

Generation of Hydrogen Production Cycles Through Water Splitting

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Abstract

A computer procedure for the automatic generation of water-splitting cycles and thermodynamic analysis is discussed in detail. The method aims at finding new water-splitting cycles that are thermodynamic feasible at lower temperatures than found in many currently well known cycles. Two methods are used to determine cycles. One method starts with a pool of 100 molecules and the other generates molecules from the combination of functional groups. In each case cycles are generated by enumerating molecules in the different configurations. Thermodynamic properties such as the Gibbs energy and enthalpy of reaction for stoichiometrically viable reactions are calculated. Finally, each thermodynamically feasible cycle undergoes a pinch analysis to determine the thermal efficiency of the cycle. Cycles with high efficiencies on a thermal basis are discussed in further detail such as the inclusion of separation work.

Purpose and Introduction

Nearly 90 percent of the world's energy is supplied from the combustion of fossil fuels. The high demand of energy, decreasing fossil fuel supply and their negative environmental impact are all reasons that have resulted in a strong initiative and significant research for alternative energy sources. One of the most promising and studied energy alternatives is the production of hydrogen. The current methods for producing hydrogen have proven to be either inefficient or require the use of fossil fuels, such as steam reforming. Steam reforming is a process that produces hydrogen from natural gas. The process uses the heat of combustion from methane to supply heat to the hydrogen production reaction. The process is used today in the petrochemical industry, but is not a long term solution for hydrogen production. The Department of Energy and various research studies have identified water-splitting cycles as a viable long term solution for the production of hydrogen.

Water-splitting cycles involve the formation of hydrogen and oxygen from the decomposition of water. The cycles utilize a combination of thermally driven chemical reactions. For the thermal decomposition of water alone, a temperature of more than 2500°C is required. If however, a two or more reaction cycle is utilized, the temperature of each reaction can be greatly reduced from 2500°C . The only net reactant of the cycle is water and net products are H_2 and O_2 . The reactants other than water are regenerated as products in other reactions in the cycle. If any reaction in the cycle is not thermodynamically feasible then it is possible that through the addition of electrical work the reaction will proceed. This is known as an electrolysis reaction. The pure electrolysis of water uses electricity to decompose it into hydrogen and oxygen, but it requires large amounts of energy. The process results in relatively low efficiencies usually around 25%.

Brown et al performed a recent study which identified and rated known water-splitting cycles for a variety of criteria. Some of the reasons cycles were downgraded was if they included largely unfavorable Gibbs energy of reactions, required the flow of solids, or were overly complex (e.g. containing more than 3 reactions). One of the most promising cycles the study identified was the Sulfur-Iodine cycle shown at the top of the next page.

Sulfur-Iodine Cycle

	Reaction Temperature
$2\text{H}_2\text{SO}_4(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$	850 °C
$2\text{HI} \rightarrow \text{I}_2(\text{g}) + \text{H}_2(\text{g})$	450 °C
$\text{I}_2 + \text{SO}_2(\text{a}) + 2\text{H}_2\text{O} \rightarrow 2\text{HI}(\text{a}) + \text{H}_2\text{SO}_4(\text{a})$	120 °C

An important aspect of the Sulfur-Iodine cycle is the high temperature required for the decomposition of H_2SO_4 into SO_2 , H_2O , and O_2 . In fact, nearly all cycles studied by Brown include at least one reaction where the required temperature exceeded 700 °C. Reactions that occur at lower temperatures likely use electrolysis. The heat requirement reduction for these lower temperature reactions is supplanted by the addition of electrical work as energy.

In general, most water-splitting reaction cycles are composed of one or more high temperature, endothermic reactions. The cycle is usually accompanied by one or more low temperature exothermic reaction/s. It is therefore a necessity that heat be provided from an outside source for the reactions to be realizable. The current solution for the practical implementation of these high temperature cycles involves the coupling of the cycles with nuclear reactors, and using the reactor waste energy as the source for heat. There are many problems in using nuclear reactors as the heat source to supply to the reactions. First, the new Generation IV nuclear reactor systems being developed are still be researched and designed. It is not expected that these reactors would be available for construction until the year 2030. Secondly, hydrogen production from nuclear reactor systems hinders production capabilities. Hydrogen could only be produced in locations where nuclear facilities with high temperature capabilities exist. Lastly, high temperature reactions require formulation of new heat exchanger design and materials which could withstand elements such as corrosion at such high temperatures. Additionally, there could be other methods for heat supply, such as a high temperature furnace, but these systems would likely not be economic.

The purpose of this report is to identify new reaction cycles in which the reactions proceed at overall lower temperatures. Reactions that are capable of occurring at lower temperatures allow more freedom into the methods for the supply of heat utility and also reduce the costs required for operation. The method enumerates molecules in different reaction

configurations and the thermodynamics of the reactions are evaluated. The temperatures of the reactions are varied until the thermodynamic constraints are satisfied or the cycle is ignored if the constraints are not satisfied. Generated cycles are analyzed further for a determination of efficiency used in cycle ranking. The following sections discuss the methods for generation and evaluation in detail.

Molecular Method

A computer program written in VBA language was developed and used to search for low temperature reaction cycles from an initial population of molecules. The flow diagram for the algorithm is presented in **Figure 1**. The program first begins by choosing a set of molecules and determines if the combination of molecules satisfy two significant parameters: atomic balance and favorable Gibbs energy of reaction. If the reaction satisfies both parameters it undergoes the pinch analysis to determine the minimum heat utility required for the cycle. The thermodynamic methods are discussed in later sections. The algorithm is constructed for different configurations of reaction cycles and the results are analyzed for each configuration.

