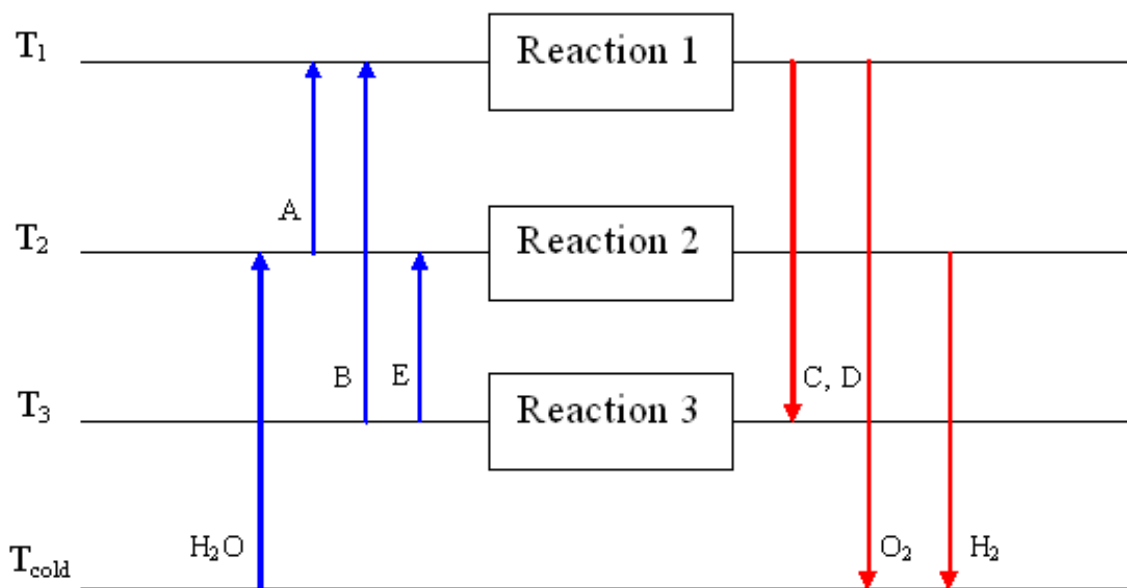
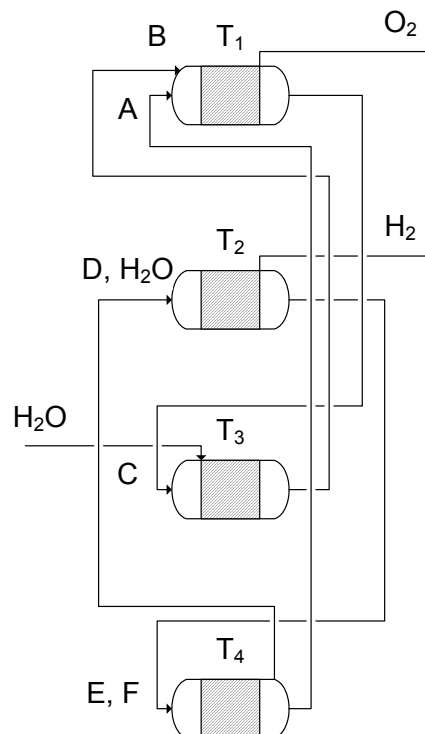


Figure 2 Cycle 2 heat cascade.

Separations are more complicated in this case, since products in the third reaction are sent to different reactors. Heat recovery is more complicated as well, since there are now multiple heating and cooling streams transferring between multiple temperatures.

T₁	$A + B \longrightarrow C + O_2$
T₂	$D + H_2O \longrightarrow E + F + H_2$
T₃	$C + H_2O \longrightarrow B + F$
T₄	$E + F \longrightarrow A + D + H_2O$

Cycle 3 Example four-step cycle. Note that cycles may have different generic reactions.



Cycle 3 requires further consideration of separation and heat recovery, and has the added feature of a reactant appearing in two separate reactions (water is added in reactions 2 and 3).

Species in other cycles may appear in multiple reactions as reactants or products, and cycling excess of the common reactant shifts equilibrium favorably in both reactions. Analysis of such cycles requires detailed optimization, but a pattern clearly develops as the generic cycles become more advanced. Two, three and four-step cycles often have different generic reactions, but our algorithm accounts for any number of species in any number of reactions.

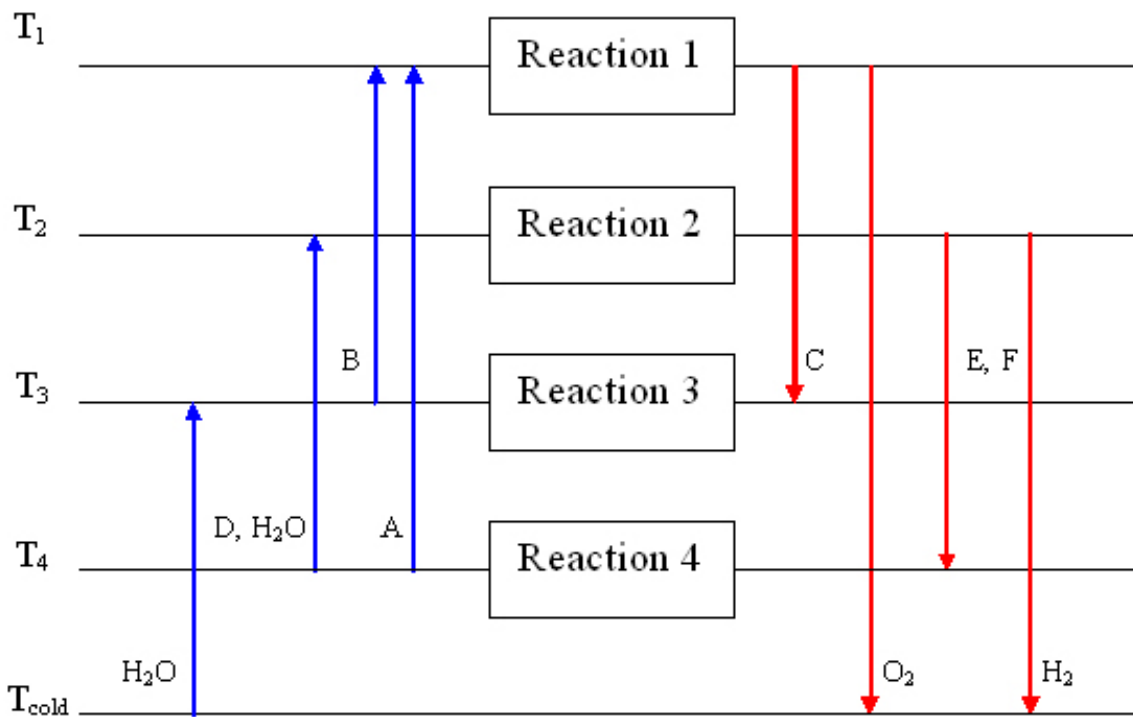


Figure 3 Cycle 3 heat cascade.

Cycles increase in complexity with additional reactions and number of species, as demonstrated by the progression from the Cycles 1-3 above. Permutations for generic four-step cycles are numerous. Connectivity depends on individual reactions, and solving intricately coupled equations. Few steps in any known cycles have more than two reactants (entropic effects limit spontaneity), but arbitrarily complex cycles can be broken into multiple steps in the solving process to solve thermochemical and the subset class of hybrid cycles.

Electrolytic reactors are subjected to the same analysis as thermochemical reactions under our methodology, with the addition of an electrical work component. Energy requirements for the electrolytic cell are found using the Nernst equation, as detailed in **Electrolysis Energy Requirement**.

Efficient designs should be operated continuously. Hydrogen must be continually supplied to a pipeline or other distribution system. Batch processes are likely to require large equipment and unsteady behavior makes batch systems difficult to control.

Cycles often contain reactions with positive ΔG values. Slightly positive ΔG reactions have been accepted in previous studies, but cycles with highly positive ΔG values for any reaction are usually ignored. Equilibrium product concentrations can be optimized by adding excess reactants, and adjusting reactor temperature and pressure. Shifting equilibrium concentrations this way makes some reactions feasible that have otherwise been discounted because their free energies are too high.

