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Method for Evaluation of Thermochemical and Hybrid Water-Splitting Cycles

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This paper presents a methodology for the preliminary evaluation of thermochemical and hybrid water-splitting cycles based on efficiency. Because the method does not incorporate sufficient flowsheet details, the efficiencies are upper bounds of the real efficiencies. Nonetheless, they provide sufficient information to warrant comparison with existing well-studied cycles, supporting the decision to disregard them when the bound is too low or continuing their study. In addition, we add features not present in previous works: equilibrium conversions as well as excess reactants are considered. The degrees of freedom of each cycle (temperatures, pressures, and excess reactants) were also considered, and these values were varied to optimize the cycle efficiency. Ten cycles are used to illustrate the method.

I. Introduction

Declining volumes of fossil fuel reserves and an increase in their demand has caused a recent rise in the cost of energy. Similarly, nations across the globe are aspirating to become less dependent on foreign resources for the fulfillment of energy requirements. Furthermore, a steady increase in greenhouse gas emissions over the past decades has brought about the reality of global warming. The need for a more environmentally friendly, renewable source of energy is evident and imminent. With the expected change to a hydrogen-based economy, research efforts toward the development of hydrogen producing processes are on the rise.

In the United States, roughly 11 million tons of hydrogen are currently produced annually, the vast majority of which (~95%) is produced using steam reforming of fossil fuel based feedstock. Most of this hydrogen is used in industrial settings, such as the production of fertilizers, hydrocracking, and hydrotreating (among other processes) in crude oil refineries, etc. However, in a hydrogen-based economy, the US hydrogen production and usage will increase significantly. The projected use of hydrogen for transportation needs is expected to be 200 million tons per year, while over 440 million tons per year would be required to fulfill the needs for all nonelectric energy.[1]

Electrolysis uses electricity to drive the decomposition of water to produce hydrogen. However, these processes have relatively low efficiencies (roughly 25% for low-temperature reactors and 37% for high-temperature reactors.[1] In turn, steam reforming of methane involves combining methane with steam at high temperature (700−900 °C) to produce carbon monoxide and hydrogen, which followed by water−gas shift reactors renders carbon dioxide and hydrogen. An obvious downside to this method is that it is dependent on fossil fuel resources. Also, the process results in the production of large quantities of greenhouse CO_2 gas.

Aside from direct electrolysis, methods that produce hydrogen from an input of only water are known as "water-splitting cycles", which use a series of chemical reactions. The net chemical reaction is the decomposition of water to form hydrogen and oxygen. After each reaction, chemical intermediates are separated and recycled to other reactions within the system, making the process cyclic in nature. Overall, the only species entering the process is water, and the only products of the process are hydrogen and oxygen. Heat and work are also transferred across the system boundaries for the heating and cooling of process streams, the separation of reactive species, and to drive the chemical reactions.

Many studies have been performed in previous years to evaluate water-splitting cycles as a means to produce hydrogen. Funk[5] provided a brief literature review of water-splitting cycles up to the year 2001. Holiastos and Manousiouthakis[6] explore the generation of reaction clusters, of which a thermochemical cycle is just one case. They prove a few interesting properties regarding the choice of temperature. In turn, Fishtik and Datta[4] provide certain means to generate new cycles and several published works focused on one or a limited number of cycles only. For example, Goldstein et al.[2] studied the efficiency of the sulfur iodine (SI) cycle, Lemort et al.[3] studied the UT-3 cycle together with two other cycles. In turn, there are only a few published works that attempted to evaluate a good number of cycles to identify promising cycles, the objective of this work. Brown et al.[7] screened and evaluated 100 cycles on a semi-quantitative basis. The purpose of that study was to determine the potential for efficient, economical, large-scale production of hydrogen. They focused on cycles that would use heat from a nuclear reactor heat source. In a separate study, Lewis[8] evaluated water-splitting cycles based on the efficiency of each cycle. The efficiency was defined on the basis of the standard enthalpy of formation of water at 298 K. The terms associated with the calculation of the efficiency were the energy of the heat and work requirements assigned to each cycle. The work term included energy contributions of both electrical work and the work associated with separation. Furthermore, an efficiency of 50% was assumed for all work requirements calculated as reversible separation work of each cycle. Although the work makes progress in introducing quantitative evaluation means, the assumption of 50% efficiency is too general. To ameliorate this shortcoming, the authors propose a detailed flowsheet simulation, which allows a better assessment of the power and heating needs. Although this process leads to accurate efficiencies, it is rather time-consuming. Another issue not explored in sufficient detail is the degree of freedom stemming from equilibrium conversions that can be manipulated using excess reactants. Finally, an optimization of temperatures, pressures, and excess reactants, when appropriate, was not performed.

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In this work, we propose a method that provides an upper bound on efficiency. The upper bound on efficiency is based on the following:

(i) A simplified process flowsheet is generated for each cycle, upon which the required amount of heat and *real* work is calculated.

(ii) Consideration of reaction equilibrium where it applies, which adds another dimension for optimization by varying the amount of excess reactants.

(iii) Process configuration (recycle structure) and operating conditions that are optimized to achieve the maximum efficiency.

The usefulness of our methodology is that it allows a quick assessment of upper bounds on efficiency and, therefore, it eneables some decision making, like disregarding a cycle when its upper bound is too low.

II. Water-Splitting Cycles

In this work, information on the cycles, including the reactions' description and the reference/nominal reaction temperatures, was obtained from Brown et al.'s GA-A24326 report.[7] There are at least two chemical reactions in a water-splitting cycle with a net result of water molecules decomposing to their individual components of oxygen and hydrogen. Cycles are composed of either only thermochemical reactions or a combination of reactions which includes thermochemical and electrolysis. The first type of cycle is called the thermochemical cycle while the combination is known as a "hybrid" cycle. Products that leave a reactor go through a separation process and a heating or cooling process at which point they become the inlets for other reactors. Only oxygen and hydrogen may leave the cycle. The other species go through a cycle of being formed and breaking down.

One example of a three-reaction thermochemical cycle is the sulfur iodine cycle:

$$H_2SO_4 \rightarrow SO_2 + H_2O + 0.5O_2 \tag{1}$$

$$I_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HI \tag{2}$$

$$2HI \rightarrow H_2 + I_2 \tag{3}$$

The first reaction is proposed to take place at 1123 K, the second at 393 K, and the third one at 723 K, all at 1 bar. In turn, one example of a two-reaction hybrid cycle is the Hallett Air Products cycle:

$$Cl_2 + H_2O \rightarrow 2HCl + 0.5O_2 \tag{4}$$

$$2HCl \rightarrow Cl_2 + H_2 \tag{5}$$

In this cycle, the first reaction takes place also at 1123 K and the second is electrolysis at room temperature (298 K). A more complex four reaction thermochemical cycle is the Ispra Mark 4 cycle, which, in addition, involves solids.

$$Cl_2 + H_2O \rightarrow 2HCl + 0.5O_2 \tag{6}$$

$$H_2S \rightarrow S + H_2 \tag{7}$$

$$2FeCl_3 \rightarrow Cl_2 + 2FeCl_2 \tag{8}$$

$$2FeCl_2 + 2HCl + S \rightarrow 2FeCl_2 + H_2S \tag{9}$$

In this cycle, the first reaction takes place also at 1123 K, the second at 1073 K, the third at 693 K, and the last at 373 K, all at 1 bar.

III. Cycle Efficiencies

Following the work of Lewis,[8] but not exactly the same way, efficiency is defined as follows:

$$\eta = -\frac{\Delta H^{\circ}_{H_2O}(298\ K)}{Q + W} \tag{10}$$

where $\Delta H^{\circ}_{H_2O}(298\ K)$ is the standard heat of formation of water at 298 K (25 °C), which is 68.3 kcal/mol. On addition, Q and W are the total heat and work required to process 1 mole of water by the water-splitting cycle. The heat term Q includes the heat utilities and the heat of separation; the work term W includes the separation work and the electrical work in electrolysis. Note that the *real* work is considered with separation efficiency $\eta_s = 0.5$ and electrical work efficiency $\eta_e = 0.9$. Lewis[8] used the overall efficiency of 0.5 for the work term.

In principle, we assume that a correct and realistic account is made for the amount of heat and work needed. We recognize the following issues:

- Thermal issues: Water needs to be heated from room temperature to the corresponding reaction temperature. Likewise, the products of the cycle (oxygen and hydrogen) need to be cooled to room temperature. In addition, products from one reaction need to have their temperature conditioned for the next. Finally, reactions that are endothermic need heat and heat from exothermic reactions can be utilized. As Lewis[8] proposed, this can be dealt with using pinch analysis.[9]
- Reaction conversion: Except in electrolysis reactions where complete conversion takes place, chemical reaction equilibrium is considered to determine the reaction conversion (assuming all reactions in cycles reach equilibrium). Excess reactants can also be used to manipulate the composition at equilibrium of reaction mixtures.
- Excess reactants: If excess reactants are present, then:

- The amount of excess reactants can be manipulated to adjust the conversion.

- The separation duty and separation work likely increase

- There are two options on how to handle these excess reactants: the excess reactants can be either immediately separated and recycled back to the reactor (recycle option) or be carried away to other reactor in the cycle as inerts before making their way back to their original place (no recycle option).

- Separation work: As noted by Lewis,[8] separation work can be estimated using the Gibbs free energy of mixing, but a better assessment of efficiency is needed. We propose to assign a separation method to each case and assign typical separation efficiencies corresponding to those methods or perform simulations to evaluate the real separation work, as suggested by Lewis.[8]
- Optimization: The reaction temperatures and pressures, as well as the amount of excess reactants, when possible, can be varied to optimize efficiency. We now discuss the appropriate tools for each of these issues.