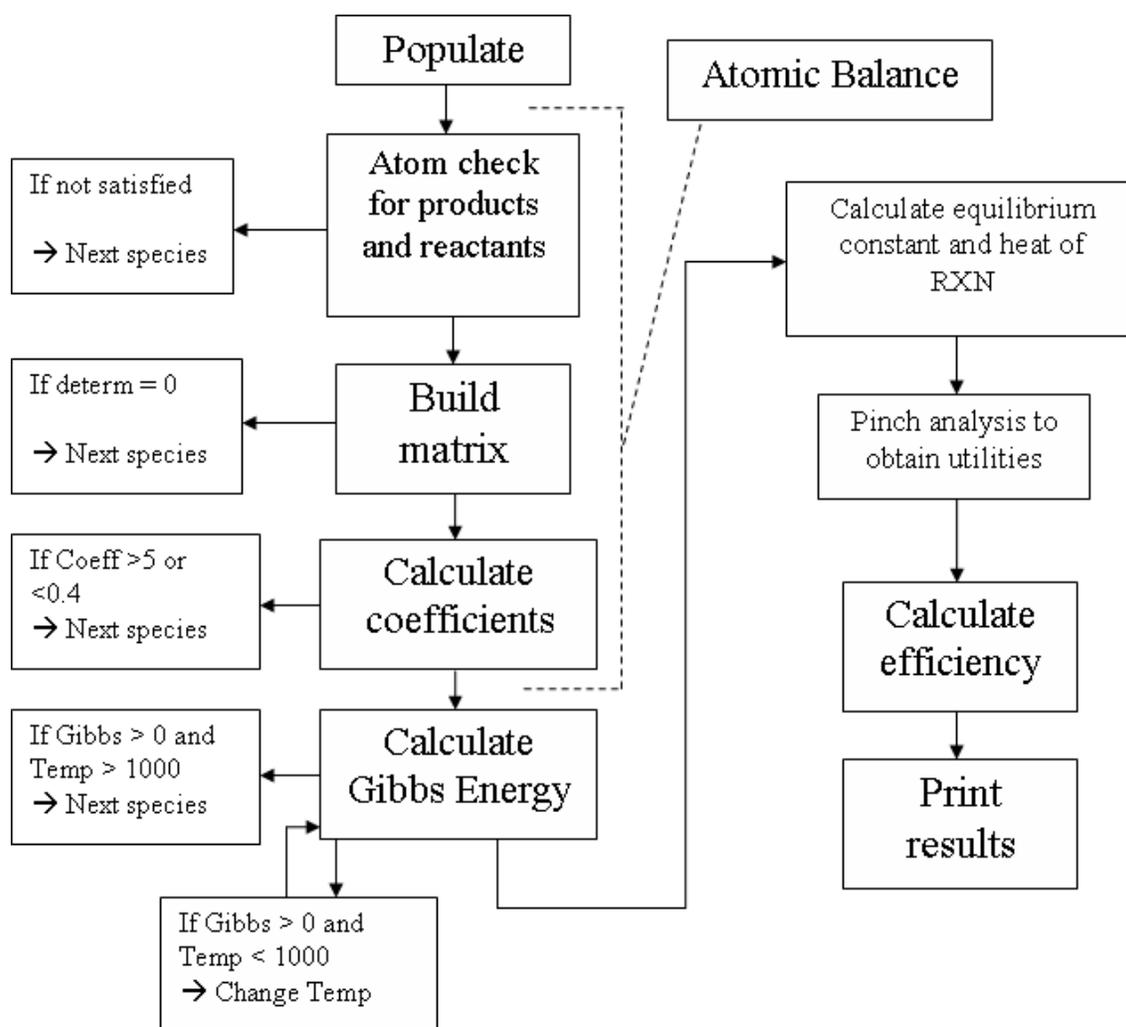


Figure 1 – Flow sheet for code

Populate

The initial step of the code is to populate a combination of molecules chosen from the total molecule population to test for the viability of a water-splitting cycle. The total molecule population consists of 100 molecules. The list of molecules is present in **Appendix A**. Organic, inorganic, cyclic, and non-cyclic molecules were considered. The code is run until every unique combination of molecules from the pool is tested. The initial constraint on enumerating the population is molecular identification. Molecular identification is used to ensure that each molecule in the species is unique.

Atomic Balance

The atomic balance consists of three steps;

1. Counts the number of each atom in the reactants and the products
2. Builds a matrix using the coefficients from each molecule
3. Calculates the solution matrix using a Gauss-Jordan elimination method.

An example using two reactants and two products is shown. For a two reactants and two products cycle, the configuration of the reactions is as follows:



The net reactant and products for any water-splitting cycle is water as the reactant and oxygen and hydrogen as the products; the other components of the cycle are continuously recycled. The pool of molecules that was used contains only 6 different atoms; hydrogen, oxygen, nitrogen, carbon, bromine, and chlorine. The program counts and identifies the atoms contained in molecules A, B, C, and D. The first constraint tests to see if the same types of atoms are present on the product and reactant side. If, for example, bromine is in the reactant side but not the product side, then the code will automatically identify this case as unsolvable and move on to the next unique combination of molecules.

Once the first reaction in a two reaction sequence is balanced, the second reaction will, by default, also be balanced using the stoichiometric coefficients determined by the first reaction balance (i.e. a, b, c, d). The following lists represent the corresponding atomic balances for Reaction 1.

$$\text{Oxygen Balance: } O_A + O_B - O_C - O_D = 0$$

$$\text{Hydrogen Balance: } H_A + H_B - H_C - H_D + 2 = 0$$

$$\text{Atom X balance: } X_A + X_B - X_C - X_D = 0$$

$$\text{Atom Y balance: } Y_A + Y_B - Y_C - Y_D = 0$$

O_A represents the number of oxygen atoms in molecule A, O_B is the amount in molecule B, and so on. The equations state simply that the difference in the number of atoms on each side of the reaction must be equal. Therefore, the differences of the reactant and product sides are equal to zero. The oxygen and hydrogen balances are always used because these atom types are always present in the cycle. The 2 found on the left hand side of the hydrogen balance represents the two hydrogen atoms found in the reactant of 1 mol H_2O . X and Y represent the corresponding balances for the remaining atoms found in the molecules A, B, C, and D hydrogen or oxygen. For instance if chlorine and nitrogen are also present in A or B, and also found in either molecules C or D, then X would be the chlorine balance and Y would represent the nitrogen balance. It is possible that there exists the situation where either one of two molecules on both the reactant and product have more than two similar atom types other than O_2 and H_2 . In this situation, the extra balances are not independent and only two balances need to be chosen.

The atomic balances in this cycle configuration represent a system of four linear equations with four unknowns. This system of equations can be solved through simple matrix algebra. Therefore, the next step in the atomic balance step builds such a matrix using the atom count from the previous step. An example of the coefficient matrix is on the following page.

$$\begin{pmatrix} O_A & O_B & -O_C & -O_D \\ H_A & H_B & -H_C & -H_D \\ C_A & C_B & -C_C & -C_D \\ Cl_A & Cl_B & -Cl_C & -Cl_D \end{pmatrix} \begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = \begin{pmatrix} 0 \\ -2 \\ 0 \\ 0 \end{pmatrix}$$

Coefficient Matrix
Variable Matrix
Solution Matrix

The above matrix represents the situation in which molecules A or B, and molecules C or D contained one or more carbon (C) and chlorine (Cl) atoms. This is the reason why these atoms appear in the coefficient matrix. The 2 appearing in the hydrogen balance now is found as -2 in the solution matrix. The sign change is due to the fact that the two excess hydrogen atoms from H₂O must be moved to the other side of the equation balance in the set up of the matrices, since the number of hydrogen atoms in 1 mole of water does not depend on the coefficients a, b, c, and d.

This first step in solving the variable matrix is finding if there is a unique defined solution to the matrix system. The determinant of the coefficient matrix is used to determine if there is a solution. If the determinant of the coefficient matrix is zero then there is no unique solution to the matrix. In that case the next set of molecules in the population is tested. Otherwise, the inverse of the coefficient matrix is calculated. The inverse coefficient matrix is then multiplied by the solution matrix to determine the values of the coefficients a, b, c, and d. Excel worksheet functions for calculating both the matrix determinant and inverse were utilized in this portion of the program.

After the coefficients were calculated for a group of molecules more constraints were applied. All coefficient values were required to be integer values and between the values of 0.5 and 5.

Balanced Coefficient Constraints

$$0.5 \leq a, b, c, d \leq 5$$

a, b, c, d must be multiple of 0.5

These coefficient constraints are implemented due to reaction feasibility possibilities. Limiting the number of molecules that are required to reactant with one mole water increases the possibility that the reactions found can actually occur from a kinetic viewpoint. The more

molecules reacting per one molecule of water the more bonding sites that are required, accompanied by very low reaction rates. If all of the discussed atomic balance and coefficient constraints are satisfied the cycle undergoes a thermodynamic analysis.

