A Systematic Methodology for the Evaluation of Alternative Thermochemical Cycles for Hydrogen Production

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1. Introduction

Hydrogen is considered to be an environmentally attractive potential alternative to fossil based fuels. It is an excellent energy carrier, particularly as a carrier of remotely generated electrical energy or as a carrier of residual waste thermal energy. Hydrogen based combustion processes are more efficient than for fossil fuels, releasing 117.6 MJ/kg, compared to only 46.36 MJ/kg for the combustion of n-octane [1]. Hydrogen is also a clean energy source. Its combustion produces no carbon or sulfur products, with water as the primary byproduct. These features characterize an ideal sustainable energy source that can be used to meet increasing residential, commercial, and industrial demands, however, there are several challenges and limitations associated with the production of hydrogen.

Electrolysis of water, a widely used method for hydrogen production, is very inefficient and involves the conversion of primary energy to electricity and electricity to hydrogen [2]. Electrolyzers have been around for centuries [2] with overall process efficiencies between 27% and 32% [3]. Electrolysis requires 140 MJ/kg hydrogen, followed by an additional 15 to 40MJ/kg to compress or liquefy the hydrogen for proper storage and transport [3]. Other methods include fossil fuel reforming, high temperature cracking paired with a high temperature nuclear energy source, and the gasification of biomass and waste [3]. Each of these methods posses distinct challenges and limitations.

Reforming fossil fuels produces low hydrogen concentrations of 70-80%, when catalytic steam reforming is used, and 40-50% for the partial oxidation and autothermal reforming on a dry basis [4]. Although catalytic steam reforming can yield 80% hydrogen it is an energy intensive process and often produces carbon monoxide [4]. The gasification of biomass, such as used edible oils [5], is another option for hydrogen production. Edible oil wastes (EOW) can be blended with high-rank coal (less than 4% moisture when air dried) and gasified to produce fuel. The gasification produces low NO_x and SO_x emissions, however the EOW is 78% carbon and so hydrogen production is limited [5].

The above obtuse production methods arise from the primary challenge with hydrogen production from water, which is the following reaction:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad \Delta G^{\circ}_{298K} = 237 \text{ kJ/mol } O_{2(g)} \qquad (1)$$
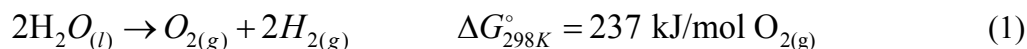
For a reaction to occur the change in Gibbs free energy (ΔG°) must be negative, therefore reaction (1) does not occur at normal temperatures. Reaction (1) will only occur at temperatures greatly exceeding 2000 K [6], which results in very energy intensive processes to generate hydrogen from water. To overcome this energy barrier a sequence of

thermodynamically feasible reactions, whose sum is the overall reaction of splitting water (1), is developed based on non-toxic, abundant compounds. This sequence is referred to as an thermochemical cycle. A representation of a thermochemical cycle is given by the figure below.
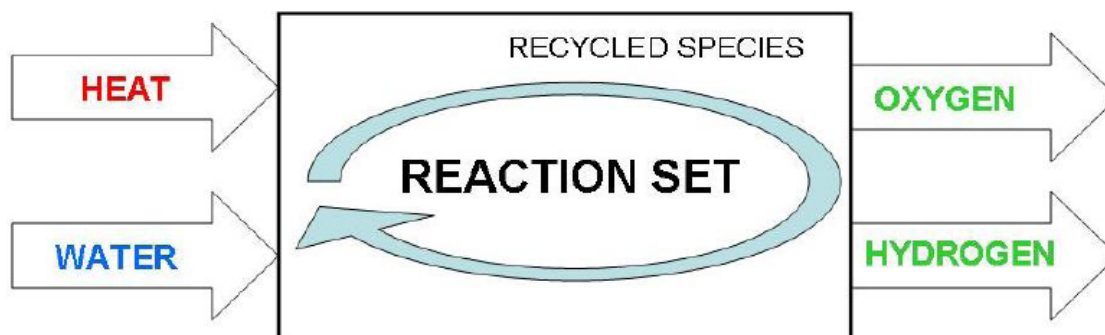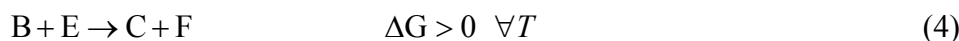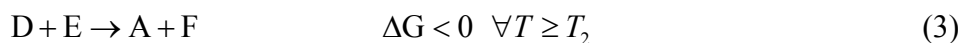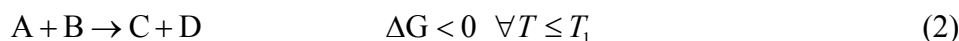