III Cycle Efficiency, η

Efficiency is the primary comparison basis for cycles using our methodology, and indicates how heat and electricity are converted into chemical energy as H_2 and O_2 . The number is a useful basis because theoretical efficiencies can be estimated for cycles without requiring physical experimentation. Energy requirements are estimated first as heat required to warm streams and power endothermic reactions, and ideal separation energies are calculated. These terms are the physical minimum energy requirement of the system. Additional energy requirement terms can only decrease efficiency. Cycle efficiencies lower than those achieved in current designs are not worthy of further consideration unless equipment costs are projected to be much less. Cycles with highest efficiencies should be explored in detail, accounting for progressively more real-world limitations for each cycle. We can estimate ideal efficiencies knowing only the chemical reactions in a particular cycle and thermodynamic behavior of each species.

$$\text{Equation 1} \quad \eta = \frac{\Delta H_f^\circ(H_2O)}{Q + W}$$

Efficiency is 1 in the ideal case, but can never be attained by a water-splitting process. Water-splitting processes ideally require only the sum of the heats of each reaction. Physical limitations require additional energy input to compensate for heat losses, separate chemicals, and power equipment. The second law of thermodynamics often restricts perfect heat recovery, since exothermic reactions cannot use their heat to power endothermic reactions that occur at higher temperatures. Heat is recovered from cooling streams and exothermic reactions as possible, but losses occur during the process as well, and are described further in the **Heat requirement** section. Practical heat, separation and other energy requirements (compression, pumps, etc.) can be considered further for best cycles.

Thermodynamic methods are detailed in **Appendix B**. Enthalpy, entropy and free energy values are calculated using the Shomate equation, and data from the JANAF tables, published by NIST [7]. State functions were calculated using pure-component averages of each stream. Heats of mixing were not considered, though mixing effects are accounted when finding the separation work requirement. Gases are under low density in most reactors. Pressures are kept low when possible, and temperatures are usually well above the critical temperature of water at 374°C. Solid-liquid interactions are considerable in some systems, and involve equilibria between various phases, including solid metal phases, oxides and electrolytes and their complexes with solvents. Intermolecular forces are attractive for most cases, and will only

increase separation requirements. Heats of mixing will affect heat cascade, since stream and reaction enthalpies are not known exactly. Accuracy of the thermodynamic model depends on individual systems, but was simplified for the basis of defining a methodology. Efficiency estimates compare favorably with literature, and trends behave as expected, as explained in **Results**. Advanced thermodynamic models will be implemented during future work.

Ideal separation work is found next for each system. Separation processes are among the largest energy requirements in each cycle. Real separation energies can be estimated for individual processes (distillation columns, membranes, etc) and optimized for best cycles. Separation work includes heat and electricity needed for a separation. For example, membrane separations require pumps to pressurize streams and distillation columns need reboiler heat. We consider heat and electricity terms to be the same value in the efficiency calculation. Value of heat usage depends on the temperature of the heat and availability of the source. Most heat will be supplied directly from the nuclear reactor. Schultz 2003 reports the most likely design will transfer process heat from the reactor via helium gas at a temperature of 950°C. Nuclear reactors generate large amounts of waste heat during electricity generation. Turbines become hot, and are cooled by water. High-temperature waste heat should be used to power reactions, if possible, to minimize total heat usage from the nuclear facility. Such operation maximizes heat available for electricity generation.

Since the amount and quality of different energy sources (nuclear reactor heat, waste heat, and electrical energy) are not known, they are weighted as the same in the efficiency calculation. Approximately, efficiency relates total power requirements and hydrogen production rates.

$$\text{Equation 2} \quad \text{Power required} \approx \frac{1}{\eta} \times \text{Production} \times \Delta H_f^\circ(\text{H}_2\text{O})$$

We assume heat and electricity are worth the same amount for this analysis. W involves electrical requirements, and electricity does not have the same value as heat energy. Alternatively, efficiency can also be expressed as a weighted function where Q and W are normalized based on their value as energy sources as in **Equation 3**.

$$\text{Equation 3} \quad \eta' = \frac{\Delta H_f^\circ(\text{H}_2\text{O})}{Q + \alpha W}$$

Where α is the value of W relative to Q. Efficiency in this definition requires complete economic analysis be performed for each cycle. Defining efficiency this way changes the basis from how much total energy is lost, to how much valuable energy is lost. For example, if hydrogen is more valuable than electricity, α will be less than 1. The opposite case is also possible, and η' will fluctuate with electricity and hydrogen demand over time. It is better to find η as in **Equation 1** and perform economic analysis separately in order to develop a systematic methodology.

IV Efficiency Models

Heat requirement, Q_{hot}

Thermal requirements account for the majority of energy input for each cycle. Heating systems are complex; including multiple reactors, heating streams, and cooling streams across large temperature zones. The heat integration method was used to optimize heat usage and determine connectivity of exchanger networks [8]. For the purposes of this model, all heat is assumed to come from a single hot utility, represented by the nuclear reactor. We are not concerned with heat exchanger costing until the economic analysis. The hot utility requirement, Q_{hot} , is the minimum amount of heat needed for a given cycle, and provides a theoretical basis for the efficiency calculation. Reaction heats and changes in stream enthalpies are known from state functions. Final designs are optimized considering exchanger sizes and availability of heat sources. Feed water enters the system at 298K, and is heated to the temperature of the input reactor. Oxygen and hydrogen are assumed to exit the system at room temperature, and are included in the heat recovery. In real cycles, the streams are sent to processing and distribution operations under pressure. Including the streams is a good estimate. Best cycles are distinguished further based on individual optimization and advanced development of the design.

Without heat integration, hot streams and endothermic reactions are supplied heat directly from the hot utility. Cold utility is used to remove heat from exothermic reactors and cool streams. Integrating the streams and reactors into a heat recovery network is energy efficient. Heat duties of both utilities decrease, and maximize the available efficiency of each cycle. Ideal requirements are found first for each cycle to provide a theoretical maximum performance. Heat can only be transferred to cooler streams and reactors. During the heat integration analysis, heat cascade diagrams are broken into temperature zones. The hottest temperature in each heat cascade is the nuclear reactor, and was assumed to be greater than 950°C. Coldest temperature is always the cold utility; assumed to be 25°C. Reactors are assumed to operate isothermally. Heat addition and removal to each reactor can be accomplished by utilities or through integration with other reactors and streams.

Many cycles include a pinch point, at which any additional heat cascaded must be removed by the cold utility. Above the pinch temperature, heat is added to the hot utility as necessary to satisfy zone and reactor requirements. Heat cascades until the pinch temperature is reached, and the total enthalpy is satisfied. Below the pinch, stream and reactor heats are adequate to cascade until all requirements are satisfied, and the cold utility removes any remaining heat.

Energy requirements for the hot and cold utilities, Q_{hot} and Q_{cold} , are minimized by cascading heat from exothermic reactors and zones with excess heat. $H_{hot, i}$ and $H_{cold, i}$ are the total enthalpy changes of heating and cooling streams in each zone.

$$\text{Equation 4} \quad H_{hot, n} = \sum_{i=0}^{\#streams} \int_{T_n}^{T_{n-1}} Cp_i dT$$

Equation 5
$$H_{cold,n} = \sum_{i=0}^{\#streams} \int_{T_{n-1}}^{T_n} Cp_i dT$$

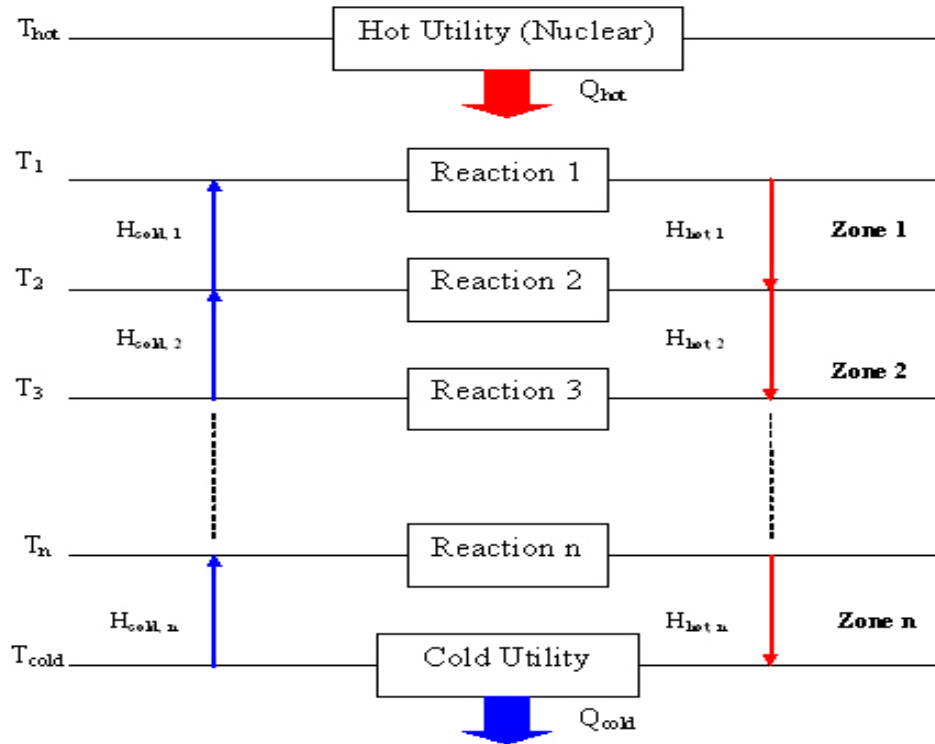


Figure 4 Generic heat cascade diagram for any number of reactors and streams.