Thermodynamic Methods

An extremely important step in the algorithm to determining unique, low temperature, water-splitting cycles is thermodynamic evaluation. Once a set of molecules for a given reaction configuration was determined to satisfy the atomic balance and stoichiometric coefficient constraints, the reactions in the cycle were subject to a thermodynamic evaluation for feasibility. The first step in the procedure analyzed the Gibbs energy of reaction for each reaction in the cycle. The Gibbs energy of reaction is given below in **Equation 1**.

$$\Delta G_r^\circ = \sum_i^n v_i \Delta G_f^\circ(T_r)_{product,i} - \sum_j^m v_j \Delta G_f^\circ(T_r)_{reactant,j}$$

Equation 1 – Gibbs Energy of Reaction

$\Delta G_f^\circ(T_r)$ denotes the standard Gibbs energy of formation of either a reactant or product species at the reaction temperature, T_r . The stoichiometric coefficients obtained from the balanced reaction equation are v_j and v_i for product species j and reactant species i , respectively. If the reaction has a Gibbs free energy that is negative, the reaction is said to be favorable and spontaneous, and will occur at the reaction conditions without additional work or heat. A reaction with Gibbs energy of over 50 kJ is thermodynamically not favorable and possibly favorable for Gibbs energy from 0 to less than 50 kJ. In the latter situation, the reaction will proceed only if work or energy is applied, such as in the form of electrical energy. The Gibbs free energy, however, does not provide any information about the rate kinetics of the reaction. In this analysis all reactions in the cycle are required to have a negative Gibbs free energy of reaction in order for the cycle to undergo further thermodynamic evaluation. This is accomplished by individually analyzing each cycle in the reaction. The reaction temperature is increased incrementally ($\Delta T = 10 \text{ K}$) until the reaction is found to have a Gibbs energy of reaction less than zero. If the maximum allowed reaction temperature of 975 K is exceeded before this constraint is met, the cycle is deemed unfit and a new set of molecules is tested back through the atomic balance. If the first reaction in the cycle satisfies the negative Gibbs energy constraint then subsequent reactions are analyzed similarly.

Once a hydrogen producing cycle is found to satisfy the Gibbs energy limitations for all reactions, a pinch analysis is automatically performed in order to find the minimum utility requirements. A generic two reaction configuration cycle is considered and pictured in the flow diagram in **Figure 2**. Again, this figure represents a cycle configuration of four randomly chosen molecules, A, B, C, and D. In the first reaction A and B are reacted with one mole H_2O and the products are C, D, and $\frac{1}{2}$ mole O_2 . The second reaction is the reaction of C and D to form A, B, and one mole H_2 . The basic set-up of this configuration can also be found in **Table 1**. The necessary stoichiometric reaction amounts for A, B, C, and D are determined earlier in the algorithm. In this example the Gibbs energy is largely negative and complete conversion of all reactants is assumed.

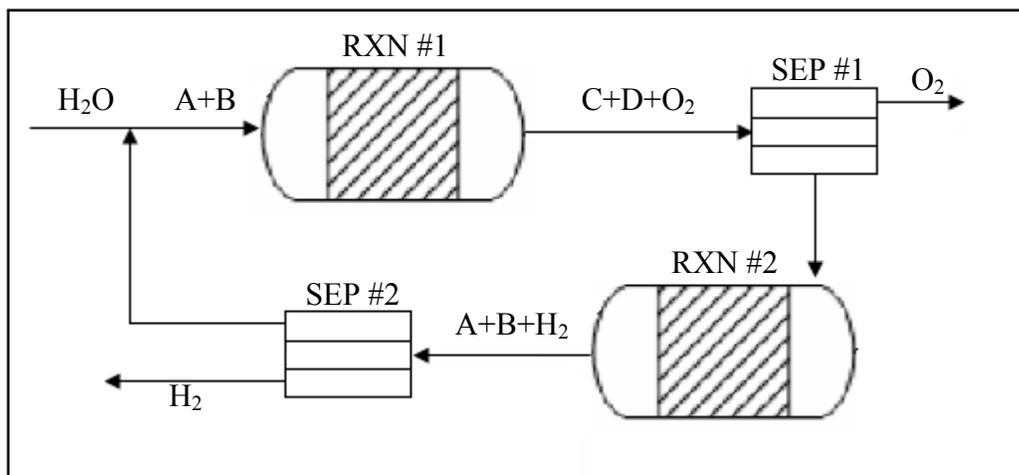


Figure 2 – Simple 2 Reaction Cycle

The pinch method design determines the minimum heat utilities by constructing intervals in which heat can only transfer from higher temperature intervals to lower temperature intervals (2nd law of thermodynamics). For a given network of streams there exists a pinch temperature (pinch point) in which only hot utility is needed above the pinch and only cold utility is required below the pinch temperature. The pinch temperature is determined by the allowed minimum approach temperature (T_{\min}). The minimum approach temperature is the lowest value of temperature difference in which any two streams in the network are allowed to transfer heat. The lower T_{\min} the more area that will be required in the heat exchanger design, however, in this analysis the heat exchanger design network is not considered and T_{\min} is equal to 10 K for all cycles considered.

Available excess heat is either from reactions with exothermic heats of reaction or from hot streams which can transfer heat to colder streams. The amount of heat that is unable to be transferred in this manner will require a hot utility to supply the remaining needed heat duty.

Pinch Analysis

An illustration of the pinch interval analysis is provided in **Figure 3**. Consider the cycle previously discussed with the same configuration as in **Figure 2**. Water is the only reactant for reaction 1. This inlet water is heated from ambient conditions because the cycle is already assumed in steady operation and A and B are already being regenerated from reaction 2. The dashed lines separate intervals in which heat is allowed to transfer without violating the 2nd law of thermodynamics. This figure represents a generic case in which the temperature of reaction 2 is higher than reaction 1. This will not always be the case and the program determines which reaction temperature is higher and adjust the calculations accordingly.

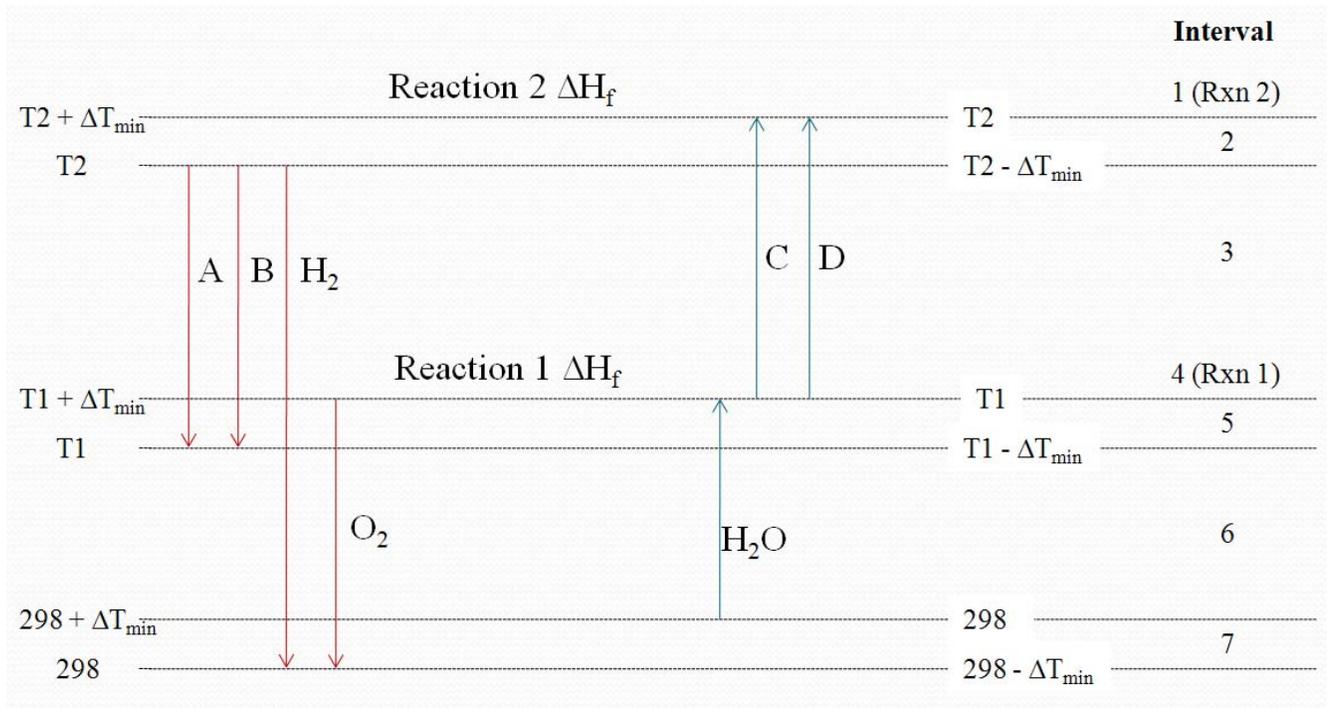


Figure 3 – Pinch Analysis

Energy Cascade

The next step after dividing the streams into temperature intervals is to construct a cascade diagram. The cascade diagram is illustrated in **Figure 4**. For each temperature interval,