Figure 1. Representation of a thermochemical cycle for the production of hydrogen

$$A + B \rightarrow C + D \qquad\qquad \Delta G < 0 \;\; \forall T \leq T_1 \qquad\qquad (2)$$
$$D + E \rightarrow A + F \qquad\qquad \Delta G < 0 \;\; \forall T \geq T_2 \qquad\qquad (3)$$
$$\overline{\rule{0pt}{1em}\hspace{8cm}}$$
$$B + E \rightarrow C + F \qquad\qquad \Delta G > 0 \;\; \forall T \qquad\qquad (4)$$

The above thermochemical cycle, equations (2) – (4), accomplishes the thermodynamically infeasible (ΔG > 0) reaction (3), with a sequence of alternative reactions, (1) and (2), which are feasible at certain temperatures as shown by Figure 2. In chemical process sequencing, species B and E are consumed producing C and F, while species A and D are recycled. Energy supplied to a thermochemical cycle is largely consumed by the regeneration of the reactants, rather than the formation of the product [1].

The above scheme can be used as a strategy for the splitting of water into hydrogen and oxygen through multiple, feasible, reaction steps at considerably lower temperatures. In such a proposed cycle water is consumed along side other reagents, producing hydrogen and oxygen, while the remaining products are recycled back as reactants. The net reaction for the cycle is (1). The appeals of the thermochemical cycle is that the waste heat from a nuclear reactor can be used to supply the necessary hot utility, as is done with an alternative thermochemical cycle (ATC) [7], and purified oxygen, a much sought after commodity, is produced as a by-product. This paper specifically deals with ATCs, in which the cycle contains no sulfur or sulfur products. A temperature limit of 1123K is imposed so that nuclear waste heat can provide the hot utility requirements. The ATCs under investigation specifically do not consist of more than five reactions, are chemically and thermodynamically viable, and do not contain noble metals or other substances with low abundances [7]. To abide by RICA standards the ATCs do not contain mercury, selenium, or cadmium.
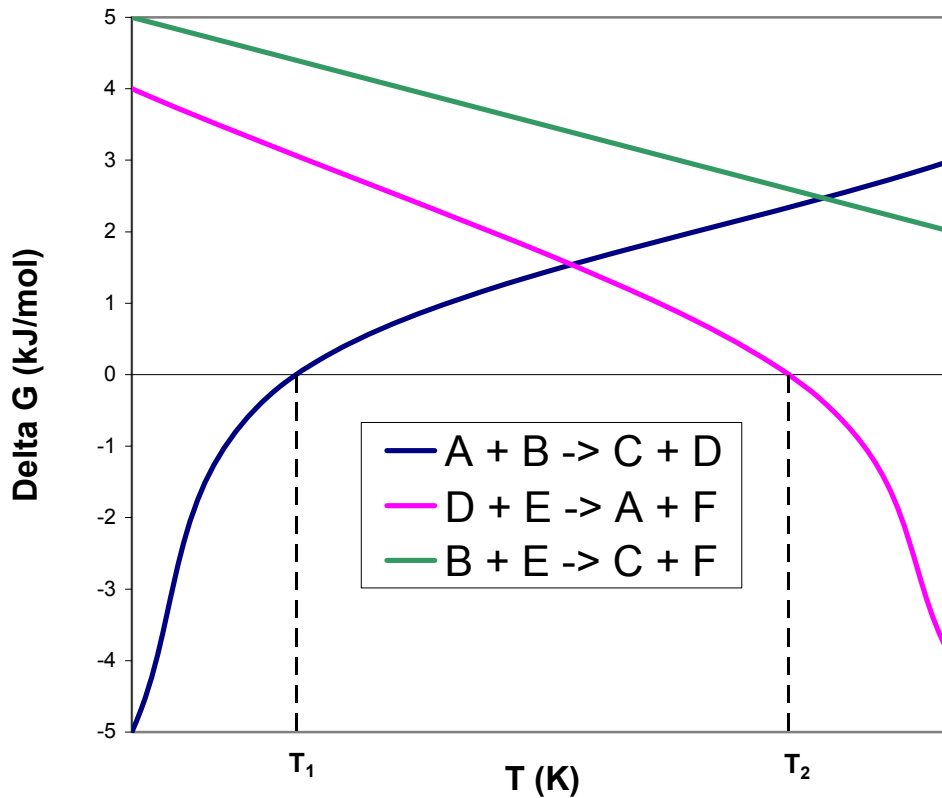
Figure 2. Plot of ΔG as a function of reaction temperature for three hypothetical reactions, where the third is the sum of the first two, which demonstrates the need for thermochemical cycles

The difficulty with thermochemical cycles is with the selection and evaluation of the reaction clusters. Traditional assessment tools have primarily included literature searches [8], inspection, and evaluation by comparison [9] to screen possible clusters. Few attempts have been made to systematically identify, screen, and evaluate hydrogen producing thermochemical cycles. A proper study should be thorough, exhausting all possible thermodynamically feasible options.