By our sign convention, cooling streams and exothermic reactions have negative enthalpies. A generic heat diagram is shown in Figure 4. The analysis accounts for any number of reactions and streams. Zone heats are found as the sum of H_{hot} and H_{cold} . If $H_{hot} > H_{cold}$, there is enough heat in the zone to heat all the streams. Excess heat can be transferred to the next zone or reactor. If $H_{hot} < H_{cold}$, heat must be added to the cooling streams. If cascade heat is available, it is added to the zone until the heat requirement is met. If there is no cascade available, heat is added from the hot utility. In cycles where the hottest reaction is endothermic, heat must always be added from the hot utility. Other endothermic reactors use cascade heat from hotter zones and reactors as much as possible. Leftover heat at the end of the cascade is removed by cooling water, which is not considered in the efficiency calculation. Nuclear reactors require abundant water supplies, and costs of obtaining and pumping water are negligible compared to other energy requirements. Cycles that reject heat to the cold utility at high temperatures can create steam for heat recovery through electricity generation, and can be considered further for best cycles.

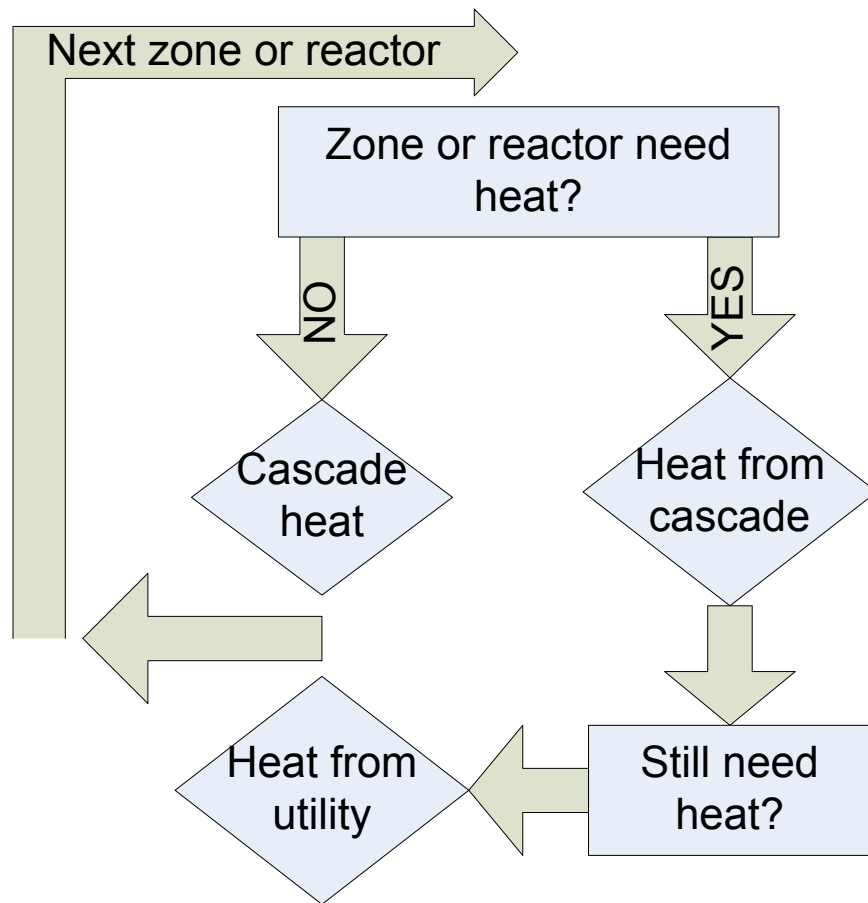


Figure 5 Algorithm for determining Q_{hot} .

Our analysis does not consider separation equipment in the heat cascade. As flowsheets are developed, zones can be further divided to account for separation processes. For example, condenser and reboiler duties can be added to the heat cascade, requiring intermediate temperature zones. In practice, hot and cold utilities will be used in most cases to avoid process instability, with little effect on the heat recovery analysis. Energy requirements for separation equipment are found separately, as accounted by the W_{sep} term in the efficiency calculation.

Detailed consideration of individual stream enthalpies (instead of zones) is considered separately to design heat exchanger networks. Heat exchanger design limits the practical amount of heat streams can transfer. Methods for determining the minimum number of exchangers and designing complete exchanger networks are described by PT&W 2003, and process flow diagrams for our best cycles are in **Appendix A**. The driving force for heat transfer decreases as streams approach the same temperature and further transfer requires increased exchanger surface area. Perfect transfer requires infinite surface area, and is not possible in practice. Minimum approach temperatures must be defined for the analysis, representing the allowable difference in stream temperatures (also called approach temperature, or pinch temperature difference). Ideally, ΔT_{min} is zero, but $Q_{hot, real}$ is always greater than $Q_{hot, ideal}$. Increasing the pinch

temperature difference always increases requirements from the hot and cold utilities, but the difference is small in some cases. PT&W recommend 10°C as a reasonable approach temperature, resulting in acceptably-sized heat exchangers. Hot utility and heat exchangers networks must be found separately for each value of ΔT_{\min} . We report the effect of ΔT_{\min} on total heat requirement in **Results**.

Multiphase flow through exchangers will cause heat transfer and transport problems. Practical designs of solid-handling heat exchangers require large approach temperatures, and use of sweep-gases as intermediate heat carriers should be considered during the design process.

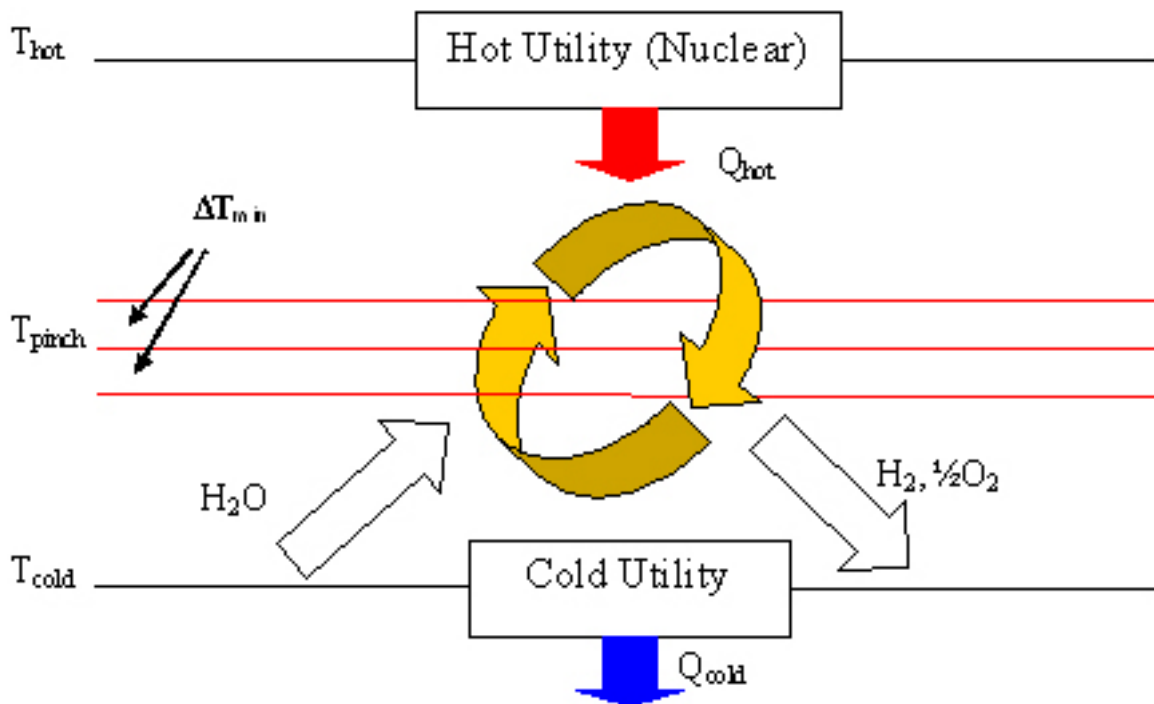


Figure 6 Heat cascade above the pinch is augmented by the hot utility. Cascade below the pinch is self-sustaining, and excess heat is removed by the cold utility. Heat cascade across the pinch goes into cold utility as waste.