IV. Heat Requirements

In this section, we discuss how data from the thermochemical cycles is conditioned so that it can be used in pinch analysis. Pinch analysis requires hot and cold streams to be provided. These are water, cycle products, and reaction products that need to be heated up or cooled down. Because reactors are supposed to be operated isothermally (an assumption that can be relaxed), these energy sources/sinks are replaced by streams spanning a small temperature range (0.1 K for example). The same is done by heat sources and sinks associated to separation operations (distillation columns for example).

Consider a generic two-reaction cycle as in Figure 1. This figure does not include separation of products and is intended to illustrate

T_1	$A \rightarrow B + C + 1/2O_2$
T_2	$B + C + H_2O \longrightarrow A + H_2$

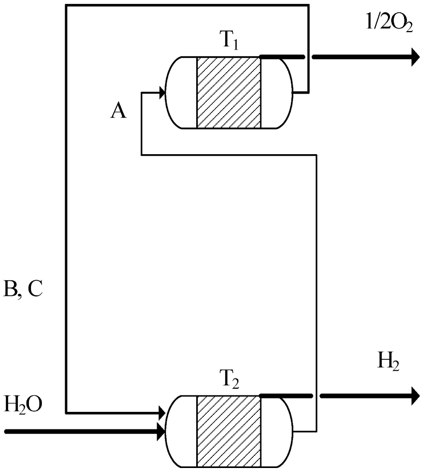


Figure 1. Example of a two-step cycle.

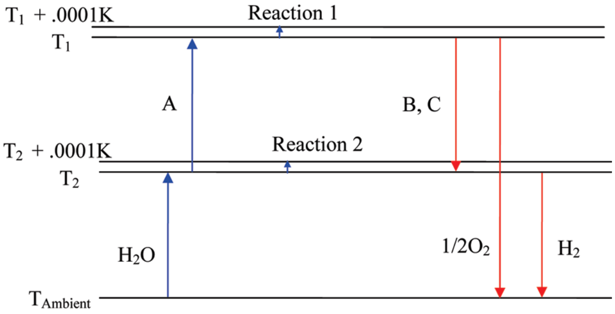


Figure 2. Temperature interval diagram for two-step cycle, without separators.

T_1	$A + B \rightarrow C + D + 1/2O_2$
T_2	$E + H_2O \longrightarrow A + H_2$
T_3	$C + D \longrightarrow B + E$

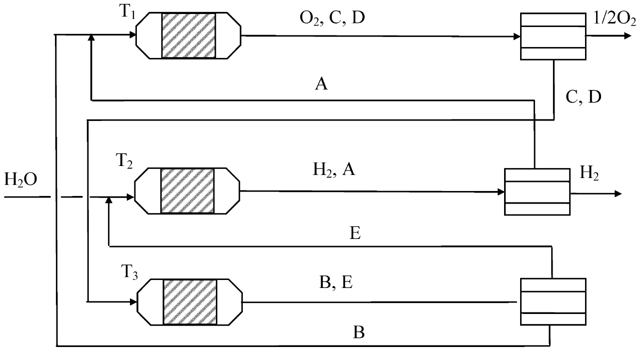


Figure 3. Example of a three-step cycle with separators.

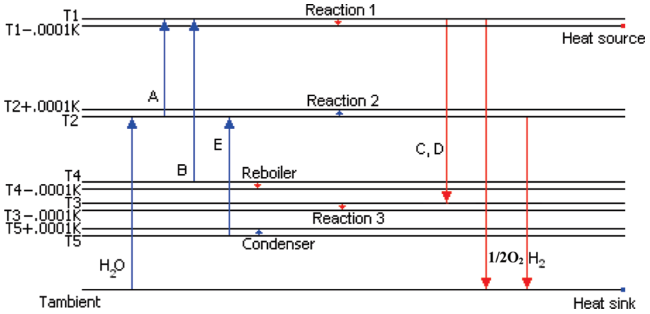


Figure 4. Temperature interval diagram for a three-step cycle with separators.

our procedure; Figure 2 depicts the temperature intervals spanned by the different streams, ready for pinch analysis.

Finally, Figure 3 shows a three-reaction generic cycle with an assumed membrane separator ($C + D$ from O_2) at the top, another assumed membrane separator after the second reactor (to separate A form H_2), and a distillation column fed by the outlet of the lower temperature reactor to separate B form E. The membranes do not require heat, only work, which goes directly to be accounted for in the term W, and the distillation column requires both heating and cooling, which is indicated in the stream−temperature diagram of Figure 4. In this figure, the temperatures of the streams containing pure B and pure E are different from the temperature of reactor 3. Without loss of generality, we have assumed that B comes from the reboiler at a temperature above the reactor temperature and E comes from the condenser at a temperature lower than the temperature of reactor 3.

V. Electrical Work

Electrochemical reactions that are present in hybrid water-splitting cycles require a supply of electrical energy to operate the electrolytic cell in which the reaction is taking place. This energy requirement needed to drive the reaction can be evaluated using the Nernst equation. This equation relates the amount of electrical work required to the number of moles of electrons transferred and the electrical potential of the reaction:

$$W_{\mathrm{ELEC,min}} = -nFE \qquad (11)$$

The potential of the cell is given by

$$E = E^{\circ} - \frac{RT}{eF}\ln K \qquad (12)$$

where K is the equilibrium constant of the electrolytic reaction. In the electrolyzer, however, the product gases are continuously removed and equilibrium is never achieved. For this reason, the second term involving the equilibrium constant in eq 12 is neglected. The standard electrical potential of each reaction can be found as follows:

$$E^{\circ} = E^{\circ}_{298\mathrm{K}} + \int_{298\mathrm{K}}^{T} \frac{\mathrm{d}E^{\circ}}{\mathrm{d}T} \qquad (13)$$

using reduction potentials listed in chemical data tables.[10] Finally, the work that is added to the term W in the efficiency equation is

$$W_{\mathrm{ELEC,actual}} = \frac{W_{\mathrm{ELEC,min}}}{\eta_{\mathrm{ELEC}}} \qquad (14)$$

We use $\eta_{\mathrm{ELEC}} = 0.9$, as it is recommended by Milliken and Ruhl.[11]

VI. Equilibrium Conversion

Equilibrium effects are of large consequence when the Gibbs energy of the reaction is slightly positive or negative. In such cases, the reactants will not spontaneously convert completely to products. Thus, to drive the reaction to larger product concentrations (or to consume at least one of the reactants), excess reactants must be fed to the reactor. For gases, the relationship between concentrations is given by the following:

$$K(T) = \exp\left[-\frac{\Delta G^\circ(T)}{RT}\right] = \prod f_i^{\nu_i} = K_y K_p K_\phi \tag{15}$$

Similar equations can be written for liquid phases. Now, the molar fraction of each species is given by

$$y_i = \frac{n_i^0 + \upsilon_i \xi}{\sum_k n_k^0 + \upsilon_k \zeta} \tag{16}$$

where n_i^0 is the initial number of moles before the reaction is allowed to proceed to equilibrium, ν_i is the stoichiometric coefficient, and ζ is the conversion (number of moles reacted of a reference reactant). After this substitution is made, one has a relationship between temperature and pressure (which are momentarily fixed), conversion (ζ), and initial number of moles (n_i^0):

$$K(T) = f(n_i^0, \xi, P) \tag{17}$$

The above does not apply to electrolysis. Indeed, water-splitting cycles that involve an electrochemical reaction will require stoichiometric feeds of chemical species to the electrolysis reactor. This requirement is necessary to prevent accumulation of reactants within the reactor, given the special arrangement to remove products in this type of units (all products of electrochemical reactions are assumed to be removed continuously from the reactor).

Some reactions involving solids do not require the use of these equilibrium conversion reactions. For example, the US chlorine cycle contains the following reaction:

$$2CuCl_2 \rightarrow 2CuCl + Cl_2 \tag{18}$$

and although the ΔG° of this reaction is slightly negative (−5.750 kJ/mol), it can be conducted by continuously removing Cl_2, and therefore, only a material balance relationship is required.

Finally, there are cycles with reactions that have a large positive ΔG°, which means that the reaction will not proceed spontaneously to the right and does not make use of electrolysis (e.g., US chlorine, UT-3, Gas de France, Ispra Mark 4, Ispra Mark 9). The fact that these are cycles that can function after all is because equilibrium is never achieved and products are removed continuously.

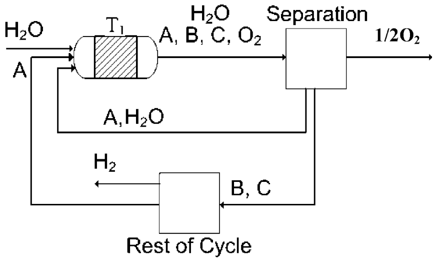
VII. Separation Work Requirement

The separation work requirement is the amount of energy associated with the separation of chemical species within the cycle. The ideal separation work term is all-encompassing, including energy required by electrical, thermal, and shaft separation processes that are performed reversibly. From thermodynamics, this energy is given by

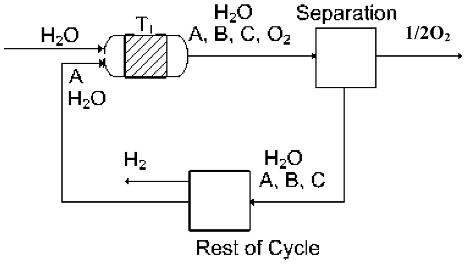
$$W_{\text{SEP,minimum}} = \Delta G_{\text{mixing}} = RT[(\sum_i n_i \ln(\gamma_i x_i))_{\text{OUT}} - (\sum_i n_i \ln(\gamma_i x_i))_{\text{IN}}] \tag{19}$$

which includes fugacity/activity coefficients depending on the reference state used. The real work added to the term W in the efficiency calculation is

$$W_{\text{SEP,minimum}} = \frac{\Delta W_{\text{SEP,minimum}}}{\eta_{\text{sep}}} \tag{20}$$



(a) Separation and recycle of excess reactants



(b) No recycle of excess reactants

Figure 5. Reactant separation options.