In this work a systems engineering approach is taken to develop a systematic methodology for the initial evaluation of ATCs for hydrogen production, as shown by Figure 3. This proposal consists of five major components, (i) conceptualization, (ii) reaction cluster synthesis, (iii) flowsheet design, simulation, and analysis, (iv) process integration and (v) performance evaluation. A formal definition of thermodynamic feasibility is given, followed by a mathematical construct for generating feasible clusters. Steps are then prescribed for design, optimization, and heat integration, along with a formal definition for efficiency and prescribed minimum threshold efficiency. After the strategy is outlined, its strength and flexibility is then demonstrated through a case study involving the Fe-Cl thermochemical cycle.
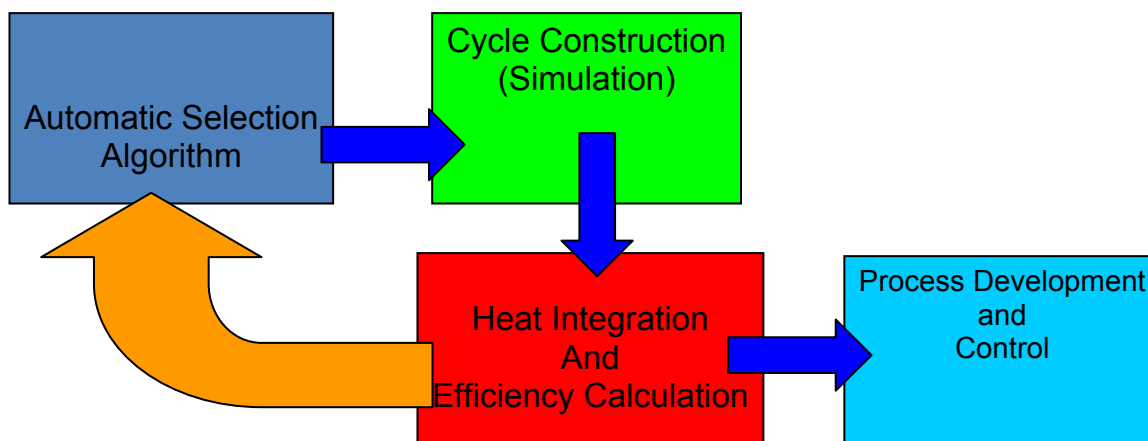
Figure 3. Flowchart of the systematic methodology for identifying, screening, and evaluating thermochemical cycles, in which the participating species are chosen for a given ATC and are supplied to an automatic selection algorithm, each identified cycle is constructed using simulation software, then a heat integration is executed and the efficiency of each cycle is determined, if a promising ATC is identified (one whose efficiency exceeds a threshold value) further research and development are conducted on that cycle, otherwise parameters in the algorithm are modified or new molecular and/or atomic species are considered for cycle construction

2. Computational Methodology

The space containing the reactions involved in a desired cycle is defined as follows, which is adapted from the work of Holiastos and Manousiouthakis [10] and Stephanopoulos ([11], [12]).

We begin by defining our reaction cluster as follows, where N^R is the number of reactions, N^S is the number of chemical species, γ_{ij} is the reactant coefficient for species Λ_i in reaction j, and δ_{ij} is the product coefficient for species Λ_i in reaction j. The molecular species Λ_i involved are contingent on the N^A desired atomic species, which satisfy criteria of safety, abundance, and affordability in accordance with an ATC [7]. The overall desired reaction has coefficients of v_i ($v_i > 0$ is a product) which the cluster must be constrained to.

To achieve a desired cycle, all of the involved reactions must be thermodynamically feasible. What follows is a derivation of thermodynamic feasibility along with the mathematical constraints for a reaction cluster.

$$\sum_{i=1}^{N^S} \gamma_{ij} \Lambda_i \rightarrow \sum_{i=1}^{N^S} \delta_{ij} \Lambda_i \qquad j \in \left\{ 1, 2, ..., N^R \right\} \qquad\qquad (5)$$

$$\sum_{j=1}^{N^R} \left(\delta_{ij} - \gamma_{ij} \right) = v_i \qquad i \in \{1, 2, ..., N^S\} \qquad\qquad (6)$$

2.1 Thermodynamic Modeling of Reaction Clusters

A reaction cluster is often evaluated based on prescribed criteria, such as process safety, environmental protection and economic viability. Process safety tends to constrain the reactants and by-products in the reaction cluster to be nontoxic and nonflammable. Environmental considerations require reducing the byproducts and eliminating hazardous compounds. Economic viability is significantly determined by the reaction yield.

Thermodynamics plays a central role in reaction yield since it sets an upper bound on a reaction attainable yield. If a process is thermodynamically infeasible, process safety and economic viability are greatly impaired. Thermodynamics can limit the process yield which is directly correlated with product yield and economic viability. With a lower yield larger flowrates and more energy will have to be used, reducing profit. Process safety and environmental concerns are also affected by unexpected, thermodynamically favored, byproducts, which could have adverse health effects. Larger operations, resulting from unfavorable reaction dynamics, also pose a threat to process safety.