the change in enthalpy of the cold streams is subtracted from the change of enthalpy of the hot streams. If there is a deficiency of available heat in any interval this value will be negative. The surplus or deficiency of heat from the highest temperature level is added to the same value for the next highest interval, and so on for each subsequent interval. The most negative value represents the magnitude (opposite in sign) of the required hot utility. If any less than the minimum hot utility is applied then in one or more temperature intervals there would be a deficiency of available heat. The cold streams would not reach their required temperature. The heats of reaction are added as the negative of their actual value. This is due to the fact that an exothermic (negative in sign) heat of reaction will donate excess (positive) heat to the lower temperature intervals and vice versa for an endothermic reaction (donates heat deficiency). The cold utility is found by subtracting the hot utility value from the sum of the last (lowest temperature) value in the cascade diagram.

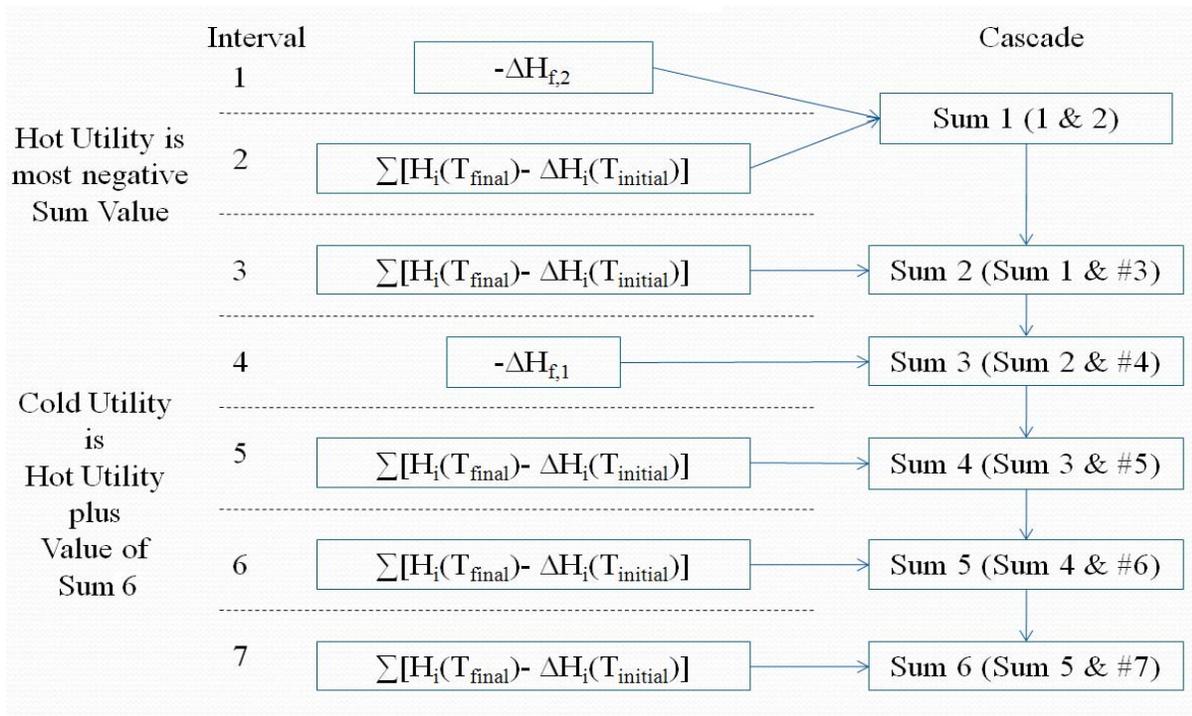


Figure 4 – Cascade Diagram

In order to construct the pinch and cascade diagrams the heat of reactions and thermal enthalpy change due to temperature difference is calculated for each species. The heat of reaction is expressed similarly to the Gibbs energy of reaction and is a function of the heat of formation of the individual molecules involved in the reaction.

$$\Delta H_r^\circ = \sum_i^n v_i \Delta H_f^\circ(T_r)_{product,i} - \sum_j^m v_j \Delta H_f^\circ(T_r)_{reactant,j}$$

Equation 2 – Enthalpy of Reaction

The thermal enthalpy change due to temperature increase or decrease of a species, i , is presented below in **Equation 3**. The thermal enthalpy change is dependent on the amount of species and on the heat capacity change, C_p , of the molecule over the temperature interval.

$$H_i^\circ(T_2) = H_i^\circ(T_1) + \int_{T_1}^{T_2} n_i C_{p,i} dT$$

Equation 3 - Thermal Heat Capacity

The use of thermodynamic correlations for all the molecules in this study over wide distribution of temperature values was of key importance. Accurate data and correlations ensure the accuracy of the thermodynamic feasibility and cycle efficiencies. A variety of sources containing this information was compared. Two references tables, the JANAF thermodynamic table and Yaws chemical properties handbook were decided to be the most accurate and useful for application in the cycle creation program. The JANAF tables are used for inorganic molecules, and the Yaws handbook is used for the molecules containing carbon atoms. The JANAF tables only contained information for organic molecules containing two or less carbon atoms. For the rest of the molecules, the Yaws handbook is used to determine thermodynamic properties. The Yaw's handbook contains thermodynamic information for molecules containing up to 28 carbon atoms.

The JANAF tables and Yaws handbook use a combination of experimental data and correlations. The JANAF tables correlate the Gibbs and enthalpy data from statistical mechanical relationships. The methods differ depending on the molecular structure. For instance, the method of calculating the Gibbs energy of formation for a compound is presented in **Equation 4**.

$$\Delta G_f^\circ(T) = \Delta H_f^\circ(T) - T \left[S^\circ(T)_{compound} - \sum S^\circ(T)_{elements} \right]$$

Equation 4 - Gibbs Energy of Formation for a compound

The JANAF data was presented in the form of data tables and required a best fit correlation to be manually created in Excel to implement a continuous temperature range of

values in the program. The correlations presented in the Yaws handbook were much easier to implement into the algorithm. The Gibbs and enthalpy data were given as constants in the following form.

$$\Delta G_f = A + B * T + C * T^2$$

$$\Delta H_f = A + B * T + C * T^2$$

Equation 5 - Gibbs and Enthalpy Correlation Equations

The constants are given for each molecule used in the code.

The figures below illustrate the comparison of two molecules found in both JANAF and Yaws in order to determine there are large deviations in the calculations of the two methods. **Figure 5** displays the heat of formation for methyl chloride determined by JANAF and Yaws. There is a slight difference in the values calculated via each method, but the deviation was only found in the enthalpy of formation correlations. The values for C_p and Gibbs energy of formation were found to match nearly exactly for all molecules examined. Another example of the slight differences found in the determination of the enthalpy of formation for water and is seen in **Figure 6**.