Separation energy requirement, W_{sep}

Separation work is a large energy requirement in most cycles, and is the amount of energy – electrical, thermal or shaft – required to operate separation equipment. The work term represents those terms collectively and with equal weight. Many species undergo phase transitions during separation or transport, and reactors include multiple phases. Reaction species can be described in three classes, given in **Table 2**.

Table 2 Common cycle species and their classification based on chemical nature. Species in each classification exhibit common phase characteristics, with exception to S and I₂. Reaction temperatures range from 25 to 950°C.

<p>Heavy solids K, C, S[†], I₂, CaO, FeO, Fe₂O₃, Fe₃O₄</p>	C and metal oxides will not melt or sublime, and separate from liquid and gas phases at equilibrium.
<p>Heavy salts CrX₂[‡], CrX₃, FeSO₄, FeX₂, FeX₃, CuX, CuX₂, CaX₂, KOH</p>	Electrolytic species form complexes with solvents and each other, and have low vapor pressures. All are soluble in water.
<p>Light components H₂, O₂, H₂O, CO₂, H₂S, S, SO₂, H₂SO₄, HX, X₂</p>	Exist as liquids at lower temperatures, and supercritical fluid at most temperatures. Acids and halides are water soluble.
<p>†K exists as solid and liquid, S exists as solid, liquid and gas ‡X = Cl, Br, I</p>	

Species are assumed to exist in pure component phases, as determined from temperature ranges in the JANAF tables. Phase transitions are assumed to occur at pure component temperatures (phase transitions do not change in mixtures), and phase separations are assumed complete. Phase interactions are negligible in most cases, and most components exist in one phase over wide temperature ranges. Other species are mostly heavy metal oxides and their salts (with a few exceptions). Separation work must be found for each phase individually, and is found from ideal mixing energies.

Equation 6 $W_{\min} = -\Delta G_{\text{sol}} - \Delta G_{\text{liq}} - \Delta G_{\text{vap}}$

Equation 7

$$W_{\text{sep}} = \Delta G_{\text{mix}} = \Delta \sum_{i=1} n_i \mu_i$$

$$= RT \left[\left(\sum_{i=0}^{\text{\#components}} n_i \ln x_i \right)_{\text{out}} - \left(\sum_{i=0}^{\text{\#components}} n_i \ln x_i \right)_{\text{in}} \right]$$

where ΔG_{mix} is free energy of mixing, n_i is number of mols, and x_i is mol fraction. In the case of full separation, the ‘out’ term is neglected. Components that are sent to the same reactor do not require separation. In this case full separation cannot be assumed and the ‘out’ term for these components must be evaluated. Connectivity of the cycle must be analyzed to determine separating requirements and conditions.

Reactions that do not reach completion at equilibrium require greater separation energies, and in some cases it is favorable to avoid separating unreacted species. Real energy requirements are much larger for many systems, depending on chemical nonidealities, separation equipment, and degree of separation. Chemical attractions are strong, and will only serve to increase the estimated W_{sep} . These effects are lumped as a single separation efficiency term, estimated as η_{sep} , and are assumed 1 in the first phase of the analysis.

Equation 8
$$W_{\text{sep}} = \frac{-\Delta G_{\text{mix}}}{\eta_{\text{sep}}}$$

Separation efficiencies are developed in general, assuming average values for individual separation processes. For example, a distillation column could be assigned an efficiency based on average performances from literature data.

Electrolysis energy requirement, W_{elec}

Large-scale hybrid cycle-based facilities require expensive electrolytic equipment, so it is in our favor to optimize the electrical to chemical efficiency. Most electrolytic reactors (electrolyzers) operate in batch mode and produce large amounts of low-quality waste heat, which will be discarded for most reactions. As product gases (O_2 , H_2 , SO_2 , etc.) evolve from the electrolytic half-cell, the activity of the remaining electrolytic solution increases. Electrolytes, in many cases, interact strongly with the anode. Increasing interactions resist potential across the cell, in a phenomenon known as overpotential.

Overpotential increases required voltages and practical electrode surface areas to sustain high current densities. Process kinetics depend on total electrons transferred – a product of surface area and current density. Electrodes are normally made of noble metals – platinum, rhodium, gold, etc. – to minimize surface interactions between electrode and electrolyte. Other materials – iron, nickel, manganese, etc. – corrode rapidly and must be replaced. It is important for processes to be operated continuously. Designs with multiple batch reactors in parallel will cause significant fluctuations in product flows, and are more susceptible to down-time if reactors must be cleaned, or electrode materials replaced. Large processes require multiple cells with large surface areas to maintain good kinetics, and costs are prohibitive of implementation.

However, overpotential problems are overcome if product and feed streams flow continuously, as shown in

Figure 7. Cell concentrations remain low; decreasing surface interactions, and sustaining high kinetics.

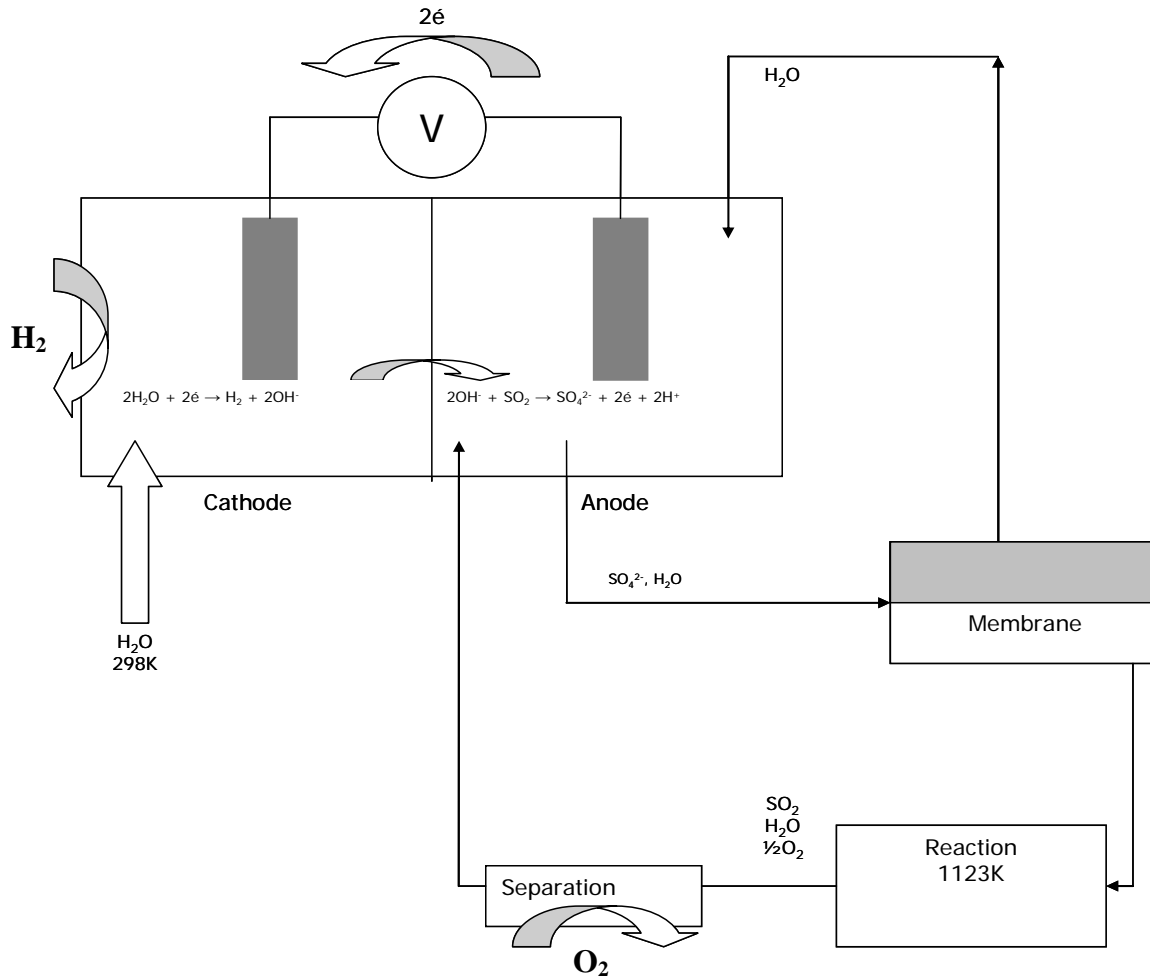


Figure 7 Continuous electrolyzer. Overall, the electrolytic reaction is $\text{SO}_{2(\text{g})} \rightarrow \text{H}_2\text{SO}_{4(\text{aq})} + \text{H}_{2(\text{g})}$, as in the Westinghouse cycle. Design decreases the amount of waste heat produced and capital costs.