Lewis[8] used $\eta_{\text{sep}} + 0.5$. Something better than this generalization needs to be used, but this unfortunately implies that each type of separation needs to be identified and its efficiency assessed. An additional difficulty is that requirements of heat addition/removal need to be removed from these calculations because, as explained above, they need to be considered in pinch analysis. Thus, this leaves compression work to be considered here only. For this reason, we opted for directly assessing the compression work. Finally, all phase separations were assumed to be complete and the amount of energy associated with phase separation was considered negligible.

Finally, hybrid water-splitting cycles that involve the production of gases through electrolysis already produce the products separately, so no additional separation step is required.

VIII. Separation Options and Recycling

Consider the reactions shown in Figure 1. After each reactor, one has two options regarding the separation of the unreacted species (Figure 5).

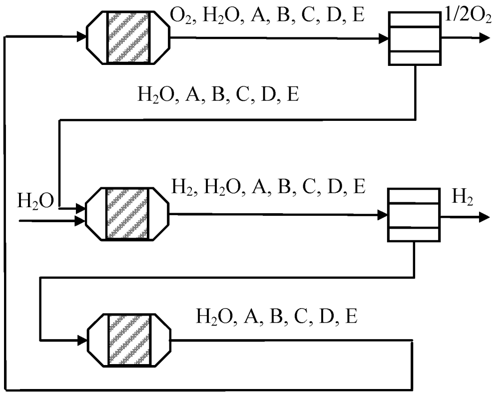
(1) Separate the excess reactants in the product and recycle it back to the reactor (recycle configuration; Figure 5a).

(2) Allow the excess reactants to travel through the rest of the reactions (no recycle configuration; Figure 5b).

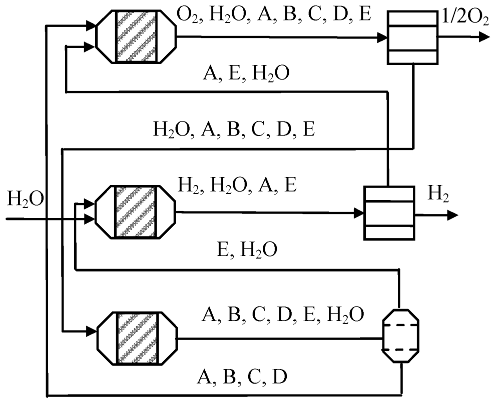
In the recycle configuration, reactor effluents are usually separated into three streams: the product stream H_2 or O_2 (if present), the other products that will go to another reactor in the cycle, and the unreacted species (excess reactants) to be recycled back to the reactor. In other words, the excess reactants are immediately separated from the products and recycled back to the reactor.

In the no recycle configuration, the excess reactants travel through the rest of cycle as inerts and eventually come back to their original reactor. There are two options related to how one manipulates the flows of reactor effluents in these no recycle configurations. We illustrate this next using the reactions of Figure 3.

- Minimum separation (Figure 6a): In this option, all the chemicals coming out of a reactor are sent to the other reactor



(a) Minimum Separation



(b) Strategic Separation

Figure 6. Product separation options for a no recycle configuration.

in the cycle, thus the only separation duty required in this option is to separate H_2 or O_2 (if present) out of the reactor effluents.

- Strategic separation configuration (Figure 6b): In this option, the effluent coming out of a reactor can be strategically separated into two (or more) streams, and each of these streams are sent as reactants to the other reactors in the cycle. Thus, the scheme involves both the separation of H_2 or O_2 from the reactor effluents and, where appropriate, the separation of a reactor effluent into two (or more) streams. There are variants of this option. For example, in this option, one could opt for more separations than the ones shown and go to the extreme of sending every specie strictly to the reactor where it belongs. For example, in the case of Figure 6b, this would mean an additional separation in each reactor to recycle excess reactans: The oxygen separator may also separate A and B and recycle it to the reactor feed and the hydrogen separator may also separate E and recycle it to the feed. Thus, several variants exist. We represented the one that requires the least separation and at the same time sends species strategically where they are main reactants.
- In some cycles, strategic and minimum separation options may be the same configuration depending on the reactions involved. We illustrate these two options in Figure 6.

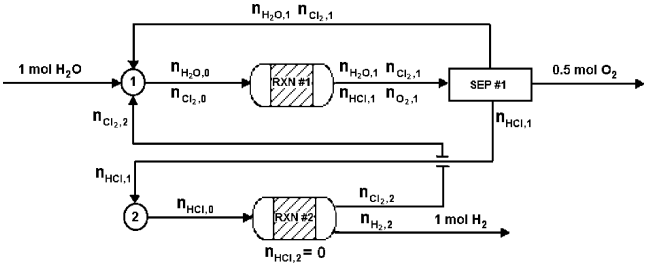


Figure 7. Hallett Air Products cycle.

It may seem from the above discussion that the required separation energy in the no recycle option is smaller than the energy in the recycle option. However, this is not always true. This is evident in the Julich cycle and the sulfur iodine cycle (these are shown below). The reason is that the recycle configuration requires the separation of unreacted reactants out of the reactor effluent while the strategic separation configuration involves strategically separating a reactor effluent into two (or more) streams (although the number of such separations is usually not more than one).

The no recycle option offers both an advantage and disadvantages. The advantage is that it usually requires lower separation energy, which results in higher efficiency. The disadvantages are direct results of having excess reactants/inerts travel internally in the cycle, which means there is more fluid circulating in the cycle. As a result:

- It requires bigger size, higher capacity as well as operating energy, more instrumentation, pumps, etc.

- The heat duty requirement would likely increase.

- The presence of excess reactants coming from the other reactor may affect reaction equilibrium in a reactor, an effect that is assumed to be negligible in this work.

- The operating energy and the investment capital cost of separation equipment could be smaller, but the operating energy and the investment capital cost of instrumentation for transporting fluid would increase.

Therefore, whether it is beneficial to use the no recycle configuration can only be determined by performing an economic analysis.

IX. Degrees of Freedom

For each cycle one can now write material balance equations in separators, as well as the equilibrium reactions and determine the degree of freedom. For example, consider the Hallett Air Product cycle, shown in Figure 7. The second reactor is an electrolysis reactor, and therefore, its conversion of HCl is 1.

The following equations are the material and equilibrium conversion equations:

First reactor

$$n_{H_2O,0} = 1 + n_{H_2O,1} \tag{21}$$

$$n_{H_2O,1} = n_{H_2O,0} - \xi_1 \tag{22}$$

$$n_{Cl_2,0} = n_{Cl_2,1} + n_{Cl_2,2} \tag{23}$$

$$n_{Cl_2,1} = n_{Cl_2,0} + \xi_1 \tag{24}$$

$$n_{HCl,1} = \xi_1 \tag{25}$$

$$n_{O_{2,1}} = \frac{1}{2}\xi_1 \tag{26}$$

Second reactor

$$n_{HCl,0} = n_{HCl,1} \tag{27}$$

$$n_{HCl,2} = n_{HCl,0} - 2\xi_2 \tag{28}$$

$$n_{Cl_2,2} = \xi_2 \tag{29}$$

$$n_{H_2} = \xi_2 \tag{30}$$

Equilibrium in the first reactor

$$K_1(T_1) = \frac{n_{HCl,1}^{\;2} n_{O_2,1}^{\;.5}}{n_{Cl_2,1} n_{H_2O,1}[n_{Cl_2,1} + n_{H_2O,1} + n_{HCl,1} + n_{O_2,1}]^{.5}} P^{0.5} \tag{31}$$

In these equations, ξ_i is the conversion of reaction i, and K_i the equilibrium constant. We note that because we assumed that the number of moles of water input is 1, then $n_{H_2} = 1$ and $n_{O_2,1} = 0.5$, which immediately fixes the conversions to $\xi_1 = \xi_2 = 1$ (eqs 26 and 30). As soon as these are replaced, one discovers that the first two equations are not linearly independent, so only one of them can be counted. The same can be said for the third and fourth equations.

We are left with 10 variables and 9 linearly independent equations, that is, one degree of freedom. After all substitutions are made, the following three equations are left:

$$n_{H_2O,0} = 1 + n_{H_2O,1} \tag{32}$$

$$n_{Cl_2,0} = n_{Cl_2,1} + 1 \tag{33}$$

$$K_1(T_1) = \frac{2^2 0.5^{0.5}}{n_{Cl_2,1} n_{H_2O,1}[n_{Cl_2,1} + n_{H_2O,1} + 2 + 0.5]^{.5}} P^{0.5} \tag{34}$$

Clearly, one can manipulate the excess water in the first reactor and eventually shift equilibrium to smaller amounts of unreacted chlorine $n_{Cl_2,1}$. In the limit for $n_{H_2O,0} \gg 1$, we have $n_{Cl_2,1} \approx 2\sqrt{2}/n_{H_2O,0}^{1.5}$, which can be convenient (or not) when a separation of water and Cl_2 from HCl is considered. Indeed, it could eventually reduce the associated energy effort. Conversely, one can consider that such separation should only entail separating only water (which cannot be introduced to the electrolysis cell) and sending the unreacted chlorine and the HCl to the electrolysis cell. This option is shown in Figure 8.