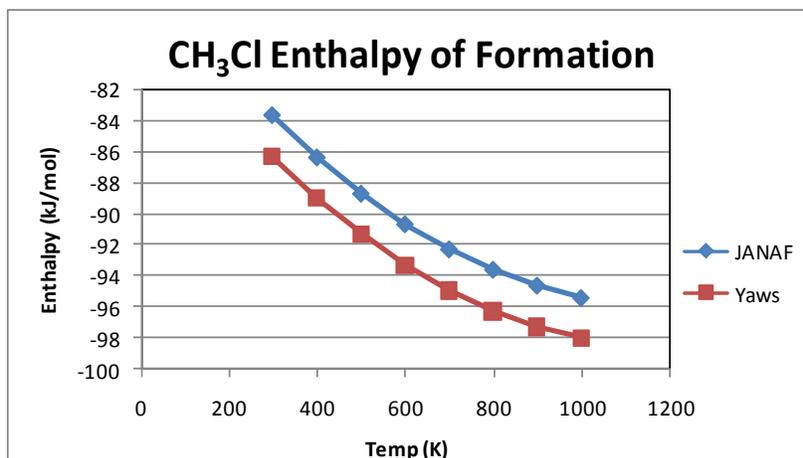


Figure 5 - Enthalpy of Formation for Methyl Chloride

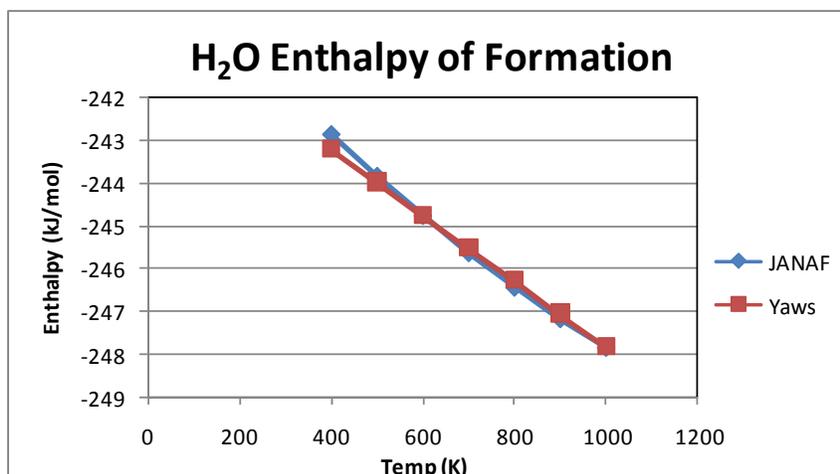


Figure 6 - Enthalpy of Formation for Water

Due to the overall similarity of the two thermodynamic sources, JANAF and Yaws, it was determined integrated use of both correlation data sets would not have a significant influence of error of the efficiency results.

The efficiency of the cycle is defined in this analysis as the standard heat of formation of one mole of water divided by the minimum hot utility for the cycle.

$$\eta = \frac{\Delta H_f^\circ(298.15 K)}{Q_{min}}$$

Equation 6 – Basis Efficiency Equation

In addition to efficiency, the equilibrium constant for each reaction in the cycle was calculated. The equilibrium constant determines the amount of conversion in each reaction and is defined as

$$K(T) = e^{\frac{-\Delta G_{rxn}}{RT}}$$

Equation 7 - Equilibrium Constant

Where R is the universal gas constant equal to $8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Separation Work and Excess Reactants

The consideration of separation work is important when further determining cycle feasibility and practicality. In this analysis, the ideal separation work is calculated from the change in Gibbs energy on mixing, shown below.

$$W_{SEP_Minimum} = \Delta G_{mixing} = R \cdot T \left[\left(\sum_i n_i \cdot \ln(\gamma_i x_i) \right)_{OUT} - \left(\sum_i n_i \cdot \ln(\gamma_i x_i) \right)_{IN} \right]$$

Equation 8 – Minimum Separation Work

This calculation is only an initial approximation for the required work to separate unreacted components and products from each reaction in the cycle. The actual work required can only be accurately determined in the final stages of the cycle design when the complete process flow diagram is constructed. An efficiency of 50% for the amount of work required from the ideal calculation to the actual calculation is recommended by Lewis et al and that value is used for this study. The inclusion of separation work also changes the efficiency calculation for the cycle as in the equation below. The work value is simply added the cycle heat requirement in the denominator of the efficiency calculation discussed previously.

$$\eta = \frac{\Delta H_f^\circ(298K)}{Q + W}$$

Equation 9 - Efficiency equation with heat and work

The equilibrium constant calculations were used to determine the overall conversion of hydrogen for cycles with high efficiencies. It is possible in cases where the Gibbs energy of reaction is not significantly favorable there is a low conversion to hydrogen product. Therefore, in addition to finding all cycles with negative Gibbs energy in each reaction, cycles were identified in which the Gibbs energy was only slightly positive and considerable conversion can be achieved via the addition of excess reactants. It is also true that in the cases where the Gibbs energy is negative, but only slightly, the addition of excess is useful in obtained overall hydrogen conversion to near 100 %. In these cases, work calculations were adjusted by the addition of excess reactant feed to the reaction with the water feed. In general, the ratio of reactant feed from stoichiometric values was 3:1 when adding excess reactants, attempting to force the reaction to the right. The separation work was recalculated in these situations and the impact on conversion and efficiency change is discussed.

Electrolysis

In the determination of new, feasible cycles the search was not limited to cycles with all reactions having a negative or slightly positive Gibbs energy. In cases where there was only one reaction with a very highly positive Gibbs energy of reaction the molecules were identified and examined for the possibility of an electrolysis reaction. Electrolysis is a procedure by which the addition of electrical work to the system allows to separate an ionic compound. If such compounds were present in the reaction, the required electrical work is calculated by the Nernst equation.

$$W_{\text{electric}} = zF\Delta E$$

Equation 10 – Nernst Equation

where z is the number of electrons transferred in the electrolysis, F is Faradays constant, and ΔE is the reduction potential or electromotive force in volts for the oxidation/reduction process. This work is included with the separation work in the efficiency calculations for cycles that possess the possibility for one reaction to occur via electrolysis.

Kinetics and Reactive Selectivity

The kinetics were not considered in any individual reactions. The only step taken to try to ensure kinetic feasibility was to limit the stoichiometric coefficients or reactants normalized to one mole water feed. In addition, in cases where cycles existed but where multiple reactants had coefficients at or near the limiting case of five the cycles were manually eliminated from further analysis and discussion. Accordingly, the reaction selectivity is an important consideration and was not studied in this report. For high potential cycles a literature search was conducted in order to find information about reaction kinetics and selectivities but was unsuccessful in yielded any useful information.

Functional Group Method

The second method for cycle generation that was considered in this project was a functional group method. In this method, a pool of functional groups were combined to form feasible molecules. Table 1 shows the functional groups and bonds present on each group. The code that was used is similar to the molecular method in the enumeration of the different possibilities. The code utilized as many as five functional group to form molecules. The main advantage to using this method over the molecular method is the ease in introducing new atoms. The current molecular method only utilizes six atoms.

Functional Groups				
	-CH ₃	>CH ₂	>CH-	>C<
=CH ₂	=CH-	=C<	=C=	≡CH
≡C-	-F	-Cl	-Br	-O-

Table 1 - Functional Groups Used

Constraints

The constraints used in this method were taken from the previous work by Joback and Stephanopoulos. Joback used these constraints to generate molecules with specific improved properties used for a variety of applications such as refrigerants, solvents, and polymers. For this project, only some of the structural constraints were used in the generation of molecules. They are as follows,

1. The number of groups having an odd number of free bonds must be even.
2. There are three types of bonds that were considered: single, double, and triple. Each of these bonds must have a complement in order for the molecule to be viable.