Water, the solvent, is continuously purified. Electrolytes in most known reactions are strong Lewis acids and bases. Inorganics such as FeCl_x and CrCl_x can be removed efficiently through membrane separations. Recycling the purified water sweeps the electrodes; keeping electrolyte concentrations low. Minimizing overpotential also decreases total waste heat generated, since less voltage is required at the interface. A steady-state is reached, and current density remains high. Steady state electrolyzers require relatively small surface areas compared to batch designs, and capital costs are considerably lower. Motupally et. al 1998 report that such continuous-flow electrolyzers have been implemented for recovery of chlorine gas from hydrochloric acid waste streams. Electrodes were made from copper catalyst-coated Nafion® membranes. Material costs are considerably lower than in designs using noble metals, and molar conversions of 70-85% per pass were reported.

Reaction heats are continuously removed to limit overpotential at higher temperatures. High temperature electrolysis is possible for unknown reactions. Reactions with large positive ΔG values should be considered to see if electrolysis is possible.

Work needed to drive an electrolytic reaction electric, W_{elec} , is calculated with the Nernst equation (**Eq. 8**). Electrolyzers are assumed perfectly energy efficient to provide a meaningful theoretical baseline. Efficiencies for individual electrolytic processes must be considered in detail for promising cycles. Values for E° and $E^\circ(T)$ can be found from literature [9].

$$\text{Equation 9} \quad \Delta G_{\text{electric}} = -nFE$$

$$\text{Equation 10} \quad E = E^\circ - \frac{RT}{eF} \ln K$$

$$\text{Equation 11} \quad E^\circ = E^\circ_{(298)} + \int_{298}^T \frac{d(E^\circ(T))}{dT}$$

$$\text{Equation 12} \quad K = \frac{[\alpha_C]^c [\alpha_D]^d}{[\alpha_A]^a [\alpha_B]^b} \text{ for reactions } aA + bB \rightarrow cC + dD$$

where E is cell voltage, E° is standard voltage at operating temperature, F is Faraday's constant: 96485 C, e is # electrons transferred, R is ideal gas constant, and K is electrolytic equilibrium constant. Gases are assumed to leave the system; therefore activity is defined as 1, and does not affect K . Approaching equilibrium increases overpotential, and slows the overall kinetics for the electrolyzer the same way it does in a PFR, CSTR or other common reactor. A similar approach should model steady-state electrolyzers for best cycles.

Equilibrium effects

Initial efficiency estimates are based on the assumption that all reactions proceed to completion using stoichiometric amounts of reactants regardless of free energy changes. We examine the effects of accounting for reactions that do not go to completion, when the free energy change of a reaction, ΔG_{rxn} , is positive or slightly negative. Provided stoichiometric amounts of reactants, equilibrium concentrations are shifted to the left, and unreacted species remain. Such reactions require larger throughput to generate the minimum amount of product needed at steady state to proceed to the next steps in the cycle.

$$\text{Equation 13} \quad \Delta G_{\text{rxn}} = \sum_i \nu_i g_i = \sum_i \nu_i (h_i - Ts_i)$$

where ν_i is stoichiometric coefficient, g_i is Gibbs free energy, h_i is enthalpy, T is reaction temperature, and s_i is entropy. Equilibrium constants are determined from ΔG_{rxn} .

Equation 14
$$K_{eq} = e^{-\frac{\Delta G_{rxn}}{RT}}$$

Equilibrium constants depend on reaction phases present, since solids and liquids phase separate from gases, and further multiphase separations are possible. Interface area between phases is negligibly small and the activities of solids and liquids are defined as one in the presence of gas. Heterogeneous equilibrium involving mixtures of solids, liquids, and/or vapors is simplified by considering only the most volatile phase in equilibrium calculations.

Equation 15
$$K_{eq} = \prod_i x_i^{v_i} P^{\sum_i v_{gas,i}}$$

Equation 16
$$x_i = \frac{n_i}{\sum n_i}$$

where x is mole fraction, P is reaction pressure and $v_{gas,i}$ is the stoichiometric coefficient for gas phases only. Product gas is disfavored at increased pressures when the sum of the stoichiometric coefficients of vapor species is greater than zero, and vice versa. Product quantity is dictated by connectivity requirements, allowing determination of the corresponding excess reactant quantities by combining equations 14-16 at constant temperature and pressure. Increased heat and separation requirements are modeled to account for excess species. Heat requirements are only affected if temperatures of excess reactants cycle near the pinch point. Additional heating required is small compared to the separation energy requirement, which is strongly coupled to the amount of excess products used.

The minimum energy required for separation must take into account the excess reactants present. If equilibrium is dependent on only one reactant, the amount of excess reactant determined as above is not variable. In this case, W_{sep} is also invariable. If equilibrium is a function of more than one reactant, however, an infinite number of solutions exist for both excess amounts and separation energy. W_{sep} is optimized by varying amounts of excess reactants while maintaining product requirements.

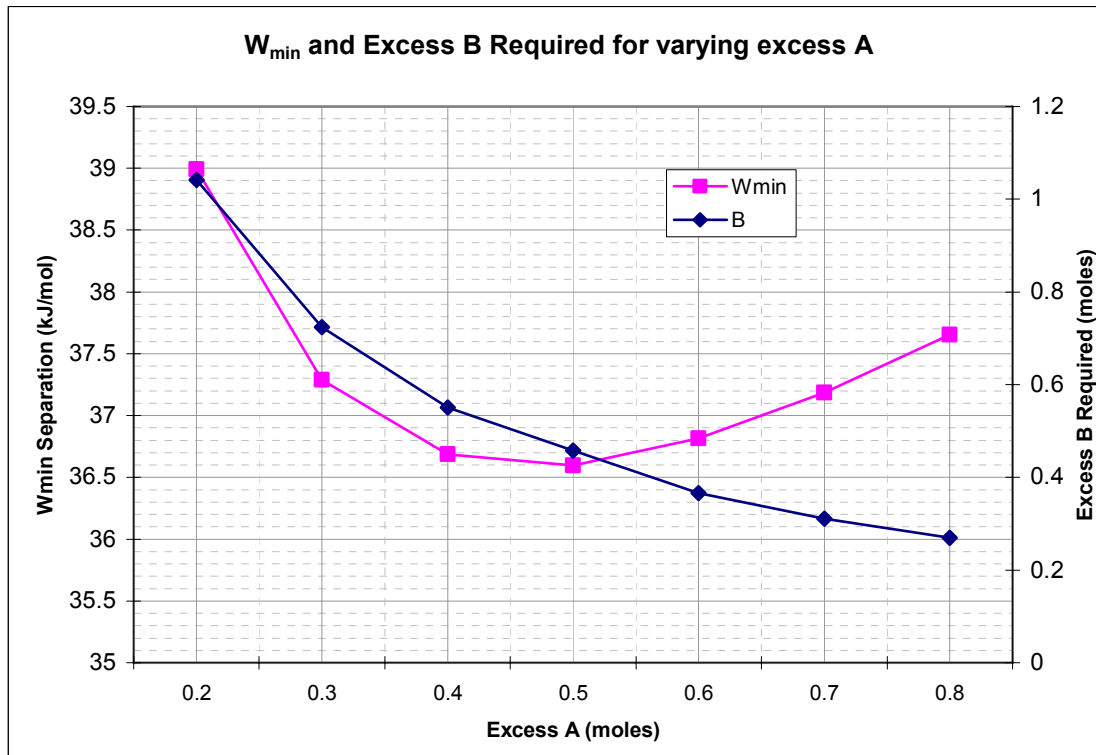


Figure 8 Example optimization for $A_{(g)} + B_{(g)} \rightarrow 2 C_{(g)} + \frac{1}{2} O_{2(g)}$ for $\Delta G_{rxn} = -17$ kJ

For the example reaction described in **Figure 8**, excess reactants are necessary despite the negative ΔG_{rxn} . Because each species present is in the gas phase, both W_{sep} and equilibrium are functions of n_A , n_B , n_C , and n_{O_2} . Equilibrium and W_{sep} can be further reduced to functions of only n_A and n_B by setting target amounts of n_C and n_{O_2} at 2 moles and $\frac{1}{2}$ mole, respectively. W_{sep} is minimized by finding the optimal n_A to n_B ratio. Reactions proceeding to completion with stoichiometric amounts of reactants do not require optimization.

