THERMOCHEMICAL ANALYSIS OF HYDROGEN PEROXIDE WITH APPLICATIONS TO ROCKET DESIGN

A Project Report

Presented to

The Faculty of the Department of Aerospace Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Masters of Science

by

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ABSTRACT

The report provided herein documents research into hydrogen peroxide rocket propellant and the subsequent computer modeling for its application.

A summary of an extensive literature search on hydrogen peroxide monopropellant is provided, with references sited. The literature search on hydrogen peroxide included, but was not limited to, propellant handling, molecular properties, dissociation through catalysis, catalyst optimization, and history of use.

The computer model addresses the thermochemical performance of hydrogen peroxide and suggests thruster dimensions for optimal performance. For reference, plotted data show the anticipated performance of ground based hydrogen peroxide thruster tests.

Accuracy of the computer model was validated for hydrogen peroxide concentrations from 70% to 98%, chamber to exit pressure ratios of 13.6 to 100, and thrust levels up to 44 Newtons. The computer model is based upon thermodynamic laws and conservation criteria, and as such, is scalable beyond the range validated.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

Parameter	Description
M_r	Molecular weight of reactants
M_{avg}	Average molecular weight of products
$\%H_2O_2$	Concentration of hydrogen peroxide (by volume) within water
n_r	Number of moles of reactants
n_p	Number of moles of products
ρ	Density
Cp_{avg}	Average Specific Heat of Products
R	Gas constant
γ	Specific Heat Ratio of Products
$\Delta_R H$	Heat of reaction
$\Delta_f H$	Heat of formation
Q	Heat released by reaction
g	Acceleration of gravity at sea level
T_c	Chamber Temperature
Isp	Specific Impulse
$\dot{m}_i$	Ideal mass flow rate
$\dot{m}$	Mass flow rate (predicted)
F_t	Thrust (theoretical)
T	Thrust (predicted)
P_c, p_1	Chamber pressure
P_e, p_2	Exit pressure
V_t	Throat velocity
V_2	Exit velocity
C_f	Coefficient of Thrust
c*	Characteristic Velocity
κ	Catalyst load factor
α	Nozzle half-angle
β	Contraction angle
ε	Expansion ratio
A_t,	Area of throat
A_e	Area of nozzle exit
A_c	Area of chamber/catalyst
L_i	Length of chamber, pre-catalyst
L_c	Length of catalyst in chamber
L_o	Length of chamber, post-catalyst
λ	Nozzle correction factor
ζ_v	Velocity correction factor
ζ_d	Discharge correction factor
ζ_F	Thrust correction Factor

INTRODUCTION

Purpose

The report contained herein partially fulfills the requirements for an Aerospace Engineering (A.E.) Masters Degree at San Jose State University (SJSU). The A.E. program requires completion of a masters project with documented analyses and results. The masters project demonstrates the student's understanding of the theoretical concepts obtained through coursework material in an area of study.

Background and Rationale for Work

The Aerospace Engineering student's area of concentration is space propulsion. An aptitude for chemistry led the student to focus upon chemical rocket propulsion for the masters project.

Upon completion of advanced space propulsion and physical chemistry courses, the student decided that the topic of the project would include thermochemistry. Hydrogen peroxide was chosen as the propellant to be analyzed, because of its properties as a versatile "green" monopropellant. Upon advisement of a review committee professor, the student extended the scope of the project to include the research and efforts involved with preliminary thruster design.

Subject

The subject of the report is the thermochemical analysis of hydrogen peroxide monopropellant with design optimization for rocket engines in low thrust applications. Supported by research, the entire subject is simulated through a computer model. Validity of the computer model is provided, by comparison to industry standards and published literature.

Literature Search

The majority of knowledge pertaining to thermochemistry and chemical rocket propulsion was obtained through coursework at SJSU. The specific details of hydrogen peroxide in its application as a monopropellant, was supported with published literature from the industry.

Published literature on hydrogen peroxide and its use as a monopropellant was obtained from SJSU and Stanford libraries, AIAA (American Institute of Aeronautics and Astronautics) Journals, Hydrogen Peroxide Conference bindings, the Teltech® technical paper publishing firm, and other credible sources.

The literature obtained and reviewed, are identified within the *References* section of this report. The *Results* section identifies the application of the literature towards the computer analysis performed.

A summary of findings from the literature search that is pertinent to hydrogen peroxide, but was not directly used by the computer program, is available within Appendix 4. The findings are categorized into handling requirements, performance, and history of use.

METHOD

Analysis Modeling

The first step to the development of the computer program was the generation of a flow chart. The flow chart of Figure 1 includes the key characteristics of input, processing, and output. The steps of Figure 1 support the purpose of the masters project, as described within the *Introduction*.