Flow sheet for code

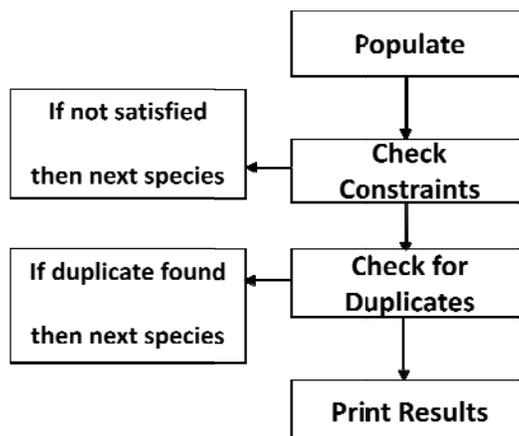


Figure 7 – Flow Sheet for Functional Group Method

Figure 7, represents the flow sheet of the code used in the functional group method. Initially, the code will populate every combination possible through enumeration. Once this has been done, the constraints will be checked, followed by a check for duplicates. Once the molecules are generated, these molecules can be placed in the molecular method and run in the same manner as before.

Results

A pool of 100 molecules, all of relatively low molecular weight, was chosen from Yaws Chemical Handbook and JANAF Thermochemical tables. Cycles were generated in a variety of different configurations; one configuration was already considered, the two reactants and two products. **Table 2** details the other configurations. The list of all molecules used and their chemical formula can be found in **Appendix A**.

Configurations	
1 reactant	$H_2O + aA \xrightarrow{T_1} bB + cC + \frac{1}{2}O_2/H_2$
2 products	$bB + cC \xrightarrow{T_2} aA + \frac{1}{2}O_2/H_2$
2 reactants	$H_2O + aA + bB \xrightarrow{T_1} cC + \frac{1}{2}O_2/H_2$
1 product	$cC \xrightarrow{T_2} aA + bB + \frac{1}{2}O_2/H_2$
2 reactants	$H_2O + aA + bB \xrightarrow{T_1} cC + dD + \frac{1}{2}O_2/H_2$
2 products	$cC + dD \xrightarrow{T_2} aA + bB + \frac{1}{2}O_2/H_2$
3 reactants	$H_2O + aA + bB + cC \xrightarrow{T_1} dD + eE + \frac{1}{2}O_2/H_2$
2 products	$dD + eE \xrightarrow{T_2} aA + bB + cC + \frac{1}{2}O_2/H_2$

3 Reaction Cycle	$H_2O + aA + bB \xrightarrow{T_1} cC + dD + \frac{1}{2}O_2$ $cC + dD \xrightarrow{T_2} eE + fF$ $eE + fF \xrightarrow{T_3} aA + bB + H_2$
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Table 2 - Configurations considered

The code used to generate the cycles analyzed many aspects of viability as addressed in previous sections. The atomic balance and negative Gibbs energy of all reactions were the major constraints for viability. Once these two criteria were satisfied, the other parameters were used to rank the generated cycles, namely the temperature of reactions, separation work, electrolysis (if applicable) and overall corresponded cycle efficiency. The following sections will analyze selected cycles for each configuration. The table below details the results of each of the cycle configurations.

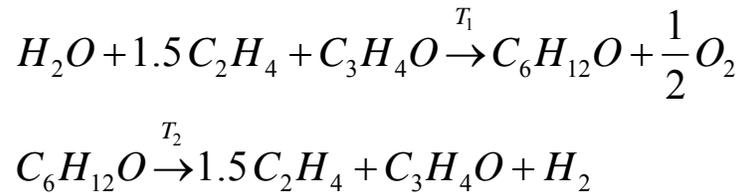
2 Reactants 2 Products	1 Reactant 2 Products	2 Reactants 1 Product	3 Reactants 2 Products	2 Reactants 2 Products (3 Reactions)
400 Unique Cycles	0 Unique Cycles	160 Unique Cycles	600 Unique Cycle	< 10 Cycles
Highest Efficiency 72.66%		Highest Efficiency 50.40%	Highest Efficiency 71.71%	Possible Electrolysis

1 reactant – 2 products

This configuration did not generate any unique cycles. When the code only analyzed the atomic balance, there were multiple cycles that were found. However, when the thermodynamics were applied to the analysis, all of the cycles were eliminated for a number of reasons. The coefficients were too high, the temperature of one or more reaction is greater than 1000, or the Gibbs energy was too high.

2 reactants – 1 product

This cycle configuration produced about 160 unique cycles with efficiencies reaching a maximum of about 50.04%. Many of the cycles generated according to this configuration had the same temperature for both reactions, about 400 K, or the minimum temperature that was tested. This could be caused by a number of things, since there were so few reactants and products the Gibbs Energy of formation for each cycle was always negative at the lowest temperature that was tested. The reaction kinetics of this and all groups of molecules are unknown, however, only from a thermodynamic analysis can these cycles are certainly feasible.



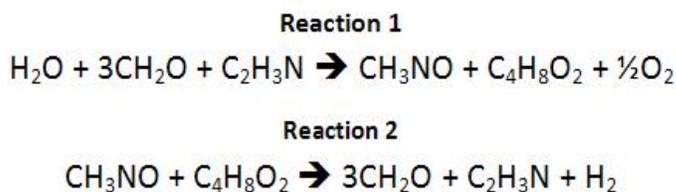
	Gibbs Energy (KJ/mol H2O)	Heat of Reaction (KJ/mol H2O)	Temperature (K)	Equilibrium Constant
Reaction 1	-43.63	-127.25	400	498994.9302
Reaction 2	-45.05	370.45	400	762959.5603

	(KJ/mol H2O)	Efficiency (%)
Hot Utility	370.45386	50.04%
Cold Utility	169.9608279	

Figure 8 - Summary of 2 reactants – 1 product Thermodynamics and Efficiency

2 reactants – 2 products

This configuration produced about 400 cycles were produced with efficiencies reaching a maximum of about 72.66%. The highest efficiency cycle is shown in **Figure 9**. The efficiency is about 73% without the inclusion of separation work. The separation work with a stoichiometric feed reduces the efficiency almost 10% with 1 mole water feed converting to about 0.6 moles hydrogen. The addition of excess reactants in a 3 to 1 ratio from stoichiometric feed lessens the efficiency down to near 60% corresponding to a 99% conversion to hydrogen. The high efficiency and conversion amounts, however, are still not enough of an indicator that this cycle would be practicable. The necessary condition for 5 molecules to react in reaction 1 is deemed unlikely to be kinetically realizable as discussed with previous cycles.



	ΔG (kJ/mol H ₂ O)	Temp (K)	Equilibrium Constant	Separation work
Reaction 1	-13.88	375	85.8	9.72
Reaction 2	-1.23	945	1.56	15.48
		Efficiency	w/ separation work (stoic)	w/ separation work (excess)
		72.66%	64.41%	58.80

Figure 9 – Highest efficiency 2 reactant and 2 product cycle

Three cycles in this configuration with the best efficiencies are compared in **Figure 10**. The efficiencies without inclusion are shown and compared to the separation requirements with stoichiometric feed and excess reactants. The required separation work reduces the efficiencies of the all three different cycles in about the same proportion. This is due to the fact that the ideal separation equation is dependent only on the mole fractions of the species and not each molecules individual activity. In each of the three cases, the addition of excess reactant feed in the reaction with water increased the conversion to hydrogen to nearly 100%. In general, the reaction temperatures for the highest performing cycles were lower than most of the cycles

currently found in the literature, however, are not significantly low to draw further potential into these configurations of reactions.