When the yield of the process, specified by thermodynamics, is greater than or equal to the yield ensuring economic feasibility, then the corresponding reaction is called thermodynamically feasible. The purpose of the work is to screen out some hydrogen producing reaction cluster that is thermodynamically feasible within a certain temperature range within a database of some selected chemical species, while meeting imposed environmental and safety criteria. The first effort in generating reaction clusters is to establish acceptable criteria for thermodynamic feasibility.

Consider a closed, reacting system, and the overall differential for internal energy (U) and its relationship to other state variables.

$$d(nU) = Td(nS) - Pd(nV) + \sum_i \mu_i dn_i \qquad\qquad (7)$$

Re-arranging (7), using the first and second laws of thermodynamics, we determine the total change in chemical potential to be negative, where μ_i is the chemical potential of species i and dn_i is the transfer rate of i to and from the system.

$$-\sum_i \mu_i dn_i = Td(nS) - d(nU) - Pd(nV) = Td(nS) - d(nQ) \geq 0 \qquad (8)$$

Given the definition of the differential of Gibbs energy (G):

$$d(nG) = -nSdT + nVdP + \sum_i \mu_i dn_i \qquad (9)$$

For an isothermal, isobaric closed reacting system, by combining (8) and (9), we find that thermodynamics constrains changes in Gibbs energy to be negative.

$$d(nG) = \sum_i \mu_i dn_i \leq 0 \qquad (10)$$

The equilibrium constant, $K(T)$ is then specified in terms of the change in Gibbs energy for a reaction ($\Delta G^\circ(T)$), which specifies the reaction to occur favorably with some driving force e^z.

$$K(T) \equiv e^{-\Delta G^\circ(T)/RT} \geq e^z \qquad z > 0 \qquad (11)$$

By assuming the equilibrium constant to be of exponential order, we know the function $K(T)$ is bounded to finite values over any temperature range [13].
Combining that with (10) gives the following:

$$\frac{-\Delta G^\circ(T)}{RT} - z \geq 0 \qquad (12)$$

Re-arranging (12) gives us our definition for thermodynamic feasibility:

$$\Delta G^\circ(T) + zRT \leq 0 \qquad (13)$$

The requirement of thermodynamic feasibility for each reaction in cluster synthesis is as follows, where T_j is the temperature of reaction j.

$$\sum_{i=1}^{N^S} \left(G_{iT_j} \right) \left(\delta_{ij} - \gamma_{ij} \right) \leq 0 \qquad j \in \left\{ 1, 2, ..., N^R \right\} \qquad (14)$$

Our formulation employs a database of ΔG° values for each molecular species within a temperatures range, T^L to T^U. This differs from the literature, where the Gibbs energy is usually assumed to be a linear function of temperature, forcing the reactions to occur at the bounds of T^L and T^U [10]. We have found the Gibbs energy of formation to be highly nonlinear, due primarily to phase changes, so by specifying Gibbs at several temperatures and assuming that the reactions can take place at any of those temperature values within the range of T^L to T^U, we can overcome the nonlinearities.

In addition to the cluster satisfying thermodynamic feasibility (14) and the overall desired reaction (6), an atomic species balance must be satisfied, where B_{ki} is the number of atoms of k in species i per molecule.

$$\sum_{i=1}^{N^S} B_{ki} \left(\delta_{ij} - \gamma_{ij} \right) = 0 \qquad k \in \{1, 2, ..., N^A\} \; j \in \{1, 2, ..., N^R\} \qquad (15)$$

Limits on the allowable reaction coefficients must now be placed.

$$\delta_j^l \leq \sum_{i=1}^{N^S} \delta_{ij} \leq \delta_j^u \qquad\qquad j \in \{1, 2, ..., N^R\} \qquad\qquad (16)$$

$$\gamma_j^l \leq \sum_{i=1}^{N^S} \gamma_{ij} \leq \gamma_j^u \qquad\qquad j \in \{1, 2, ..., N^R\} \qquad\qquad (17)$$

$$\delta_{ij} \in \{\phi_1, ..., \phi_n\} \qquad\qquad i \in \{1, 2, ..., N^S\} \; j \in \{1, 2, ..., N^R\} \qquad (18)$$

$$\gamma_{ij} \in \{\varphi_1, ..., \varphi_m\} \qquad\qquad i \in \{1, 2, ..., N^S\} \; j \in \{1, 2, ..., N^R\} \qquad (19)$$

$$0 \leq \delta_{ij} \leq \delta_{ij}^u \qquad\qquad i \in \{1, 2, ..., N^S\} \; j \in \{1, 2, ..., N^R\} \qquad (20)$$

$$0 \leq \gamma_{ij} \leq \gamma_{ij}^u \qquad\qquad i \in \{1, 2, ... N^S\} \; j \in \{1, 2, ..., N^R\} \qquad (21)$$

Inequalities (16) and (17) limit the overall sum of product and reactant coefficients, in each reaction, to lie between upper and lower bounds. Equations (18) and (19) constrain δ_{ij} and γ_{ij} to be integer values, while (20) and (21) put bounds on the allowable integer values.