For reactions that favor product formation at higher pressures, efficiency is increased by neglecting to separate excess non-reacting vapor species from previous reactions. Increasing the total number of moles present by adding an inert gas drives equilibrium to the right. With this optimization, production requirements are met with lower separation energy expenditures since equilibrium is shifted favorably, and less energy is spent separating excess species. Cycles with one or more reactants appearing in multiple reactions benefit from the same procedure. Avoiding separation of the excess reactants decreases separation energy requirements, and equilibrium concentrations shift to the right. Cycling excess reactants to the rest of the cycle in this manner shifts equilibria to the left in most cases, since reactants originate as products in other steps of the cycle.

Kinetic considerations

Kinetic effects are distinct from thermodynamic models, and have no effect on idealized efficiencies. Catalysts are assumed to remain in fixed beds, and separation requirements to

remove catalyst from product streams are assumed negligible. Reaction kinetics relate strongly to process economics through two effects:

1. Reactor sizing
2. Catalyst costs

Fast reactions reach equilibrium conditions with smaller reactor volume. Accelerating reaction kinetics – either through better catalysts or higher temperatures – decreases reactor volume. However, higher temperatures require more expensive equipment, and improving catalysts requires research. Furthermore, cycles requiring expensive catalysts, such as noble metals, cost drastically more to implement than systems using Ni, Fe or other base metals. Harsh environments in water-splitting reactions prohibit most transition elements from performing as acceptable catalysts. Reactor optimization considers these economic effects.

V Results

Nine thermochemical and three hybrid cycles were evaluated. Details for each cycle are found in **Appendix C**.

Hot utility is the largest requirement for most cycles, and was considered first in the analysis **Figure 9**. Zone and reaction heats must add up to 285.8 kJ. On the basis of ideal heat requirements, several cycles have 100% thermal efficiency. Heat from exothermic reactions in these cycles is at high enough temperature to be recovered. Other cycles experience a pinch point, and reject energy to the cold utility. Cycles exhibiting good heat recovery characteristics are worthy of further exploration, and distinctions between the best cycles are already becoming apparent.

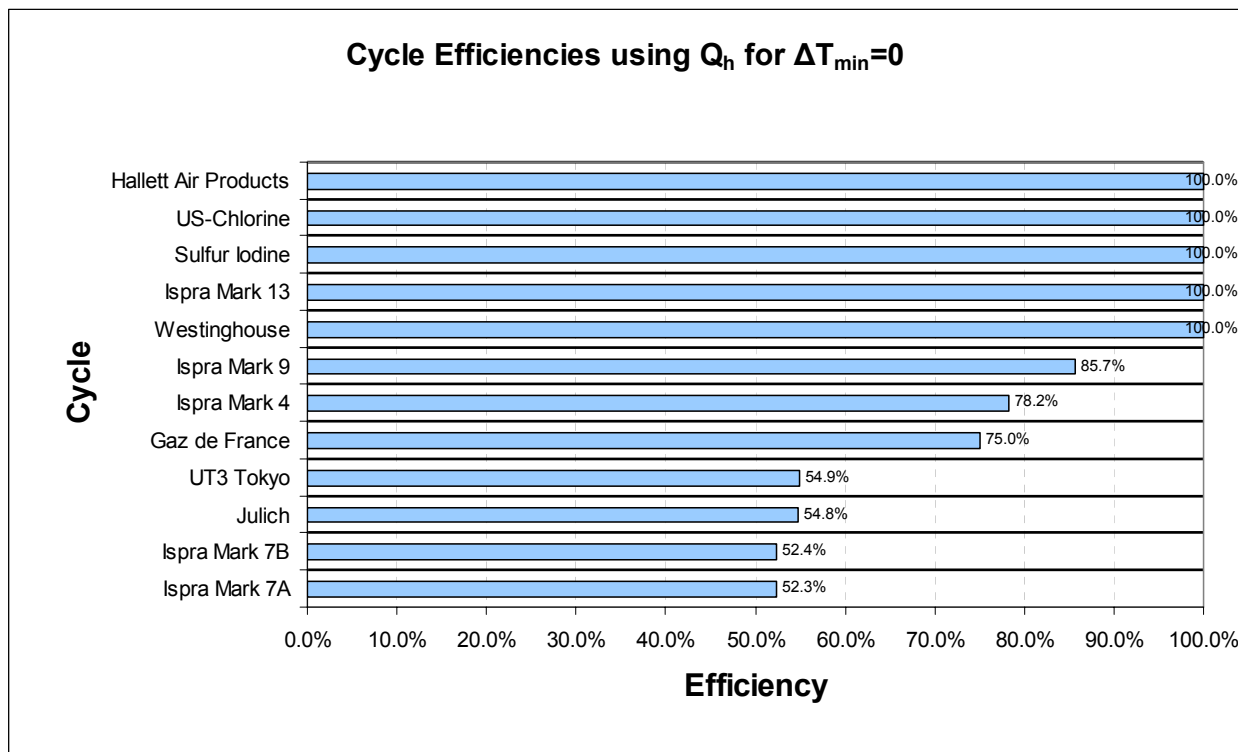


Figure 9 Efficiency on the basis of ideal heat requirements. Cycles with large thermal requirements are distinguished early in the analysis.

Perfect thermal efficiency is possible when stream and reactor heats are recovered in the heat cascade, assuming there is no approach temperature. Cycles with the smallest heat requirements recover heat from cooling streams and exothermic reactors through heat cascade, and are affected minimally by the pinch point. Endothermic reactions at high temperatures increase the amount of heat required, since heat produced by low-temperature exothermic reactors in these cycles is too low quality for recovery. Thermal efficiency for the UT-3 cycle, 55%, compares favorably to the 49% reported by Brown et. al 2000. Thermal efficiency is defined as similarly to our efficiency, except only the heat requirement is considered. Reported values were determined from a bench-scale process, and are below theoretical performance by 6%. Real efficiencies must be less than ideal, and the small difference between the two indicates the UT-3 flowsheet, in its current optimized state, is operating near its ideal thermal efficiency limit.

Electrical work accounts for a large energy requirement in hybrid cycles, and is considered next in the analysis. We are assuming ideal efficiencies in electrolysis equipment, as described in **Electrolysis energy requirement**.

Table 3 Electrochemical energy requirements for hybrid cycles.

	W_{elec} (kJ/mol)	Efficiency
Westinghouse	38.3	87.6%
Ispra Mark 13	210.1	57.0%

Hallett Air Products	262.5	52.1%
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The three hybrid cycles all have ideal heat cascade, but efficiencies of the Ispra Mark 13 and Hallett Air Products cycles decrease significantly once electrical requirements are considered. Westinghouse cycle efficiency only decreases by 12.4%, and will operate at 75% efficiency in the worst-case scenario that 50% of the electrical energy is lost. Hybrid cycles have potential for good heat recovery, as indicated by the three studied. Hallett Air Products and Westinghouse cycles are simple two-step cycles and have reduced capital costs because of their simplicity. Hybrid cycles have great potential for high-efficiency operation, and electrochemical reactions should be examined when discovering new cycles.

Separation work is a large requirement in most cycles, and is considered next in the analysis. First, reactions are assumed to go to completion. Separation work is idealized in this case, since unreacted species are not yet considered. Even with idealized separation estimates, best cycles are distinguished **Figure 9**. All cycles now exhibit efficiencies lower than 100%, with the UT-3 cycle decreasing to about 50%, with a new rank of 10th place overall. Notably, the Gaz de France has zero ideal separation energy. Reactants and products all phase separate, and the process can ideally be operated without separation equipment. In practice, phases will not separate perfectly, and species will instead equilibrate between multiple phases. Particularly, the potassium gas product in the 1098K reaction will interact with the K₂O and K₂O₂ oxide species. However, mixed fractions do not necessarily have to be separated, and the process should be optimized using experimental data. It is also of note that the Westinghouse cycle requires little separation energy, since the top reaction goes to completion, and the only separation required is the removal of O₂ from other product gases. The low-temperature reaction is electrolytic, and is assumed to operate continuously through advanced electrolytic cell design. Continuous flow will be used to remove sulfuric acid products, and use of Nafion® or other ion-selective electrodes eliminates the need for separation equipment during the electrolysis step. Effectively, the H₂SO₄ concentration at the electrode will reach a steady-state concentration, and is assumed to be at equilibrium. Removing the product acid through the electrode requires additional cell potential; accounting for separation energy in that step, which is included in the analysis of the electrical energy requirement when determining the cell efficiency.