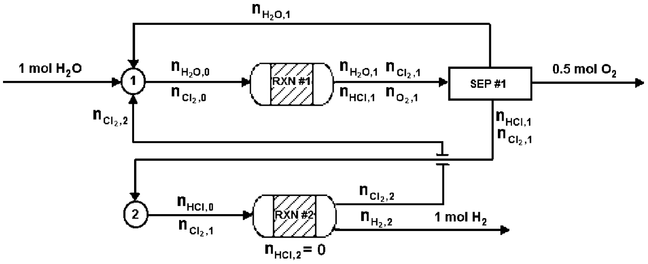


Figure 8. Hallett Air Products cycle—alternate recycle configuration.

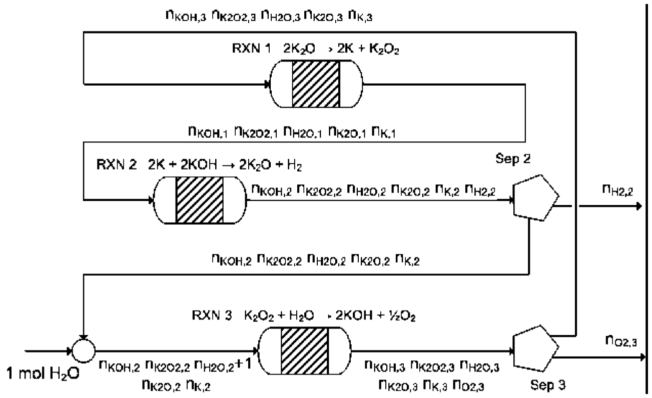


Figure 9. Gaz de France cycle—no recycle configuration.

The material and equilibrium conversion equations are the same except that eqs 23 and 29 are replaced by

$$n_{Cl_2,0} = n_{Cl_2,2} \tag{35}$$

$$n_{Cl_2,2} = n_{Cl_2,1} + \xi_2 \tag{36}$$

which does not alter the degrees of freedom but should have significant effect on the energy expenditure (minimum heat utility and separation work).

We now examine the degrees of freedom involving a system in which excess reactants are allowed to travel through the entire cycle. Consider for example the Gaz de France thermochemical cycle involving three reactions.

The following equations are the material and equilibrium conversion equations:

First reactor

$$n_{KOH,1} = n_{KOH,3} \tag{37}$$

$$n_{K_2O_2,1} = n_{K_2O_2,3} + \xi_1 \tag{38}$$

$$n_{H_2O,1} = n_{H_2O,3} \tag{39}$$

$$n_{K_2O,1} = n_{K_2O,3} - 2\xi_1 \tag{40}$$

$$n_{K,1} = n_{K,3} + 2\xi_1 \tag{41}$$

Second reactor

$$n_{KOH,2} = n_{KOH,1} - 2\xi_2 \tag{42}$$

$$n_{K_2O_2,2} = n_{K_2O_2,1} \tag{43}$$

$$n_{H_2O,2} = n_{H_2O,1} \tag{44}$$

$$n_{K_2O,2} = n_{K_2O,1} + 2\xi_2 \tag{45}$$

$$n_{K,2} = n_{K,1} - 2\xi_2 \tag{46}$$

$$n_{H_2,2} = \xi_2 \tag{47}$$

Third reactor

$$n_{KOH,3} = n_{KOH,2} + 2\xi_3 \tag{48}$$

$$n_{K_2O_2,3} = n_{K_2O_2,2} - \xi_3 \tag{49}$$

$$n_{H_2O,3} = n_{H_2O,2} + 1 - \xi_3 \tag{50}$$

$$n_{K_2O,3} = n_{K_2O,2} \tag{51}$$

$$n_{K,3} = n_{K,2} \tag{52}$$

$$n_{O_2,2} = \frac{1}{2}\xi_3 \tag{53}$$

Equilibrium in third reactor

$$K_3(T_3) = \frac{n_{O_2,3}^{\;.5}}{n_{H_2O,3}[n_{H_2O,3} + n_{O_2,3}]^{-0.5}} P^{-0.5} \tag{54}$$

Due to the fact that the water feed to the system is 1 mol, we have $n_{H_2} = 1$ and $n_{O_2,1} = 0.5$, which fixes the conversion of reactions two and three; that is, $\xi_2 = \xi_3 = 1$. The conversion of the first reaction is $\xi_1 = 1$, obtained by combining eqs 41, 46, and 52. When the values of conversions are replaced in the equations above, it becomes apparent that eqs 40 and 45, 38 and 43, and 42 and 48 are not linearly independent, forcing one of the equations of each of these pairs of equations to be eliminated. Similarly, only two of the equations from eqs 39, 44, and 50 written for water are linearly independent.

We are then left with 15 variables (excluding reaction temperatures) and 11 linearly independent equations and 4 degrees of freedom. Upon substitution and elimination, the five following equations and nine variables remain:

$$n_{K_2O,1} = n_{K_2O,3} - 2 \tag{55}$$

$$n_{K,2} = n_{K,1} - 2 \tag{56}$$

$$n_{KOH,1} = n_{KOH,2} + 2 \tag{57}$$

$$n_{K_2O_2,3} = n_{K_2O_2,2} - 1 \tag{58}$$

$$K_3(T_3) = \frac{0.5^{.5}}{n_{H_2O,3}[n_{H_2O,3} + 0.5]^{-0.5}} P^{-0.5} \tag{59}$$

To be able to solve the above system of equations, four of the nine variables must be assumed as design parameters. Taking variables, $n_{K_2O,3}$, $n_{K,1}$, $n_{KOH,1}$, and $n_{K_2O_2,2}$ as design parameters and specifying their values, we can solve for the other five unknowns.

All three of the cycle configurations considered for the Gaz de France cycle were found to have four degrees of freedom.

X. Evaluation Methodology

Instead of aiming at accurately evaluating the cycle efficiencies, we are proposing to preliminarily identify cycles with good potential. Simplified assumptions are used to facilitate the optimization of important variables (process configurations, operating variables) at the expense of less accurate cycle efficiencies evaluation. The simplified assumptions are summarized next:

- The standard thermodynamic calculation $\Delta G_{rxn} = \sum\Delta G_{products} - \sum\Delta G_{reactants}$ is used for all reactions where the data ΔG of chemical species are obtained from published literature sources, the ΔG_{rxn} is then used to determine chemical equilibrium. Water-splitting cycles are complex nonideal systems usually involving complicated chemical reactions, thus an appropriate thermodynamic model should be used to determine chemical equilibrium in each reaction system (e.g., NRTL models for aqueous ionic systems, etc).
- If the ΔG_{rxn} (obtained by standard thermodynamic calculation) of a thermochemical reaction (i.e., not an electrolysis one) is found to be positive, we assume that the reaction can proceed by means of a phase separation and a continuous removal of products. The assumption is needed to proceed with efficiency calculations (all the cycles under consideration have at least one reaction with positive ΔG_{rxn}). In reality, actual reaction operating conditions have to be considered to validate the stated assumption and the feasibility of reactions with positive ΔG_{rxn}.
- A simple separation method (membrane separation) is used for all separation tasks (other than the phase separation).
- Simplified process flowsheets are developed for the cycles. Detailed process flowsheets are needed to better evaluate the efficiency. Obviously, when the stated assumptions are used, the obtained efficiency is an upper bound of the cycle efficiency. The discrepancy depends on the gap between the simplified representation used in this work and the detailed/realistic process configuration, For example, the calculated efficiency of the UT-3 cycle (37.3%) is comparable to the efficiency reported in the work of Brown et al.[7] (35−40%) while the calculated efficiency of the sulfur iodine cycle (72%) is much higher than the efficiency reported in the same report (52%). Thus, in this screening method, any cycle with low efficiency is certainly not a good candidate (the upper bound of its efficiency is already small, so the more accurately evaluated efficiency is even smaller). In addition, cycles with high efficiency have to be studied in more detail to obtain a better estimate of their efficiency. Cycles with low efficiency can be easily disregarded. The important issue is that we calculate the best upper bound possible through optimization, which is covered in the next section.

Table 1. Results of Degree of Freedom Analysis

cycle	degree of freedom
US chlorine	4
sulfur iodine	3
Westinghouse	0
Gaz de France	4
Hallett Air Product	1
Julich	5
UT-3 Tokyo	6
Ispra Mark 4	5
Ispra Mark 9	4
Ispra Mark 13	3

XI. Optimization

The existence of the degrees of freedom leads to the possibility of manipulating excess reactants to minimize/maximize some objective. In our case we maximize efficiency, but cost could be a sensible alternative. Temperatures and pressures, which are usually considered fixed, can also be varied within practical ranges. Clearly, all these affect the separation work as well as the minimum heating utility associated to the cycle. Details of this optimization are given in the illustration section.

XII. Illustrations

The methodology was implemented on 10 thermochemical and hybrid water-splitting cycles. Details for each individual cycle considered can be found in the Appendix. These cycles were chosen because of their popularity in the discussion of water-splitting cycles.[7] The phases and Gibbs free energies of each chemical species for various temperatures at pressure of 1 bar were found from the JANAF data.[12] The pressure for all reactions is 1 bar. While other pressures can be used, which would improve efficiency through altering equilibrium, these are not explored and are left for future work. However, we must note that while advantages can be obtained by running reactions at different pressures, compression work will be needed reducing or even eliminating the aforementioned advantages. Neglecting this, of course, does not alter the upper bound nature of our calculated efficiencies.