Next we define flag variables, β_{ij} and θ_{ij}, that indicate whether species i is a product or a reactant in reaction j, respectively. These variables eliminate redundancy within a particular solution. With these new variables we rewrite our coefficient constraints, so that if a species i is involved as a product in reaction j then $\beta_{ij} = 1$ and if it is a reactant in reaction j then $\theta_{ij} = 1$.

$$\beta_{ij} \in \{0,1\} \qquad\qquad i \in \{1,2,...N^S\} \ j \in \{1,2,...,N^R\} \qquad (22)$$

$$\theta_{ij} \in \{0,1\} \qquad\qquad i \in \{1,2,...N^S\} \ j \in \{1,2,...,N^R\} \qquad (23)$$

$$0 \le \delta_{ij} \le \delta_{ij}^u \beta_{ij} \qquad\qquad i \in \{1,2,...N^S\} \ j \in \{1,2,...,N^R\} \qquad (24)$$

$$0 \le \gamma_{ij} \le \gamma_{ij}^u \theta_{ij} \qquad\qquad i \in \{1,2,...N^S\} \ j \in \{1,2,...,N^R\} \qquad (25)$$

To ensure that a species does not occur as both a product and a reactant in the same reaction we add the following, which is not evident in [10].

$$\beta_{ij} + \theta_{ij} \le 1 \qquad\qquad i \in \{1,2,...N^S\} \ j \in \{1,2,...,N^R\} \qquad (26)$$

Limits on the total number of species involved in a reaction are then invoked, and the range of possible reaction temperatures is enforced.

$$\sum_{i=1}^{N^S} \beta_{ij} \le s_P \qquad\qquad j \in \{1,2,...,N^R\} \qquad (27)$$

$$\sum_{i=1}^{N^S} \theta_{ij} \le s_R \qquad\qquad j \in \{1,2,...,N^R\} \qquad (28)$$

$$T_j \in \{\psi_1,...,\psi_n\} \qquad\qquad j \in \{1,2,...,N^R\} \qquad (29)$$

$$T^L \le T_j \le T^U \qquad\qquad j \in \{1,2,...,N^R\} \qquad (30)$$

2.2 ILP Formulation

The above model is the foundation for a structured definition of a feasible thermochemical cycle. To screen and identify all feasible clusters, the algorithm is formulated as the following minimization problem:

$$(P1) \qquad\qquad \min \sum_{i=1}^{N^S} \sum_{j=1}^{N^R} \left(d_i \delta_{ij}^2 + c_i \gamma_{ij}^2 \right)$$

subject to:

$(6), (14) - (30)$

The objective function presented here, featuring adjustable weights on the reaction coefficients, is used only as a tool for identifying the clusters. Constraining the objective to be greater than a known minimum allows for additional cycles to be generated. $P1$ is an integer

linear program (ILP), because each constraint, including the objective function, is linear, and the decision variables can only assume integer values. The reaction coefficients are confined to integer values, so as to eliminate unrealizable and obtuse solutions. The reaction temperatures are also integer values as we have data for Gibbs energy at specific integer temperature values.

With this flexible definition one can search for both the reactions and their temperature, or the reaction temperatures can be specified as a parameter, leaving only the reaction coefficients as the variables. With the conceptualization in place, we now put forth the necessary tools for evaluating generated ATCs.

2.3 Cycle Evaluation

A systematic method must also be employed in the evaluation of the cycles. This includes reaction cluster construction, process integration, and an efficiency calculation. This section describes such a process for the methodic evaluation of generated ATCs.

For the purpose of initial ATC screening, it is assumed that each reaction in a generated cycle goes to completion within the thermodynamically feasible temperature range and that there are no competing products. The analysis assumes that the entrance and exit streams to the system are at a temperature of 298K and a pressure of 1 bar. Each reactor is sequenced appropriately in a simulation software, with heat exchangers and reactors in between the key reactions to model temperature and phase transitions, respectively. The details of flow separation and pumping are not considered in any stage of the presented analysis.

Once the cycle has been constructed a heat integration is performed and the cluster's efficiency is determined. Taking the latent, sensible, and reaction heats from the simulated flowsheet, a pinch analysis is implemented to aid in process integration. Temperature intervals, which break at phase transitions and reaction temperatures, are determined for the hot (i.e. require cooling) and cold (i.e. require heating) process streams. Overall heating and cooling requirements are determined for each temperature interval and then the two streams are plotted against each other, as temperature versus heat duty. The two curves can be moved horizontally in enthalpy so that the hot curve lies above the cold curve. Maximum overlap should be ensured while satisfying a minimum approach temperature or pinch. This will give the designer the areas where heat can be integrated between processes.