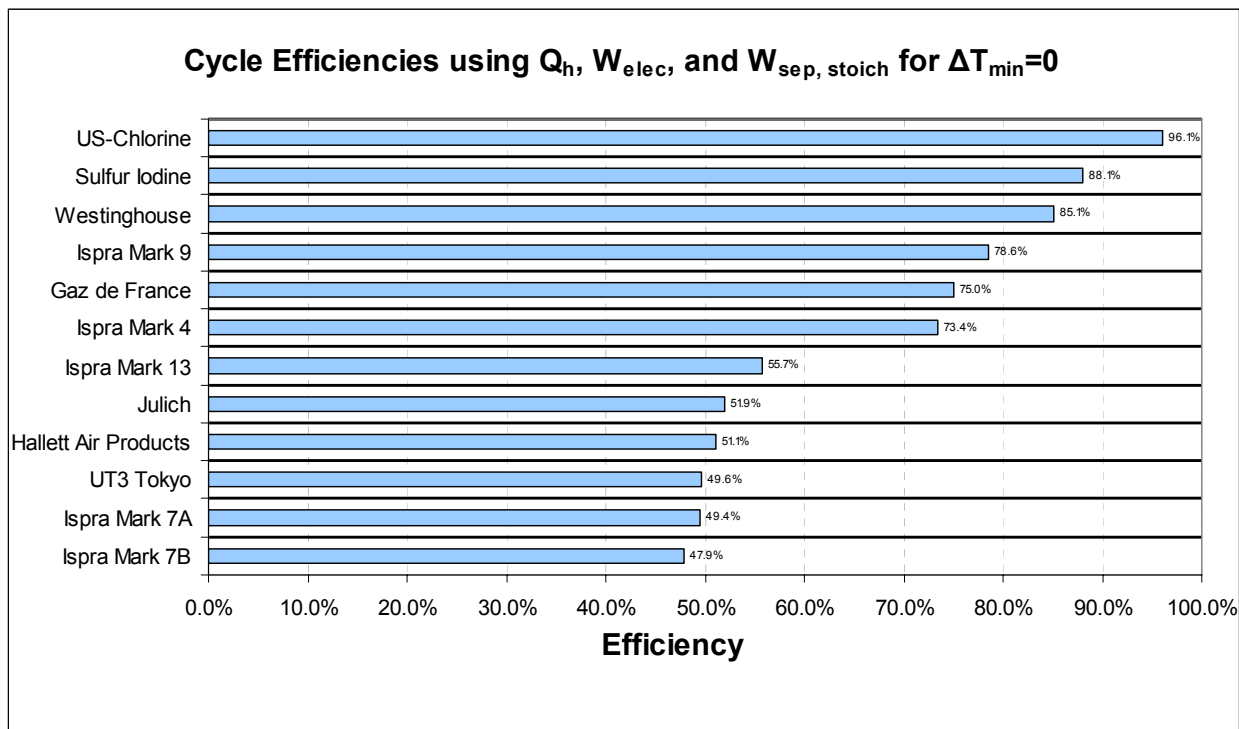


Figure 10 Electrolysis work and minimum separation work terms are now accounted.

All cycles studied have one or more reactions that do not go to completion, and the effect of separating unreacted species was optimized for each case, as described in **Equilibrium effects**. Accounting for non-stoichiometric conversion, the separation work increases significantly in most cycles. Minimum separation requirements were more than ten times greater than ideal for the US Chlorine cycle, and increased energy requirements over 100 kJ for several cycles **Figure 11**. The disparity between ideal and the true minimum separation energy is large enough that incomplete reactions must be studied to determine a meaningful efficiency estimate for each cycle. The Gaz de France and Westinghouse cycles are again of note. Gaz de France does not require any separation, and the Westinghouse separation step is unaffected, since the high-temperature reaction goes to completion. Efficiency of the UT-3 cycle drops to 33% once separation energy requirements are determined. Thermal efficiencies reported for the cycle are misleading, since separation equipment requires a large amount of energy. Using our efficiency basis, the cycle ranks too low for further consideration.

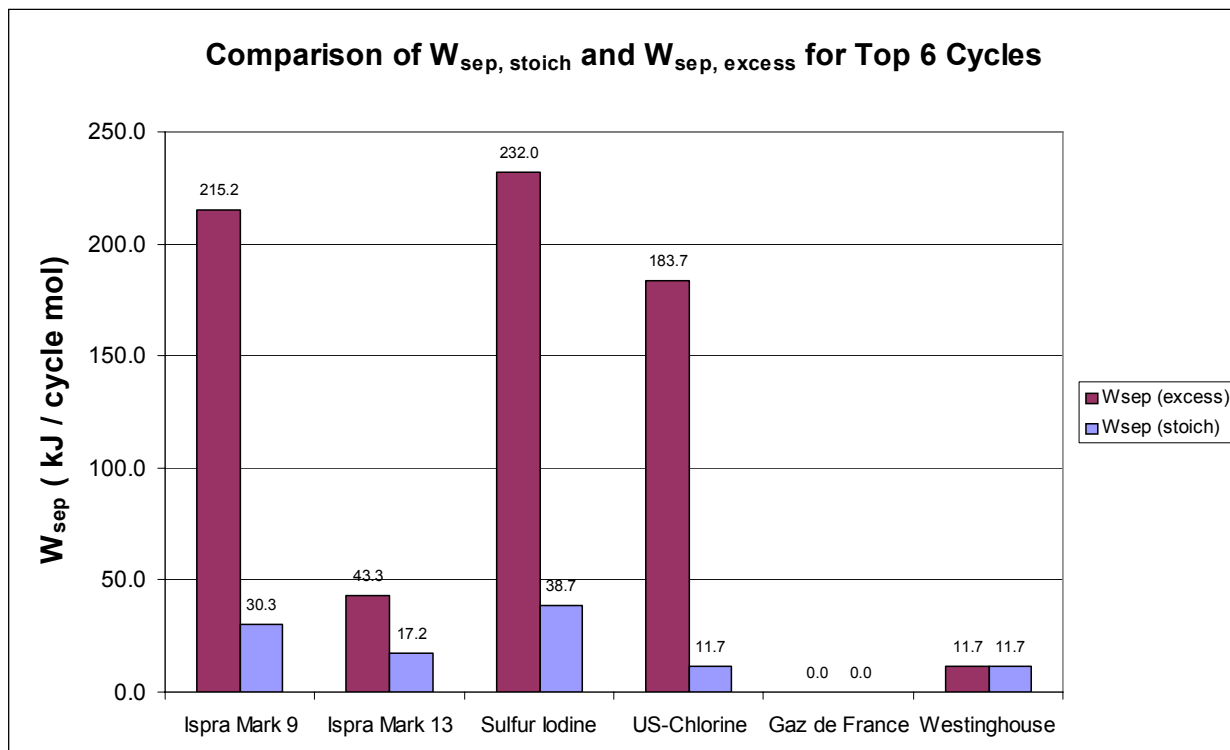


Figure 11 Minimum separation work when non-stoichiometric reactions are considered. Unreacted species increase separation requirements significantly for some cycles.

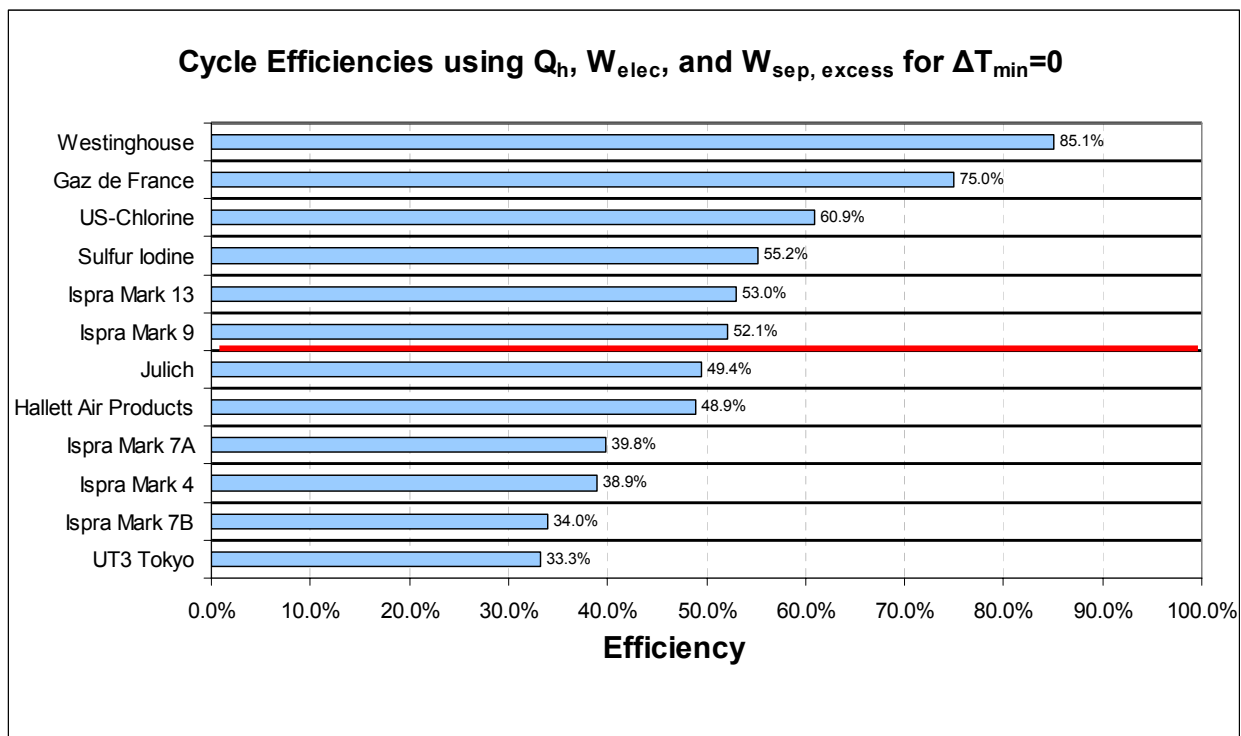


Figure 12 Major energy terms for each cycle are accounted, and the top six cycles are selected for further study.