Table 1 summarizes the degrees of freedom of each cycle. When possible, three different recycle configurations were considered and applied to each of the cycles. As discussed above, the number of degrees of freedom remained constant for all cycle configurations considered.

Heat Requirements. The location of the pinch has an important impact on cycle efficiency. If the pinch temperature is located at a relatively high temperature, the amount of energy required as the minimum hot utility will increase. This effect is heightened when exothermic processes occur at a temperature

Table 2. Efficiency of Selected Cycles Based on Heating Utility Electrical Work (Recycle Option and Stoichiometric Feed Ratios)

cycle	W_{elec} (kJ)	minimum utility (kJ)	pinch point (K)	efficiency[a]
US chlorine	0	286.26	308	99.90%
sulfur iodine	0	286.26	308	99.90%
Westinghouse	35.5	286.26	353	88.70%
Gaz de France	0	383.4	1098	74.60%
Hallett Air Product	291.6	286.55	308	49.40%
Julich	0	528.23	973	54.10%
UT-3 Tokyo	0	696.25	493	41.10%
Ispra Mark 4	214.9	508.22	1073	39.50%
Ispra Mark 9	0	647.1	433	44.20%
Ispra Mark 13	224.2	288.67	360	55.70%

[a] This efficiency ignores separation work.

below the pinch. This is evident in processes such as the UT-3 Tokyo, Ispra Mark 9, and Julich cycles. These exothermic reactions will produce heat that can cascade through the system and eventually be rejected by cold utility. On the other hand, the presence of exothermic reactions at high temperatures above the pinch is a source for heat, serving to lower the hot utility requirement of a cycle.

Conversely, cycles which have only endothermic reactions exhibit a pinch temperature that is relatively low compared to the other intervals. This can be seen in the US chlorine, sulfur iodine, and Westinghouse cycles. The endothermic reactions which occur at a low temperature allow for heat added by the hot utility to continuously cascade down the temperature intervals. This in effect decreases the cold utility and lowers the pinch temperature. Ideal thermal efficiency is possible when all stream and reaction heats are completely recovered in the heat cascade using a minimum approach temperature of 0 K. It is also noteworthy that three of the hybrid cycles show very good heat cascade properties.

The efficiencies calculated using minimum utility and electrical work for hybrid cycles together with the pinch points, the minimum utility, and the electrical work are shown in Table 2. In this table, whenever the degree of freedom allowed it, stoichiometric feeds to the reactors were considered. In addition, recycling of reactants to the feed (but not accounting for the separation work) was considered.

Although the hot utility requirements of the Hallett Air Product, Ispra Mark 13, and Westinghouse cycles were practically identical, the high amounts of electrical work associated with the first two processes lowers their efficiency by a sizable amount. Although the Ispra Mark 13 and Ispra Mark 4 cycles have roughly the same amount of electrical work, the low thermal efficiency of the Ispra Mark 4 cycle results in a lower overall efficiency.

One important question that one should pose is if changing the excess reactants in the different reactions taking advantage of the degrees of freedom each cycle has would change the efficiency. The answer to this question is negative for cycles featuring the recycle configuration. This is now illustrated using the Hallett Air Products cycle, which has only one degree of freedom.

The pinch point location and minimum utility do not change when the excess reactant flow is modified. This is because the recycle stream is assumed to operate under isothermal conditions. Thus, there is no heating or cooling of excess reactants to alter the hot utility or pinch point location. For example, in reaction 1 of the Hallett Air Product cycle, the excess H_2O and Cl_2 are all recycled back to the inlet stream of reactor 1 at the reaction temperature of 1123 K. Since the separation of the product stream of the reactor also occurs at 1123 K, the amount of heat lost or gained is zero. Therefore, the hot utility requirement results presented above are valid for both stoichiometric feeds and for optimized excess feeds with equilibrium considerations for the recycle separation configuration only.

Table 3. Efficiency Based on Hot Utility and Electrical Work[a]

cycle	reactants recycle	no recycle strategic sep	no recycle minimum sep
US chlorine	99.9%	99.9%	99.9%
sulfur iodine	99.9%	99.9%	99.9%
Westinghouse	86.8%	86.8%	86.8%
Gaz de France	74.6%	74.6%	74.2%
Hallett Air Product	49.4%	49.4%	49.4%
Julich	54.1%	54.1%	54.1%
UT-3 Tokyo	41.1%	41.0%	39.8%
Ispra Mark 4	47.8%	49.0%	47.9%
Ispra Mark 9	44.2%	43.3%	43.1%
Ispra Mark 13	55.7%	55.7%	55.7%

[a] This efficiency ignores separation work.

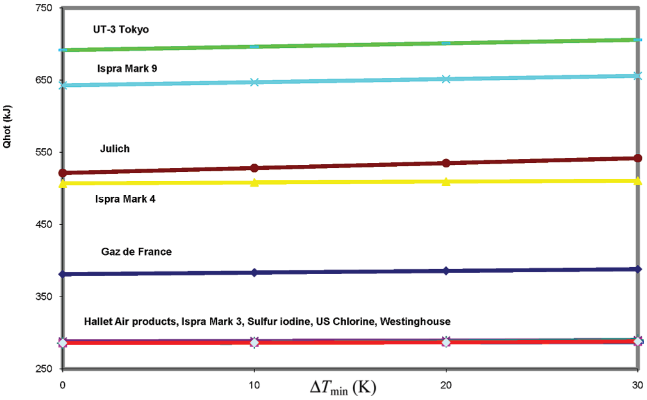


Figure 10. Influence of minimum temperature difference on hot utility.

The two configurations for the no recycle option were applied to all cycles. In the case of Ispra Mark 13, Hallett Air Product, and Westinghouse cycles, the configuration was the same for strategic and minimum separation. Table 3 showed the efficiency based on just hot utility requirements for all three configurations.

As seen in Table 3, all three configurations for each cycle have roughly the same efficiency based on hot utility and electrical work only. Due to the assumption of isothermal reactor/separator operation and the fact that intermediate chemical species travel internally inside the cycle in the cyclic manner, the effect of a recycle option on heat requirement is insignificant. Occasionally, for some cycles the configuration of minimum separation has a slightly lower efficiency than the other configurations, which can be attributed to the heating and cooling of inerts. For example, the Ispra Mark 9 cycle has the highest efficiency for the recycle configuration and the lowest efficiency for the minimum separation configuration. This is because minimum separation has the most heating and cooling of inerts due to the excess amounts of HCl, Cl_2, $FeCl_2$, and H_2O that are cycling through the system. Conversely, it would have the lowest amount of separation work, a topic which will soon be discussed. In the same manner, the strategic separation option of the Ispra Mark 9 cycle has a lower efficiency than the recycle option because it has some heating and cooling of inerts, but not to the large extent required for the minimum separation option.

Effect of Minimum Temperature Difference. Figure 10 shows the change in the hot utility for all processes as the ΔT_{min} varies by 10 deg from 0 to 30 K.

We conclude that the minimum approach temperature barely has any effect on the hot utility. The biggest change was in the Julich process where the hot utility increases by about 20 kJ from a ΔT_{min} of 0 to 30 K. The minimum hot utility for the

Table 4. Comparison of Efficiencies, Recycle Separation Configuration

$Q_h + W_{elec}$		$Q_h + W_{elec} + W_{sep}$	
US chlorine	99.9%	US chlorine	82.1%
sulfur iodine	99.9%	sulfur iodine	72.0%
Westinghouse	86.8%	Westinghouse	81.1%
Gaz de France	74.6%	Gaz de France	74.6%
Hallett Air Product	49.4%	Hallett Air Product	44.7%
Julich	54.1%	Julich	44.5%
UT-3 Tokyo	41.1%	UT-3 Tokyo	37.3%
Ispra Mark 4	47.8%	Ispra Mark 4	43.5%
Ispra Mark 9	44.2%	Ispra Mark 9	30.1%
Ispra Mark 13	55.7%	Ispra Mark 13	52.2%

Julich cycle at the ideal approach temperature is 528 kJ; the efficiency decrease is about 3%. The UT-3 Tokyo and Ispra Mark 9 also show some change in the hot utility, but all these cycles hardly have any change that would affect the reaction.

Finally, we note that a large ΔT_{min} leads to a smaller heat exchanger area, which has an effect on the cycle economics.

Separation Energy Requirement. Cycles that contain fewer reactions have an efficiency that has a smaller propensity to be decreased by the inclusion of the separation energy term. Furthermore, reactions that involve primarily phase separations are less affected, as the work required by a phase separation is zero. Table 4 shows the results of including separation work for the recycle configuration of the cycles.

When stoichiometric feeds are supplied to the reactor and the equilibrium constant is very high ($\Delta G°$ very large negative), the separation work is at a minimum because there is no excess of at least one reactant to separate. Conversely, when the equilibrium constants are moderate, the inclusion of excess reactants increases the separation work and tends to decrease the overall efficiency of the cycle. Thus, reactions with moderate $\Delta G°$ values require optimization. Indeed, excess reactants may reduce the concentration of certain reactants that are difficult to separate, but they may also increase the throughput of the separation units, which may still need to separate the excess reactant. The only term effected by this optimization is the separation work required.