The efficiency (η), defined below, is prescribed by Argonne National Laboratory (ANL) [7] and considers the cycle heat duty (Q) and required work (W) against the standard heat of formation of water $(\Delta H^{\circ}_{298K}(H_2O))$. The heat duty, determined from the pinch analysis, is the summation of the needed hot and cold utility requirements (i.e. the areas where the curves do not overlap). The definition of work can include separation, chemical, electrochemical, mechanical, and electrical requirements [7].

$$\eta = \frac{-\Delta H^{\circ}_{298K}(H_2O)}{Q + \dfrac{W}{0.5}} \qquad (31)$$

The primary work to be considered is the work of separation which is equal to ΔG_{sep}, the resulting change in Gibbs energy.

$$\Delta G_{sep} = -RT\sum_i n_i \ln y_i \qquad\qquad (32)$$

This simplistic definition, provided by ANL [7], allows for the calculation of ΔG_{sep} (which is the required work for an ATC that does not involve electrochemical steps, for a base efficiency calculation), where R is the gas constant, T is the absolute temperature, n is the molar flow of each component, and y is the mole fraction. Equation (31) assumes an efficiency of 50% for the thermal equivalent of the required work, which we feel to be a conservative estimate. In the initial, ideal analysis, only the separation costs for obtaining hydrogen and oxygen are included in the work calculation. A promising cycle has a base efficiency that exceeds the threshold value of 35% $(\eta > 0.35)$ [7].

Using this analysis, to identify, screen, and evaluate hydrogen producing ATCs, we have the tools to locate a cluster that is competitive with current technologies. A case study on the iron-chlorine cycle is now presented, which demonstrates the strength and flexibility of the proposed methodology.

3. Results and Discussion: A Case Study on the Fe-Cl Thermochemical Cycle

We now apply the proposed methodology to a case study to assess the performance of iron-chlorine based ATCs for hydrogen production. The atomic species involved in the cycle are Fe, Cl, H, and O, which are ideal elements in terms of economic and environmental concerns. From these species we develop a list of 14 molecular species to be included in the cluster synthesis:

$FeCl_2$, $FeCl_3$, Fe_3O_4, H_2O, HCl, Cl_2, H_2, O_2, Fe, FeO, Fe_2O_3, $Fe(OH)_2$, $Fe(OH)_3$, Fe_2Cl_6

The algorithm $P1$, which is an ILP, is solved using an AMPL based solver, Cbc, available through the NEOS Server at Argonne National Laboratories. Given thermophysical data from Aspen Properties for the above species, at 100 degree temperature intervals between 400K and 1200K, 10 cycles are identified using the parameter set shown in Table 1. The value of zRT is chosen as to allow for the largest possible set of cycles while avoiding null reactions.

This set of cycles is generated by assuming that at least one reaction occurs at 400K and that at least one reaction occurs at 1200K, which allows for better heat exchange. Additional cycles can be generated using the same parameters by constraining the objective function to be greater than the observed minimum.
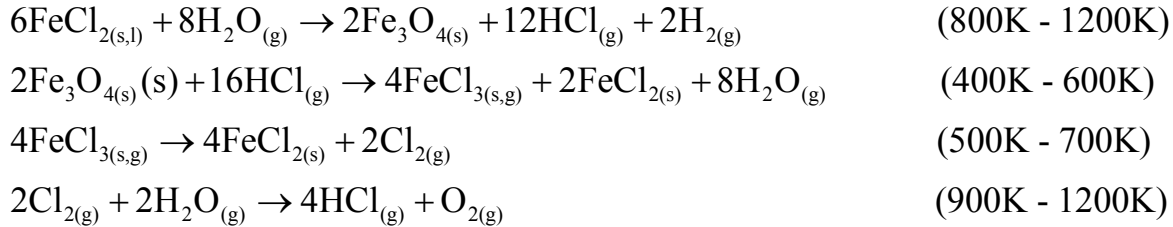
Table 1. List of parameters for $P1$

Parameter	Value
N^A	4
N^S	14
N^R	4
d_i	1
c_i	1
zRT_j	100 J/mol
δ_j^l	1
δ_j^u	20
γ_j^l	1
γ_j^u	20
δ_{ij}^u	16
γ_{ij}^u	16
$\{\phi_1,...,\phi_n\}$	$\{1,2,...,16\}$
$\{\varphi_1,...,\varphi_m\}$	$\{1,2,...,16\}$
s_P	3
s_R	2
T^L	400 K
T^U	1200 K
$\{\psi_1,...,\psi_n\}$	$\{400,500,...,1200\}\,K$

This set of cycles is generated by assuming that at least one reaction occurs at 400K and that at least one reaction occurs at 1200K, which allows for better heat exchange. Additional cycles can be generated using the same parameters by constraining the objective function to be greater than the observed minimum.