The top cycles are now selected for further study. Efficiency of the Sulfur-Iodine cycle, 55%, is close to the 52% reported by Brown et. al 2000, based on a detailed, optimized flowsheet. Separation is facilitated in the optimized design because of a liquid-liquid phase separation between HI/I₂ and H₂SO₄ – approaching the ideal efficiency limit.

Next, the effect of approach temperature is studied **Figure 13**. Cycles with pinch points at 298K were unaffected by increasing approach temperature, and others were affected minimally, though the hot utility requirement did increase as expected. Even at large approach temperatures of 25K, the biggest increase was in the Sulfur Iodine cycle, and was only about 10 kJ. The top cycles have little heat cascade, since the reactions are mostly endothermic and are supplied directly by the hot utility. Increasing approach temperature for cycles with relatively poor cascade characteristics, such as the Julich and Ispra Mark 9, decreases efficiency by only a few percent. Relatively, approach temperatures are insignificant for most cycles, though sensitivity analysis should be performed for each cycle.

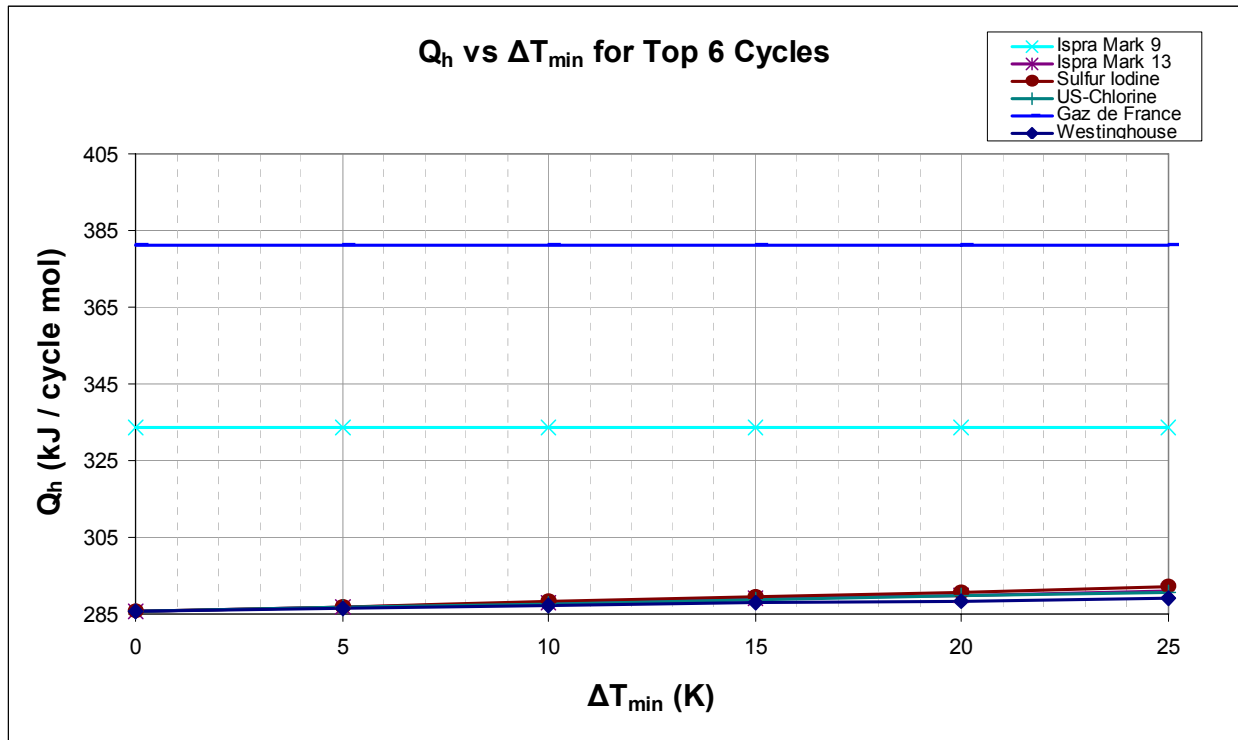


Figure 13 Effect of approach temperature (ΔT_{min}) on hot utility requirement.

Solids handling in some cycles limits heat transfer between streams. Direct transfer between solids and other streams in an exchanger is slow, and transporting solids is difficult. In one possibility, sweep gases can be used as intermediate energy carriers to transfer heat from solids. Heat transfer in such a scenario can be modeled by assuming a large approach temperature to account for heat losses. Sensitivity analysis shows that losses due to such heat exchange have minimal effect. Therefore solids handling will not cause significant heat losses, though physical transport problems are still of concern. Several scenarios exist for handling solids, and cycles should not be discounted because they involve solids. In the case of the Gaz

de France, for example, high efficiencies are obtainable if solids handling issues can be resolved. Fixed beds can be used in which fluid product species are removed and sent to other beds in a batch process. Such a solution has been used for the UT-3 cycle, and should be considered if distribution problems from using an unsteady process are resolved.

Economics were evaluated for the top three cycles: Westinghouse, Gaz de France, and US Chlorine. See **Appendix A** for details.

VI Conclusions

A standardized methodology has been developed for rapidly evaluating efficiencies of thermochemical and hybrid water-splitting cycles without the need for process flow diagrams. Using pure component enthalpy and entropy correlations to determine heating and separation requirements, cycle efficiencies are calculated within reasonable proximity to reported literature values. The scoping nature of the methodology allows quick dismissal of impractical cycles and detailed consideration for promising cycles.

Our methodology suggests that the Westinghouse, Gaz de France, and US Chlorine are capable of attaining the highest efficiencies of the 12 cycles assessed. Closer scrutiny reveals fundamental advantages within heating duties for the Westinghouse and US Chlorine cycles and within separation work requirements for the Gaz de France. No pinch point was observed within the heat integration for the Westinghouse and US Chlorine cycles at low approach temperatures, resulting in ideal heat requirement and high efficiencies. Assuming that no interaction occurs between phases, separation work is eliminated within the Gaz de France cycle due to the distinct phase purity resulting from each reaction.

It can be concluded that ideal heat requirements are realized for cycles lacking a pinch point, while separation work can be greatly minimized by ensuring phase purity within reactors at equilibrium. These conclusions outline a strategy for future cycle synthesis:

1. Exothermic reactions should be positioned at sufficiently high temperatures to fully cascade released heat to colder zones rather than reject it to cold utility.
2. Reactions temperatures should be investigated to exploit phase differences between equilibrium species.

Provided a comprehensive thermodynamic database our methodology could be modified to systemically synthesize undiscovered cycles exhibiting these characteristics. Economic analysis could be performed on the most efficient to determine the best practical cycle.

Future development of the methodology would necessitate improvement to the thermodynamic model. The current thermodynamic database has a limited number of species, so only select cycles can be modeled. Inclusion of thermodynamic data for more compounds would allow for the screening of a larger number of candidate cycles. Furthermore, calculating thermodynamic properties with the NRTL or similar model would give results that are more accurate by taking into account non-idealities. This would produce better estimates for the heats of mixing, heats of reaction, and minimum work for separation.

The efficiency estimate could be modified to include extra work performed by any excess heat generated in the cycle. A simple algorithm could be devised to determine whether this excess heat is at a sufficiently high temperature to vaporize water; if it is, then conditions exist for the cogeneration of electricity. A more realistic estimate of peak cycle efficiency would necessarily include this cogeneration. Accuracy could be improved further by considering compression and expansion work involved with vapor species. Separation energy needs could be better approximated by considering the performance of the specific unit operation performing the separation.

Continued development of the methodology, accurate efficiency estimates for known cycles, and detailed economic evaluations of the top cycles determined will be published in future work.

VII Acknowledgements

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