To illustrate the effect of separation work, we discuss the third reaction of the Ispra Mark 9 cycle (Figure 11). The amount of excess chlorine fed to the third reactor was chosen as a design parameter to fulfill one of the four required degrees of freedom. The illustration shows that there is a minimum in the separation work requirement with respect to changes in the amount of excess chlorine fed to the reactor. Such critical points reflect the presence of optimum operating conditions within the cycle.

When separation work is included in the calculation of the cycle efficiency, the stoichiometric and optimized feeds may give different results depending on the cycle. Table 5 presents the efficiency results of the recycle separation configuration for the two different feed scenarios.

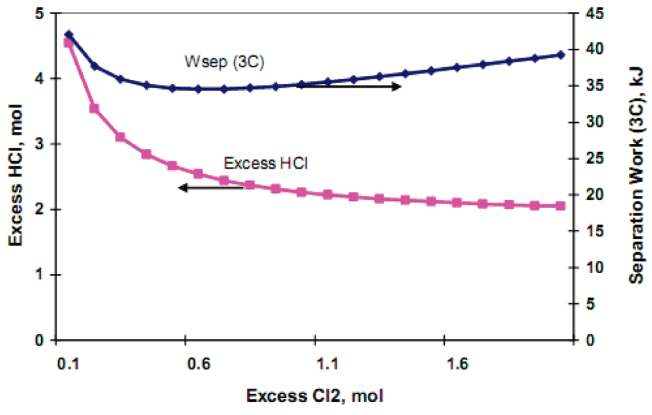


Figure 11. Feed optimization of Ispra Mark 9 reaction no. 3.

Table 5. Comparison of Feed Scenarios for Recycle Separation Configuration

cycle	efficiency	
	stoichiometric feed	optimized feed
US chlorine	82.1%	82.1%
sulfur iodine	72.0%	72.0%
Westinghouse	81.1%	81.1%
Gaz de France	74.6%	74.6%
Hallett Air Product	44.7%	44.7%
Julich	40.0%	44.5%
UT-3 Tokyo	37.1%	37.3%
Ispra Mark 4	43.5%	43.5%
Ispra Mark 9	29.9%	30.1%
Ispra Mark 13	52.2%	52.2%

Figure 12 compares the minimum theoretical separation work (obtained using the change in Gibbs free energy) associated to the cycles for the recycle separation option for stoichiometric feeds neglecting equilibrium and for optimized feeds of excess reactants considering equilibrium.

The Ispra Mark 9 cycle has the largest amount of separation work of any of the cycles evaluated. This result can partially be attributed to the number of components that require separation (by means other than phase separation) within two of the reactions. Alternatively, the Westinghouse (Figure 13) and Gaz de France cycles experience no increase in separation work required between the stoichiometric (nonequilibrium) and excess (equilibrium) amounts of feed. This can be attributed to the fact that all of the reactions in each of the two mentioned cycles are either phase-driven reactions (reactions that are driven by continuous removal of products via phase separation), electrochemical reactions, or reactions with highly negative values of Gibbs free energy. As a result, stoichiometric feeds (or near stoichiometric feeds) can be supplied to the reactor because equilibrium conditions are either not present or highly favor the product side of the reaction. In addition, the Gaz de France cycle has a required separation work of zero because all the reaction products are separated naturally.

We now consider the effect of recycling options when the separation work is included in the efficiency calculation, the cycle efficiency for all three configurations decreases. Table 6 shows in bold the maximum efficiency among the options.

When separation energy is included, the extent of decrease in efficiency of the no recycle configurations (strategic and

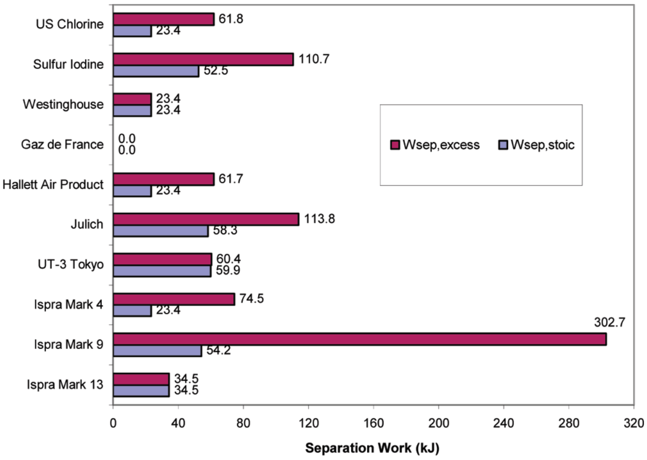


Figure 12. Separation work comparison for stoichiometric feeds (complete conversion, neglecting equilibrium) and optimized excess feeds (considering equilibrium).

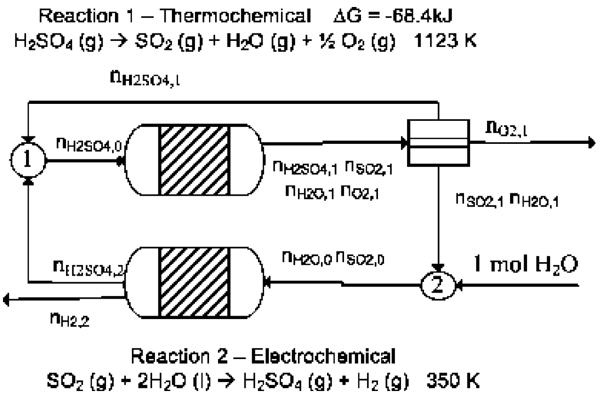


Figure 13. Westinghouse cycle illustration.

Table 6. Overall Efficiency

	recycle	no recycle strategic sep	no recycle minimum sep
US chlorine	82.1%	**91.3%**	**91.3%**
sulfur iodine	72.0%	70.4%	**76.5%**
Westinghouse	81.1%	81.1%	81.1%
Gaz de France	**74.6%**	**74.6%**	74.2%
Hallett Air Product	44.7%	**45.4%**	**45.4%**
Julich	44.5%	43.6%	**45.9%**
UT-3 Tokyo	**37.3%**	37.2%	36.3%
Ispra Mark 4	43.5%	**46.9%**	45.9%
Ispra Mark 9	30.1%	37.1%	**38.8%**
Ispra Mark 13	52.2%	**53.3%**	**53.3%**

minimum separation) is usually less than that of the recycle configuration for a simple reason: the no recycle configurations usually require less separation energy than the recycle configuration. However, as explained above, the exception to this generalization does exist: the separation energy of the strategic separation configuration is more than the energy of the recycle configuration in the two cycles Julich and sulfur iodine (126.9 vs 113.8 kJ for Julich and 119.6 vs and 110.7 kJ for sulfur iodine). Moreover, even though the no recycle configurations usually give better efficiency, it is not necessary that they are more economically beneficial, which is the ultimate factor in determining the best configuration.

Next, a better evaluation of the separation work for the first four cycles (which happen to have the highest efficiency) was attempted by calculating the real separation work instead of the ideal one. For a membrane separator, the real work is approximated as the required compressor work to pass the stream through the membrane. For phase separations, work was assumed to be zero. As Table 7 shows, this leads to a slight decrease in their overall efficiencies. These values will not be as accurate as creating a detailed flowsheet and calculating the actual separation work, but they will provide a useful upper bound on overall efficiencies of cycles.

Of the cycles that have been studied in detail and shown in Table 7, only the sulfur iodine and the Westinghouse cycles were studied in detail with reported heat and work calculations for the entire process. Goldstein[2] used distillation as a separating method in their proposed flowsheet for the sulfur iodine cycle and reported the cycle efficiency of only 36%; the separation work is not known since thermal separation (distillation) was used. Jeong et al.[13] presented the hybrid sulfur cycle that was modified from the Westinghouse cycle. They studied the effect of pressure in the reactor and obtained an optimal separation energy of 11 kJ/mol-H_2 for separating SO_2 and O_2. This energy is below the 16.25 kJ/mol-H_2 calculated for the membrane used in this report. The degree of separation for this system is also greater than for the selected membrane. Jeong et al.[13] also provide the corresponding flowsheet for the SO_2/O_2. We conclude that, without the detailed flowsheet of the cycle, the real separation work can not be accurately calculated. However, as will be shown later in Table 9, the separation work is a relatively small contributor to the overall energy requirement.

Temperature Optimization for Maximum Efficiency. All prior results regarding cycle efficiencies have been carried out at reaction temperatures specified by the literature. To improve the overall cycle efficiency, the temperatures of each reaction in each cycle were optimized. The only constraint placed on the variation of reaction temperatures was that each species present in all reactions does not deviate from its listed phase. Such constraints are made based on the assumption that the outcomes and feasibilities of reactions will not vary as long as the phases of reacting species are not changed from the phases defined by temperatures given in literature. Results are shown in Table 8.

The results of the optimization show that most cycles experienced only a small change in overall efficiency (Table 9). When all cycles and recycling options are included, an average overall increase of only 1.5% was observed. The Julich cycle shows the largest efficiency improvement with a 6.3% increase, with the vast majority of the increase coming as a result of the separation work requirement decreasing from 126.9 to 44.8 kJ.

Table 9 shows the 5 most promising processes with highest *maximized* efficiency (obtained after the process configuration and operating condition have been optimized) among the 10 cycles. Two of the cycles, Westinghouse and Ispra Mark 13, are hybrid cycles while the rest are composed solely of thermochemical reactions.

Screening Process. There are over 200 documented water-splitting cycles. Examining all the cycles in detail is time-consuming. In order to find a quicker way to examine if a process has a good efficiency, a screening process is suggested next.