Each cluster is evaluated by the methodology outlined above, using a pinch of 20 K in the heat integration, and their efficiencies are given in Table 2. A cycle, found in the literature

as one of the most promising Fe-Cl cycles [14], is generated, in addition to the other ten cycles, with an objective value of 81, using the same parameter set and letting $T_1 = 1200K$, $T_2 = 500K$, $T_3 = 700K$, and $T_4 = 1000K$. This cycle, shown below with literature suggested temperature intervals [14] and represented by Figure 4, has a base efficiency of 35.6%, which is comparable with the literature.

$$6FeCl_{2(s,l)} + 8H_2O_{(g)} \rightarrow 2Fe_3O_{4(s)} + 12HCl_{(g)} + 2H_{2(g)} \qquad \text{(800K - 1200K)}$$

$$2Fe_3O_{4(s)}(s) + 16HCl_{(g)} \rightarrow 4FeCl_{3(s,g)} + 2FeCl_{2(s)} + 8H_2O_{(g)} \qquad \text{(400K - 600K)}$$

$$4FeCl_{3(s,g)} \rightarrow 4FeCl_{2(s)} + 2Cl_{2(g)} \qquad \text{(500K - 700K)}$$

$$2Cl_{2(g)} + 2H_2O_{(g)} \rightarrow 4HCl_{(g)} + O_{2(g)} \qquad \text{(900K - 1200K)}$$

This study demonstrates the power of our methodology to identify pre-existing ATCs and unknown cycles. The methodology can also be modified to generate and evaluate hybrid ATCs [15], or thermochemical cycles with electrochemical steps. This flexible systems engineering approach will no doubt result in the discovery of economically feasible ATCs for the production of hydrogen. Once a promising cycle is identified then further analysis will be conducted, including detailed parametric studies on reaction thermodynamics and kinetics, along with the design of reactors and separation processes to give a full energy and economic evaluation of the proposed cycle.
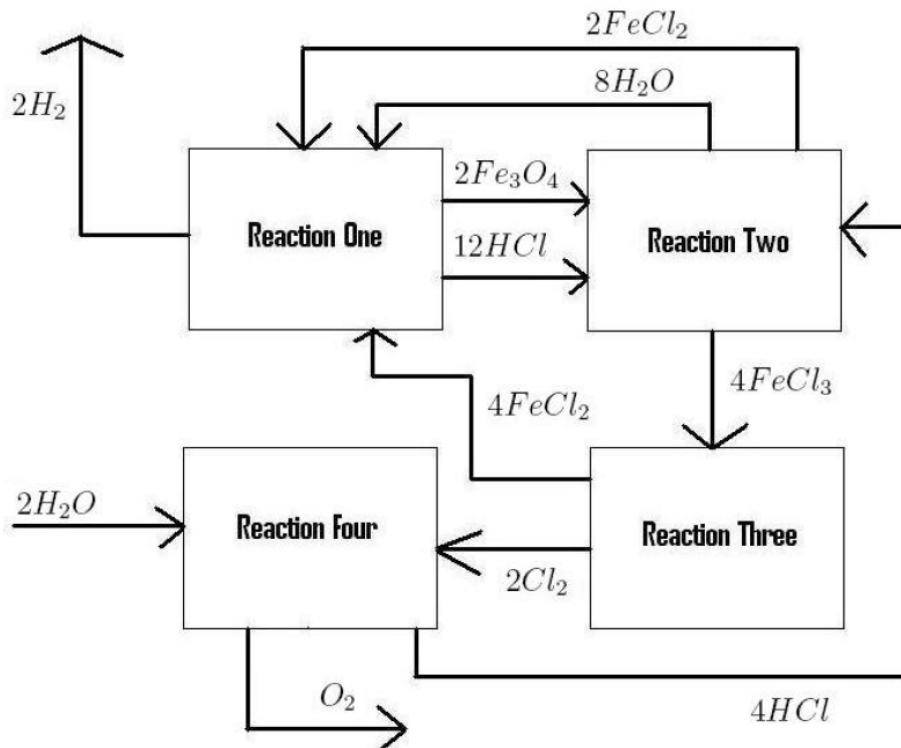
Figure 4. Diagram of the identified Fe-Cl ATC for hydrogen production, that can be found in the literature [14]

Table 2. Base efficiencies of the 10 identified Fe-Cl ATCs using $P1$ with the parameter set from Table 1, and assuming that at least one reaction occurs at the upper temperature limit and that at least one reaction occurs at the lower temperature limit