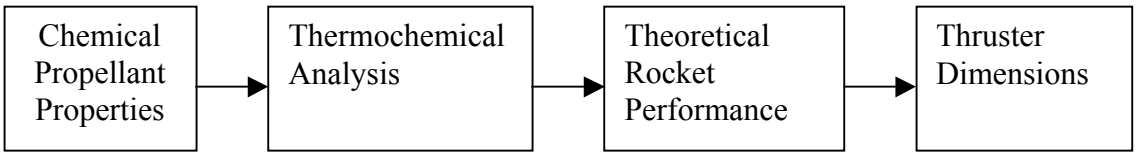

Figure 1 Chemical Rocket Preliminary Design Flow Chart

Two iterations of the computer program were required to achieve the full process and output of the flow diagram. The iterations are identified as the *first computer simulation* and f*inal computer simulation*.

The goal of the first computer simulation was to confirm a functional program with all points of errors removed. The first stage of computer simulation was based upon reasonable assumptions to simplify the code.

The goal of the final computer simulation was to achieve maximum accuracy in the results, and provide a complete set of output for preliminary thruster design.

The three major stages of the computer program are *Thermochemistry, Theoretical Rocket Performance*, and *Preliminary Thruster Design*. The following subsections, which coincide with the three major stages, identify the pertinent assumptions that are used within the computer program.

Thermochemistry.

It was assumed that the reaction for the dissociation of hydrogen peroxide was stoichiometric. According to Sercel (2000), Yamada and Nisioka (1965), and SJSU Advanced Space Propulsion Course Notes, the products of dissociation are water vapor and oxygen.

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2} O_2 \qquad (1)$$

The stoichiometric assumption was enhanced to better describe the concentration of hydrogen peroxide (by weight).

$$a\ H_2O_2\ (liquid) + b\ H_2O\ (liquid) \rightarrow c\ H_2O\ (vapor) + d\ O_2\ (gas) \quad (2)$$

The mole values of the products (c, d) and reactants (a, b) were calculated based upon molecular weight and the given concentration by weight. Details of the calculation method are available within Appendix 2.

Theoretical Rocket Performance.

With respect to the thrust chamber, it was assumed that the system was adiabatic, and all available energy released from the dissociation was transferred entirely into the prod (3) 1992). Flow through the throat and nozzle was assumed to be quasi-one dimensional frozen flow (Sutton, 2001). The assumptions provide sufficient accuracy for preliminary thruster design per Sutton (2001).

To account for actual (non-ideal) thruster performance, established correction factors (Sutton, 2001) were utilized. A description of the correction factors, and their implementation is available within the *Results* section, and Appendix 1 and 2.

Preliminary Thruster Design.

The design of a monopropellant thruster, which includes the chamber, throat, and nozzle, is partially dependant upon empirical data. The first computer simulation addressed the non-empirical data, which was limited to the throat and nozzle.

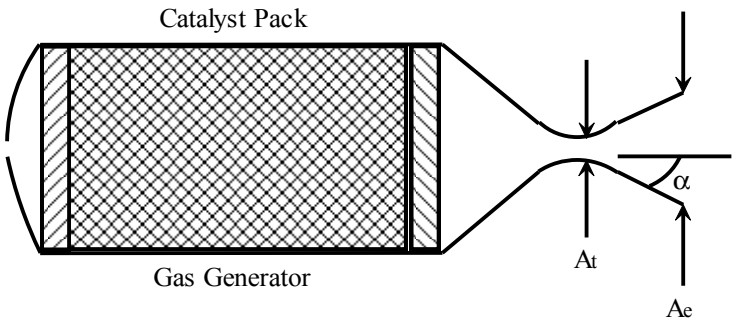

Figure 2 Nozzle Dimensions, Low Thrust Application

Based upon nozzle theory (Sutton, 2001; Hill, 1992), the throat area (A_t) and exit area (A_e) are derived from the properties of the gaseous products (temperature, pressure, molecular weight, and specific heat), the laws of thermodynamics, and conservation criteria. The resultant equations are shown within Appendix 1 and 2.

For low thrust applications and manufacturing simplicity, the computer program models a conical nozzle (Sutton, 2001; Hill, 1992, Huzel & Huang, 1992). Loss to exhaust momentum, based upon the nozzle half angle (α), is calculated through λ (nozzle correction factor). The equation for λ, and the application to Thrust (T), is provided within Appendix 1 and 2.

The final computer simulation derived the remainder of internal thruster dimensions that were dependant upon empirical data. Figure 3 identifies the dimensions from the final computer simulation.

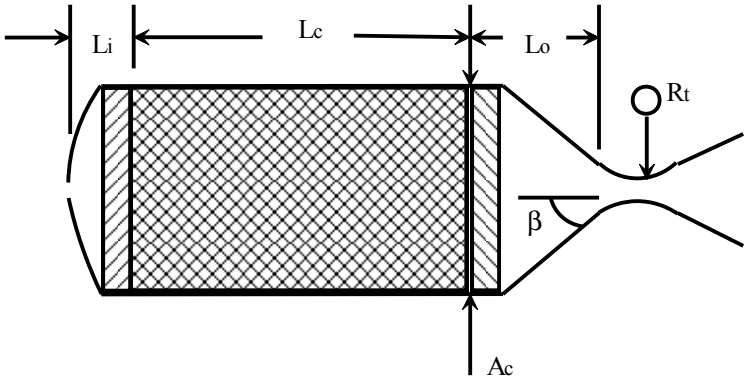

Figure 3 Empirically Determined Thruster Dimensions

Sutton (2001) identified that the throat contour, or radius of curvature (R_t), is not critical for performance, and "any radius is usually acceptable." The designer is suggested to define a radius that meets manufacturability requirements, and the angles of α (nozzle half-angle) and β (contraction angle).