First, the total energy requirement was broken down into three components: hot utility, electrical work, and separation work, to see which one plays the biggest role in the overall efficiency. As can be seen in Tables 10 and 11, the hot utility is the biggest factor for 9 of the 10 cycles. In the hybrid Hallett Air Product cycle where it is not the biggest factor due to a large electrical work requirement, it is still 45% of the total energy requirement.

Thus, examining the process based solely on the hot utility would be a good screening method. In general, the separation work is considerably smaller than the hot utility (Table 12).

When examining the individual intervals for pinch point analysis, there was a trend in the heat requirement of the individual reactions. Table 13 shows the individual heat requirement above and below the pinch for all the cycles.

The most noticeable trend is that if a cycle has a highly exothermic reaction at low temperature, it will have a low efficiency such as in the Julich, UT-3 Tokyo, and Ispra Mark 9 cycles (these cycles are highlighted in Table 13). The heat source of exothermic reaction at low temperature is virtually unrecoverable through heat exchange, which leads to high cold and hot utilities and thus low efficiency. These cycles will not need to be examined further. Another characteristic is that processes that only have endothermic reactions have a good efficiency as evident in the top 3 cycles and the Ispra Mark 13 cycle. Processes that have an exothermic reaction occurring at a high temperature tend to be hit or miss like Gaz de France and Ispra Mark 4. In conclusion, cycles with a highly exothermic reaction at low temperature should not be studied further.

Discussion

Water-splitting cycles are complex processes with several inherent difficulties: a high temperature reaction, containing

Table 7. Cycle Efficiencies for the Recycle Configuration, Real Separation Work

cycle	reaction1	reaction2	reaction3	W_{sep} ideal (kJ)	W_{sep} real (kJ)	efficiency w/W_{sep} real
US chlorine	membrane HCl, $O_2 \rightarrow HCl/O_2$	phase $CuCl_2$, $H_2 \rightarrow CuCl_2/H_2$	phase CuCl, $Cl_2 \rightarrow CuCl/Cl_2$	61.75	83.28	77.4%
sulfur iodine	membrane H_2O, SO_2, $O_2 \rightarrow H_2O$, SO_2/O_2	phase HI, $H_2SO_4 \rightarrow HI/H_2SO_4$	phase I_2, $H_2 \rightarrow I_2/H_2$	110.68	119.80	70.4%
Westinghouse	membrane H_2O, SO_2, $O_2 \rightarrow H_2O$, SO_2/O_2	phase H_2SO_4, $H_2 \rightarrow H_2SO_4/O_2$	NA	23.36	32.5	79.0%
Gaz de France	phase K_2O, $H_2 \rightarrow K_2O/H_2$	phase K, $K_2O_2 \rightarrow K/K_2O_2$	phase KOH, $O_2 \rightarrow KOH/O_2$	0	0	74.6%

Table 8. Overall Efficiency with Temperature Optimization

	recycle	no recycle strategic sep	no recycle minimum sep
US chlorine	82.1%	**92.1%**	92.0%
sulfur iodine	73.6%	71.9%	**81.3%**
Westinghouse	82.7%	82.7%	82.7%
Gaz de France	**76.0%**	**76.0%**	75.5%
Hallett Air Product	44.7%	**45.4%**	**45.4%**
Julich	49.9%	49.9%	**51.9%**
UT-3 Tokyo	**38.1%**	38.0%	37.2%
Ispra Mark 4	44.4%	**47.7%**	46.5%
Ispra Mark 9	31.1%	37.9%	**39.5%**
Ispra Mark 13	52.5%	**53.8%**	**53.8%**

Table 9. Top Cycles and Their Efficiencies

cycle	efficiency	configuration(s)
US chlorine	92.10%	no recycle—strategic sep
Westinghouse	82.70%	all
sulfur iodine	81.30%	no recycle—minimum sep
Gaz de France	76.00%	recycle or no recycle—strategic sep
Ispra Mark 13	53.80%	no recycle—strategic or minimum sep

Table 10. Distribution of Energy Requirement for Recycle Configuration

cycle	percentage of overall energy requirement		
	hot utility	electric work	separation work
US chlorine	82%	0%	18%
sulfur iodine	72%	0%	28%
Westinghouse	81%	12%	7%
Gaz de France	100%	0%	0%
Hallett Air Product	45%	46%	10%
Julich	82%	0%	18%
UT-3 Tokyo	91%	0%	9%
Ispra Mark 4	77%	11%	11%
Ispra Mark 9	68%	0%	32%
Ispra Mark 13	53%	41%	6%

Table 11. Distribution of Energy Requirement for No Recycle Configurations

Percentage of Overall Energy Requirement—No Recycle				
	hot utility		separation work	
cycle	strategic sep	minimum sep	strategic sep	minimum sep
US chlorine	91.5%	91.5%	8.5%	8.5%
sulfur iodine	70.5%	83.5%	29.5%	16.5%
Westinghouse	81.2%	81.2%	6.6%	6.6%
Gaz de France	100.0%	100.0%	0.0%	0.0%
Hallett Air Product	45.5%	45.5%	8.1%	8.1%
Julich	80.6%	84.9%	19.4%	15.1%
UT-3 Tokyo	90.7%	91.1%	9.3%	8.9%
Ispra Mark 4	83.4%	83.8%	4.4%	4.3%
Ispra Mark 9	85.7%	89.9%	14.3%	10.1%
Ispra Mark 13	53.8%	53.8%	4.4%	4.4%

Table 12. Effect of the Inclusion of the Work Term (Recycle Configuration)

Q_h		$Q_h + W_{elec} + W_{sep}$	
US chlorine	99.9%	US chlorine	82.1%
sulfur iodine	99.9%	sulfur iodine	72.0%
Westinghouse	99.9%	Westinghouse	81.1%
Gaz de France	74.6%	Gaz de France	74.6%
Hallett Air Product	99.8%	Hallett Air Product	44.7%
Julich	54.1%	Julich	44.5%
UT-3 Tokyo	41.1%	UT-3 Tokyo	37.3%
Ispra Mark 4	56.2%	Ispra Mark 4	43.5%
Ispra Mark 9	44.2%	Ispra Mark 9	30.1%
Ispra Mark 13	99.0%	Ispra Mark 13	52.2%

Table 13. Heat Requirement of Reactions in Each Cycle (Recycle Configuation)[a]

cycle	heat of individual reactions (kJ)				
	above pinch			below pinch	
US chlorine	−59.30	−156.60	−50.70		
sulfur iodine	−184.84	−12.59	−102.51		
Westinghouse	−184.84	−129.28			
Gaz de France	−381.05			−96.51	70.64
Hallett Air Product	−59.30	−184.62			
Julich	−517.17			37.26	232.88
UT-3 Tokyo	−181.81	72.64	−379.17	411.79	
Ispra Mark 4	−200.79	−306.26		−14.50	56.08
Ispra Mark 9	−333.58	−21.76		360.92	
Ispra Mark 13	−184.84	−129.49			

[a] Highest temperature reactions are on the left while the lowest temperature reactions are on the right. Negative heat is for endothermic reaction while positive is for exothermic reaction.

unfavorable reactions (high positive value of Gibss free energy), multistage process with multiple reactors and separators. Thorough evaluation of cycle efficiency considering all the factors and all the practical issues is very time-consuming, hence a few factors (deemed to be less important than the factors presented above) have to be disregarded and a few simplified assumptions like perfect separation have to be made. Qualitative analysis of the effect of including the neglected factors and relaxing the assumptions on the cycle efficiency is briefly discussed below:

Cold Utility Requirement. The cold utility requirement is neglected in this work because the results show a tendency that processes with high cold utility requirement are usually inefficient, while with highly efficient processes, the cold utility requirement is usually small (less than 1 kJ/mol-H_2 produced). Thus the differentiation between the efficient and the inefficient cycles does not change by including the cold utility requirement since the efficiency gap between the efficient and the inefficient ones expands but does not decrease. Including the cold utility requirement, however, gives a better estimate for the cycle efficiency. The cold utility requirement can be roughly accounted for as the required work to pump/transport the cooling water.

Effects of Pressure on Reaction Equilibria. Another factor that could be optimized is the reaction pressure. Such optimization would only affect reactions that have a vapor phase. For reactions containing only solid and/or liquid phases, there is no significant effect expected. It is well-known that adjusting the reaction pressure will change the equilibrium of a gas phase reaction if the reaction involves a change in the number of moles between the reactants side and the products side. Thus, the reaction pressure can be optimized so as to maximize the amount of product and cycle efficiency. In addition, including the reaction pressure factor requires that the compressor's operating energy (if any) has to be considered as well.

Nonideal Separation Recovery. Throughout this study, it was assumed for all separation processes that perfect separation was obtained. Because this is not the case in practice, the overall efficiency and functioning of the cycles would be affected. First, nonideal separation means that a dilute amount of species that failed to be separated will travel through the cycle of reactions. The presence of such inert species may shift the equilibrium of the reaction, depending on the phases of the reacting species. However, because the amount of these inert species would be relatively low, their presence should have a miniscule affect on the overall efficiency of the process. The same can be said for any additional heating requirements which may arise from the circulation of such inert species. Second, without perfect separation there is a possibility that the intermediate chemical species that are designed to be nonaffluent are allowed to exit the system through the hydrogen or oxygen product streams. Such species will need to be replenished in order for the cycle to continue to operate. It is of crucial importance to keep the loss of such species minimal to avoid large increase in production costs.