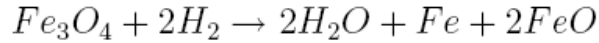| Cycle Number	Reactions	Base Efficiency (%)
1	$6H_2O + 10FeO \rightarrow 2Fe_3O_4 + 2H_2 + 4Fe(OH)_2$	42.5
	$2Fe_3O_4 + 3Fe(OH)_2 \rightarrow 3H_2O + O_2 + 9FeO$	
	$Fe(OH)_2 \rightarrow H_2O + FeO$	
2	$8H_2O + 4Fe \rightarrow 4H_2 + 4Fe(OH)_2$	44.1
	$2H_2 + 4Fe(OH)_2 \rightarrow 6H_2O + O_2 + 4Fe$	
3	$8H_2O + 4Fe \rightarrow 5H_2 + 2FeO + 2Fe(OH)_3$	48.8
	$H_2 + 2Fe(OH)_3 \rightarrow 4H_2O + O_2 + 2Fe$	
	$H_2O + 2FeO \rightarrow H_2 + Fe_2O_3$	
	$3H_2 + Fe_2O_3 \rightarrow 3H_2O + 2Fe$	
4	$2H_2O + Fe \rightarrow H_2 + Fe(OH)_2$	$Inordinate$ [2]
	$Fe + 3Fe(OH)_2 \rightarrow 3H_2 + O_2 + 4FeO$	
	$3H_2O + 5FeO \rightarrow H_2 + 2Fe(OH)_2 + Fe_3O_4$	
	$Fe_3O_4 + 3H_2 \rightarrow 3H_2O + 2Fe + FeO$	

5     $3H_2O + 5FeO \rightarrow Fe_3O_4 + H_2 + 2Fe(OH)_2$ 35.0

$$2H_2 + 4Fe(OH)_2 \rightarrow 6H_2O + O_2 + 4Fe$$

$$5H_2O + 3Fe \rightarrow 3H_2 + FeO + 2Fe(OH)_2$$

$$Fe_3O_4 + Fe \rightarrow 4FeO$$

6     $9H_2O + 4Fe \rightarrow 6H_2 + Fe_2O_3 + 2Fe(OH)_3$ $Inordinate^2$

$$Fe_3O_4 + 3H_2 \rightarrow 3H_2O + 2Fe + FeO$$

$$FeO + Fe_2O_3 \rightarrow Fe_3O_4$$

$$H_2 + 2Fe(OH)_3 \rightarrow O_2 + 2Fe + 4H_2O$$

7   $6H_2O + 10FeO \rightarrow 2Fe_3O_4 + 2H_2 + 4Fe(OH)_2$ 43.0

$$2Fe_2O_3 + 3Fe(OH)_2 \rightarrow 3H_2O + O_2 + 7FeO$$

$$Fe_3O_4 + Fe(OH)_2 \rightarrow H_2 + 2Fe_2O_3$$

$$Fe_3O_4 + H_2 \rightarrow H_2O + 3FeO$$

8   $6H_2O + 10FeO \rightarrow 2Fe_3O_4 + 2H_2 + 4Fe(OH)_2$ 41.7

$$2Fe_3O_4 + 3Fe(OH)_2 \rightarrow 3H_2O + O_2 + 9FeO$$

$$FeO + Fe(OH)_2 \rightarrow H_2 + Fe_2O_3$$

$$H_2 + Fe_2O_3 \rightarrow H_2O + 2FeO$$

$$9 \quad 5H_2O + 9FeO \rightarrow 2Fe_3O_4 + 2H_2 + 3Fe(OH)_2 \quad Inordinate^2$$

$$Fe + 3Fe(OH)_2 \rightarrow 3H_2 + O_2 + 4FeO$$

$$Fe_3O_4 + H_2 \rightarrow H_2O + 3FeO$$

$$Fe_3O_4 + 2H_2 \rightarrow 2H_2O + Fe + 2FeO$$

$$10 \quad 8H_2O + 4Fe \rightarrow 4H_2 + 4Fe(OH)_2 \quad Inordinate^2$$

$$4Fe(OH)_2 \rightarrow 4H_2 + O_2 + 2Fe_2O_3$$

$$6H_2 + 2Fe_2O_3 \rightarrow 6H_2O + 4Fe$$

^{2} For $\Delta G < 0$, $T_j > 1123K$

4. Conclusions

In this paper we outline a methodology that can be used to identify, screen, and evaluate hydrogen producing alternative thermochemical cycles. The process is five fold, giving rigorous instructions for (i) conceptualization, (ii) reaction cluster synthesis, (iii) flowsheet design, simulation, and analysis, (iv) process integration and (v) performance evaluation. Starting with a formal definition of thermodynamic feasibility , an automatic selection algorithm is proposed, followed with a base level of analysis using simulation software, the use of a pinch analysis for heat integration, and ending with a standard definition for an efficiency calculation.

The promise of the process is then demonstrated through a case study involving the Fe-Cl thermochemical cycle. We are then able to identify a, with our algorithm, a cycle that can be found throughout the literature, and determine an efficiency for that cycle that is comparable with the literature. This method allows for a standard and efficient procedure for the future evaluation of alternative thermochemical cycles for hydrogen production and can be extended to hybrid cycles and to higher order evaluations.

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