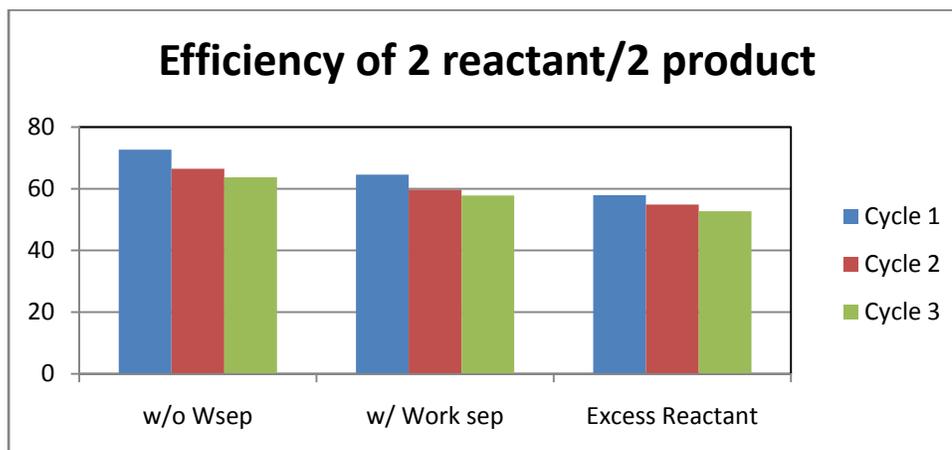
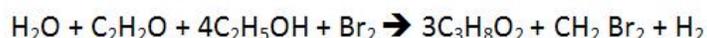


Figure 10 – Comparison of three 2 reactant/2 product cycles with work separation

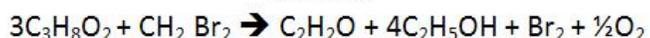
3 reactants – 2 products

This configuration produced about 600 amount with a maximum efficiency of 71.71%. The highest cycle efficiency appears in **Figure 11** along with the thermodynamic calculations. For most of the same reasons in the 2 reactant, 2 product configuration this cycle appears practical from the thermodynamic viewpoint, but it is most likely kinetically hindered. The conversion to hydrogen for this particular cycle was only 33% for stoichiometric feed and increased to 75% with additionally reactants to the first reaction.

Reaction 1



Reaction 2



	ΔG (kJ/mol H ₂ O)	Temp (K)	Equilibrium Constant	Separation work
Reaction 1	-3.95	425	3.06	13.14
Reaction 2	-5.07	975	1.87	11.11
		Efficiency	w/ separation work (stoic)	w/ separation work (excess)
		71.71%	63.93%	65.10%

Figure 11 – Best Efficiency Cycle for 3 reactants and 2 products

Two of the highest rated cycles in this configuration appear in Figure 12 and compare their efficiency dependency on the inclusion of separation work and excess reactants. Similar trends

are seen as with the other cycle configuration resulting in about a 8-10% decrease in efficiency for each case.

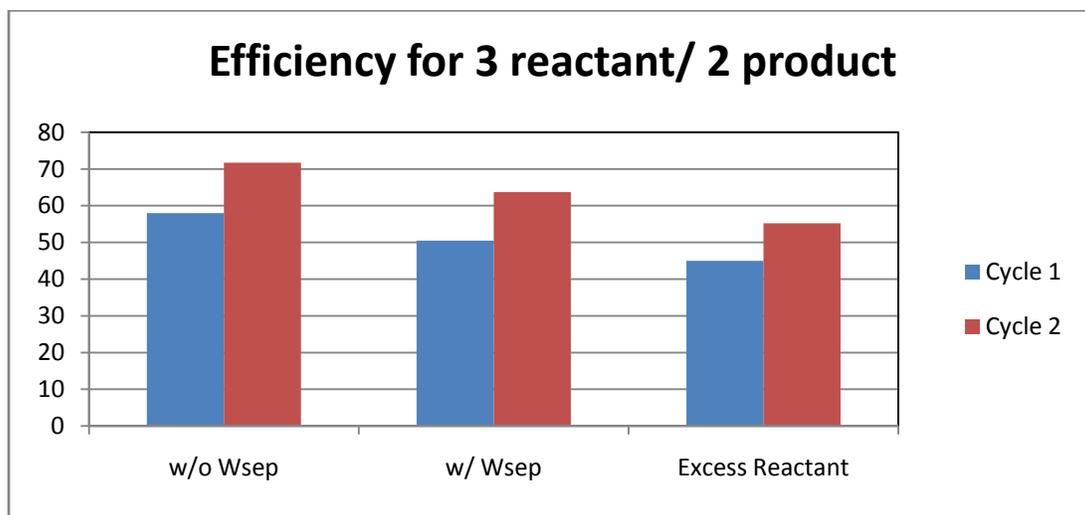
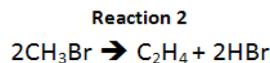
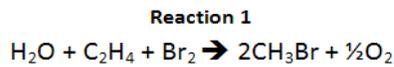


Figure 12 – Comparison of two 3 reactant/2 product cycles with separation work

3 Reaction Configuration

The most promising result was generated from a cycle that included 3 reactions. In general, most of the cycles produced from this configuration were not thermodynamically feasible. There were a number of cycles in which only two of the reactions had negative Gibbs energies, but the third reaction in many cases had a very large positive Gibbs value. The most realistic cycle actually is of a similar condition, but is practicable only because one reaction proceeds by means of electrolysis which is symbolized by the E in the table for reaction 3. The cycle is seen in **Figure 13**.



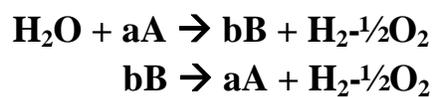
	ΔG (kJ/mol H ₂ O)	Temp (K)	Equilibrium Constant	Separation work
Reaction 1	28.1	375	.00012	12.8
Reaction 2	-1.83	450	1.63	2.15
Reaction 3 (E)	175.5	298	--	0.64
			Efficiency w/ electric work	w/ separation work (excess)
			99.4%	89.8%

Figure 13 – The most promising cycle produced, 3 reactions with electrolysis

This cycle is promising for a number of reasons. First of all, it has the highest efficiency of any cycle found for all configurations. It also has the least amount of reactants of any cycle, which would likely improve the kinetic feasibility as opposed to other cycles discussed. The temperatures of all the reactions proceed at very low temperatures as well, the initial goal of this study. This being said, there are aspects that could hinder this cycle's large scale application. The equilibrium constant for the first reaction is very low, and this cycle requires large excess feeds in order to achieve a considerable conversion. The excess feed in this case was increased by a factor of 10 to stoichiometric amounts. This still only resulted in a 5% conversion to hydrogen. Additional analysis to find ways to force the reaction to the products should be investigated such as a continual removal of products in addition to excess reactants. No information regarding the selectivity of reactions 1 or 2 was found in the literature, but it is also likely a significant amount of side products could result.

Functional Group Method

The results of the functional group method was the generation of 308 unique molecular formulas using only the 15 functional groups listed in **Table 1**. Using only 15 functional groups took about an hour to enumerate every possibility and to eliminate the duplicates. So the addition of more functional groups, atoms, and bond types would extend the runtime of this code exponentially. The generated molecules were used in the generation of a simple one reactant-one product cycle, shown below



Many of the reactions produced in this manner were not thermodynamically viable. The reason for this cycle generation step is to test whether the two cycle generation methods could be coupled seamlessly.