Deviation of Separation Temperatures from Reaction Temperatures. In practice, the optimum operating temperature of a separator is usually different from the optimum operating temperature of reactor. In the water-splitting cycle, the excess reactants from a reactor in one stage of the cycle are fed into the separator of that stage and, then, are either immediately recycled back to the reactor (recycle configuration) or travel to the other stages of the cycle before making their way back to the reactor (no recycle configuration). Thus, it can be seen that, in the recycle configuration, if the separator and the reactor in one stage of the cycle operate at different temperatures, then temperature conditioning of the excess reactants is needed (usually the excess reactants from the reactor are cooled down to the separator temperature and, then after leaving the separator, are heated up to the reactor temperature). The results are the following:

- more heat duty for the heat exchanger network, which leads to larger heat exchanger area.
- a greater hot and cold utility requirement, which leads to a decrease in efficiency, although the increase in the utility requirement and the decrease in efficiency is usually small thanks to the heat recovery possible when the temperature of the excess reactants is conditioned in two opposite directions: heating up and cooling down. In the no recycle configuration, the effect is even less recognizable because the temperature of the excess reactants is conditioned in a closed loop fashion: cooling down and heating up, independent of whether the separator and the reactor operate at the same temperature or not.

Separator Selection for Real Separation Work Calculations. The 10 cycles we looked at involve either phase separation or membrane separation, or both. It was assumed that the separation work for phase separation is zero. For other types of separation that are not phase separations, membrane separators were used. They were chosen because

- required separation work for membrane separators can be easily calculated; for other types of separation processes, the calculation is not straightforward;
- literature search reveals that the membrane separators are commonly used or suggested to be used in water-splitting cycles;
- membrane separators are reasonably priced, low maintenance devices with high recovery of product; some disadvantages to using membranes are the downtime to clean/purge the membrane and the high pressure requirement needed to push streams through the membrane; this may not be the best option for all separations, but it does form a useful upper bound; if any other separation is more efficient, then it can be used, but if not, membranes can always be used at this efficiency. Among the factors stated above, the factor of a better real separation work calculation is likely to have a significant impact on efficiency. Ultimately, to obtain a better estimate for efficiency, a detailed process flowsheet and detailed calculations are needed. Detailed calculations are possible only if a limited number of cycles are studied because they are too time-consuming. A literature search may help narrow down the list of candidate cycles for consideration. Thus, to obtain better results, we can do as follows:

- Eliminate from consideration any cycle that has been confirmed to be inoperable, inefficient, or thermodynamically infeasible.
- More accurate thermodynamic calculation by using appropriate thermodynamic models.
- More accurate evaluation of separation work based on a more detailed process flowsheet.

XIII. Conclusions

A methodology has been developed to evaluate thermochemical and hybrid water-splitting cycles based on the efficiency of the process. Using classical pinch point analysis, the Nernst equation, and minimum Gibbs energy of mixing of ideal mixtures, the hot utility, electrical work, and separation work requirements can all be found, respectively. This method can be applied to all thermochemical and hybrid cycles to give upper bounds on efficiencies that can be used on a comparative basis. The estimates found from this method have shown to be on par with those provided in the literature.

While this methodology is an effective way to screen hydrogen producing cycles by providing upper bound on their efficiencies, there is still room for improvements. The method made use of simplified assumptions and approximate calculations so that the detailed flowsheets of the cycles, which are usually not available, are not needed. It considered several factors for optimization purposes: the reaction temperature, the amount of excess reactants, and the recycle configuration. Thus, the method provides upper bounds on the cycle efficiencies and gives insights on the optimum operating condition and the process configuration based on the criterion of maximum efficiency. To improve the accuracy of the cycle efficiency calculation, it is necessary to obtain a detailed process flowsheet, which allows a more accurate calculation of energy requirement (especially the real separation work). This can be done for a limited number of promising cycles after the inefficient cycles have been screened out by using the method presented in this paper.

It can be concluded that ideal heat requirement characteristics are realized for cycles lacking a pinch point, while separation work can be greatly minimized if phase separation is made possible rather than other types of separation methods. These conclusions outline a strategy for future cycle synthesis as follows:

(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) Reaction temperatures should be investigated to exploit phase differences between equilibrium species.

Economic analysis could be performed on the most efficient cycles to find the cycle that is most economically feasible.

Appendix

The operating temperature, heat of reactions, and Gibbs free energy of reactions are given in Table A.1. The pressure for all reactions is 1 bar.

Table A.1. Details of Water-Splitting Cycles[a]

	cycles	T (K)	ΔH_{rxn} (kJ/mol)	ΔG_{rxn} (kJ/mol)
	Gaz de France			
rxn 1	$2K_2O(s) \rightarrow 2K(v) + K_2O_2(s)$	1098	381.1	159.5
rxn 2	$2K(l) + 2KOH(l) \rightarrow 2K_2O(s) + H_2(v)$	1023	96.5	118.4
rxn 3	$K_2O_2(s) + H_2O(v) \rightarrow 2KOH(s) + (1/2)O_2(v)$	398	−70.6	−98.2
	Hallett Air Products			
rxn 1	$Cl_2(v) + H_2O(v) \rightarrow 2HCl(v) + (1/2)O_2(v)$	1123	59.3	−17.4
rxn 2	$2HCl(v) \rightarrow Cl_2(v)+H_2(v)$	298	184.6	190.6
	Ispra Mark 4			
rxn 1	$Cl_2(v) + H_2O(v) \rightarrow 2HCl(v) + (1/2)O_2(v)$	1123	59.3	−17.4
rxn 2	$H_2S(v) \rightarrow S(v) + H_2(v)$	1073	306.3	189.1
rxn 3	$2FeCl_3(l) \rightarrow Cl_2(v) + 2FeCl_2(s)$	693	14.5	15.9
rxn 4	$2FeCl_2(s) \rightarrow 2HCl(v) + S(s) \rightarrow 2FeCl_3(s) + H_2S(v)$	373	−56.1	105.4
	Ispra Mark 9			
rxn 1	$3FeCl_2(s) \rightarrow 4H_2O(v) \rightarrow Fe_3O_4(s) + 6HCl(v) + H_2(v)$	923	333.6	48.7
rxn 2	$3FeCl_3(l) \rightarrow (3/2)Cl_2(v) + 3FeCl_2(s)$	693	21.8	23.9
rxn 3	$(3/2)Cl_2(v) + Fe_3O_4(s) + 6HCl(v) \rightarrow 3FeCl_3(s) + 3H_2O(v) + (1/2)O_2(v)$	423	−360.9	−20.1
	Ispra Mark 13			
rxn 1	$H_2SO_4(v) \rightarrow SO_2(v) + H_2O(v) + (1/2)O_2(v)$	1123	184.8	−68.4
rxn 2	$Br_2(v) + SO_2(v) + 2H_2O(l) \rightarrow 2HBr(v) + H_2SO_4(v)$	350	25.3	117.5
rxn 3	$2HBr(v) \rightarrow Br_2(v) + H_2(v)$	350	104.2	111.2
	Julich			
rxn 1	$Fe_3O_4(s) + 3FeSO_4(s) \rightarrow 3Fe_2O_3(s) + 3SO_2(v) + (1/2)O_2(v)$	1073	517.2	−90.3
rxn 2	$3FeO(s) + H_2O(v) \rightarrow Fe_3O_4(s) + H_2(v)$	973	−37.3	19.3
rxn 3	$3Fe_2O_3(s) + 3SO_2(v) \rightarrow 3FeO(s) + 3FeSO_4(s)$	473	−232.9	−18.0
	sulfur iodine			
rxn 1	$H_2SO_4(v) \rightarrow SO_2(v) + H_2O(v) + (1/2)O_2(v)$	1123	184.8	−68.4
rxn 2	$2HI(v) \rightarrow I_2(v) + H_2(v)$	723	12.6	23.9
rxn 3	$I_2(l) + SO_2(v) + 2H_2O(v) \rightarrow 2HL(v) + H_2SO_4(v)$	393	102.5	47.8
	US chlorine			
rxn 1	$Cl_2(v) + H_2O(v) \rightarrow 2HCl(v) + (1/2)O_2(v)$	1123	59.3	−17.4
rxn 2	$2CuCl_2(s) \rightarrow 2CuCl(l) + Cl_2(v)$	773	156.6	−5.75
rxn 3	$2CuCl_2(s) \rightarrow 2HCl(v) + 2CuCl_2(s) + H_2(v)$	473	50.7	143.6

Table A.1. Continued

	cycles	*T* (K)	ΔH_{rxn} (kJ/mol)	ΔG_{rxn} (kJ/mol)
	UT-3 Tokyo			
rxn 1	$CaBr_2(l) + H_2O(v) \rightarrow CaO(s) + 2HBr(v)$	1033	181.8	100.65
rxn 2	$Br_2(v) + CaO(s) \rightarrow CaBr_2(s) + (1/2)O_2(v)$	945	−72.6	−34.9
rxn 3	$3FeBr_2(s) + 4H_2O(v) \rightarrow Fe_3O_4(s) + 6HBr(v) + H_2(v)$	833	379.2	133.87
rxn 4	$Fe_3O_4(s) + 8HBr(v) \rightarrow Br_2(v) + 3FeBr_2(s) + 4H_2O(v)$	483	−411.8	−75.56
	Westinghouse			
rxn 1	$H_2SO_4(v) \rightarrow SO_2(v) + H_2O(v) + (1/2)O_2(v)$	1123	184.8	−68.4
rxn 2	$SO_2(v) \rightarrow 2H_2O(l) \rightarrow H_2SO_4(v) + H_2(v)$	353	129.3	119.1

[a] Notation: (s) solid phase, (l) liquid phase, (v) vapor/gas phase.

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