Conclusions

A computer algorithm using VBA was developed to generate low temperature water-splitting cycles. The program was successful in generating cycles for five different configurations. The program initiated combinations from 100 molecules, and also generated molecules from functional groups. The molecules were enumerated into a given reaction configuration the program checked the cycle feasibility by evaluation of both atomic balance considerations and thermodynamic constraints.

A total of over 1000 unique cycles were found from all of the configurations tested. For instance, cycles generated from the 2 reactant/2 product configuration reached a maximum efficiency of 72 % and other configurations yielded high efficiencies, but most had a high number of reactant molecules. These cycles likely will not be practical on a large scale because the kinetics are assumed to be very low. The best reaction found with the most practical potential was generated in a 3 reaction scheme with one reaction proceeding via electrolysis. The efficiency was near 90% with a small number of reactant molecules, possibly indicating favorable kinetics. The inclusion of separation work into the higher efficiency cycles reduced the efficiency by about 10% for each case. When excess reactants were used in situations with low reaction conversion, the conversion increased as much as 60%.

This study has demonstrated the ability to produce feasible water splitting cycles to generate hydrogen; however, potential cycles will require further analysis to realize the practical application. Foremost is the determination of reaction kinetics, selectivity, and more accurate predictions of separation work. The results from this work are promising and the expanse of the work could lead to important developments for the production of hydrogen to replace fossil fuel energy supply.

Works Cited

Bagajewicz, M., Cao, T., Crosier, R., Mullin, S., Tarver, J., & Nguyen, D. (2007). *On a Method for Evaluation of Thermochemical and Hybrid Water Splitting-Cycles*. Department of Chemical, Biological, and Materials Engineering - University of Oklahoma.

Brown, L., Besenbruch, G., Schultz, K., Marshall, A., Showalter, S., Pickard, P., et al. (2002). *Nuclear Production of Hydrogen using Thermochemical Water-Splitting Cycles*. US DOE Grant.

Chao, R. (1974). *Thermochemical Water Decomposition Processes*. Department of Chemical Engineering - University of Puerto Rico.

Chase, M., Davies, C., Downey, J., Frurip, D., McDonald, R., & Syverud, A. (1985). *JANAF Thermochemical Tables, Third Edition (Parts I and II)*. Midland, Michigan: American Chemical Society.

Holiastos, K., & Manousiouthakis, V. (1998). Automatic Synthesis of Thermodynamically Feasible Reaction Clusters. *AIChE Journal* , 164-173.

Lewis, Michele. (2005). *High-Temperature Thermochemical Processes*. Argonne National Laboratory. Department of Energy.

Nuclear Hydrogen Initiative. (n.d.). Retrieved March 10, 2008, from United States Department of Energy: <http://nuclear.energy.gov/NHI/neNHI.html>

United States Department of Energy. (2002, December). A Technology Roadmap for Generation IV Nuclear Energy Sources.

Yaws, C. (1999). *Chemical Properties Handbook*. McGraw-Hill.

Appendix A - List of Molecules used

1	Br ₂	Bromine
2	C ₂ Cl ₄	Tetrachloroethylene
3	HBr	Hydrogen
4	C ₂ H ₂ Cl ₂	1,1 – Dichloroethylene
5	C ₂ H ₂ O	Ketene
6	C ₂ H ₃ Br	Vinyl Bromide
7	C ₂ H ₃ Cl ₃	1,1,1 – Trichloroethane
8	C ₂ H ₃ Cl	Vinyl Chloride
9	C ₂ H ₄	Ethylene
10	C ₂ H ₄ Br ₂	1,1 – Dibromoethane
11	C ₂ H ₅ Br	Bromoethane
12	C ₂ H ₅ Cl	Ethyl Chloride
13	C ₂ H ₅ OH	Ethanol
14	C ₂ H ₆	Ethane
15	NO ₂	Nitrogen
16	C ₂ H ₅ NH ₂	Ethylamine
17	C ₂ H ₅ NO ₂	Nitroethane
18	C ₃ H ₆ O	Dimethyl Ether
19	CH ₂ Br ₂	Dibromoethane
20	C ₃ H ₈	Propane
21	CH ₂ O	Formaldehyde
22	CH ₃ Br	Methyl Bromide
23	CH ₃ Cl	Methyl Chloride
24	CH ₃ NH ₂	Methylamine
25	CH ₃ NO ₂	Nitromethane
26	CO	Carbon Monoxide
27	CO ₂	Carbon Dioxide
28	Cl ₂	Chlorine
29	N ₂ O	Nitrous Oxide
30	N ₂	Nitrogen
31	C ₄ H ₉ NO	Morpholine
32	C ₆ H ₁₂	Cyclohexane
33	C ₁₂ H ₁₀	Biphenol
34	C ₆ H ₅ Br	Bromobenzene
35	C ₆ H ₅ Cl	Chlorobenzene
36	C ₆ H ₆	Benzene
37	C ₆ H ₆ O	Phenol
38	C ₆ H ₇ N	Aniline

39	C7H6O2	Benzoic
40	C7H8	Toluene
41	C8H10	Ethylbenzene
42	C9H12	Mesitylene
43	C2H4O	Acetaldehyde
44	C4H10	N-Butane
45	CH2Cl2	Dichloromethane
46	C2H4O2	Acetic Acid
47	C2H6O	Dimethyl
48	C4H4O	Furan
49	C4H8	1-Butene
50	CCl2O	Phosgene
51	C2Cl4O	Trichloroacetyl
52	C2Cl6	Hexachloroethane
53	C2H2	Acetylene
54	C2H2O4	Oxalic Acid
55	C2H3N	Acetonitrile
56	C2H3NO	Methyl Isocyanate
57	C2H4Cl2	1,1 – Dichloroethane
58	C2H4O2	Methyl Formate
59	C6H11OH	Hexanol
60	C2H6O2	Ethylene Glycol
61	C2N2	Cyanogen
62	C3H2N2	Malononitrile
63	C3H3Cl	Propargyl Chloride
64	C3H3N	Acrylonitrile
65	C3H4	Methylacetylene
66	C3H4	Propadiene
67	C3H4Cl2	2,3 – Dichloropropene
68	C3H4O	Propargyl Alcohol
69	C3H4O3	Pyruvic Acid
70	C3H5Br	3 - Bromo - 1 – Propene
71	C3H5Cl	2 – Chloropropene
72	C3H5Cl	3 – chloropropene
73	C3H5N	Propionitrile
74	C3H5NO	Acrylamide
75	C3H6	Propylene
76	C3H6Br2	1, 2 – Dibromopropane
77	C3H6Cl2	1,2 – Dichloropropane
78	C3H6O2	Ethyl Formate
79	C3H6O3	Lactic Acid

80	C3H7Br	1 – Bromopropane
81	C3H7Cl	Isopropyl Chloride
82	C3H7N	Allylamine
83	C3H8O	Isopropanol
84	C3H8O2	1,2 - Propylene Glycol
85	C4H10O	n – Butanol
86	C4H4O4	Maleic Acid
87	C4H5Cl	Chloroprene
88	C4H6	1,2 – Butadiene
89	C4H8O2	n - Butyric Acid
90	C4H9Br	1- Bromobutane
91	C5H10	1 – pentene
92	C5H8	1 – pentyne
93	CH2O2	Formic Acid
94	CH3NO	Formamide
95	CH3NO2	Methyl Nitrite
96	CH3NO3	Methyl Nitrate
97	CH4	Methane
98	CH4O	Methanol
99	CHBr3	Tribromomethane
100	CHCl3	Chloroform
101	H2O	Water
102	H2	Hydrogen
103	O2	Oxygen