Sutton (2001) also provided that the contraction angle may approach 90 degrees without significant performance loss. Thus, the designer should focus upon the requirements of L_o (chamber length, post-catalyst).

Relative to the chamber, special considerations for hydrogen peroxide monopropellant thrusters were incorporated into the program. Three stages to the chamber exist. The first stage (L_i) is where liquid hydrogen peroxide is introduced. The second stage is the catalyst, which is assumed to completely dissociate the hydrogen peroxide per Equation (2). The third stage (L_o) is where the gaseous products are accelerated into the throat. The dissociation of hydrogen peroxide is completed within the catalyst, and there is no combustion occurring within L_o. Hence, the length of the chamber after the catalyst (L_o) should be minimized to limit heat transfer and starting transients (Davis & McCormick, 1960).

The cross sectional area of the catalyst (A_c), which coincides with the chamber, and the length of the catalyst (L_c), are entirely dependent upon the catalyst design. For samarium oxide coated silver screen catalysts, the cross sectional area may be calculated per Davis and McCormick (1960). The equation for A_c is available within Appendix 1 and 2.

The length (L_i) of the chamber between the flow orifice and the catalyst is entirely dependant upon the catalyst design. L_i must be of sufficient length to allow for uniform hydrogen peroxide flow through the catalyst. However, to limit start-up transients, the pre-catalyst length (L_i) should be minimized (Davis and McCormick, 1960).

Numerical Modeling - Equation Derivation and Implementation

Taken from the steps of the analysis model, a detailed flow diagram of the computer program is provided within Figure 4.

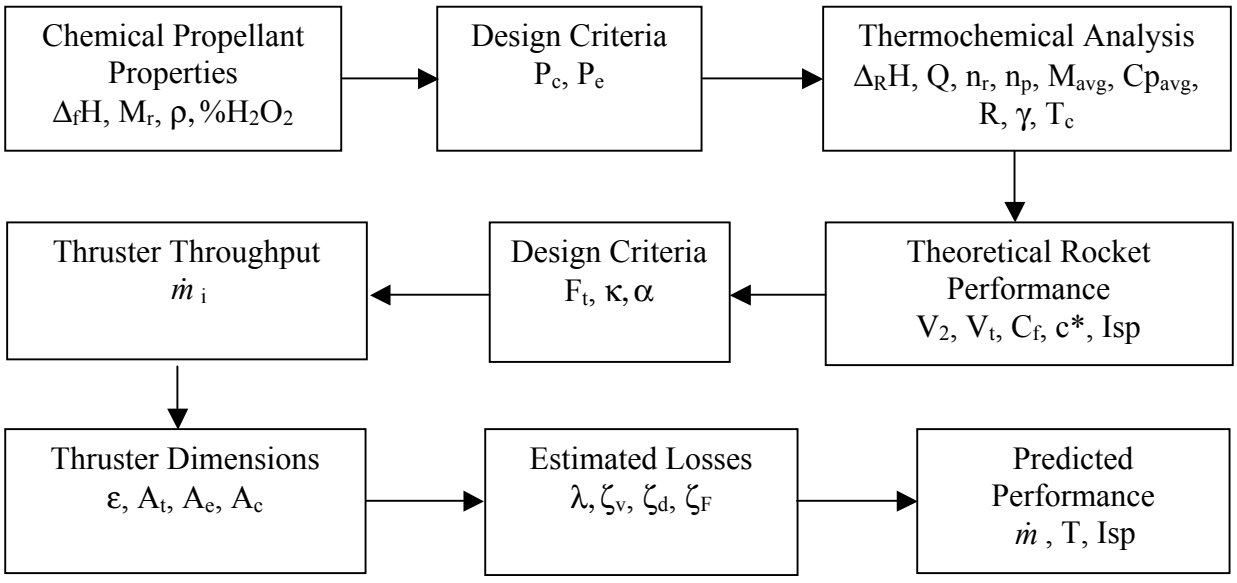

Figure 4 Computer Program Flow Diagram

Given the assumptions previously identified within the analysis model, the equations for the program were derived or taken directly from textbooks (with confirmation of correct assumptions). The equations were sequenced to provide the desired output. The individual equations and the stages of the computer analysis are provided in Appendix 1.

The computer analysis was performed through Matlab®. Appendix 2 contains the final computer program.

The method employed to validate each stage of the computer program was to compare the output to published literature or other industry standards. The details of all validation techniques are provided within the *Results* section.

RESULTS AND DISCUSSION

Thermochemistry

The thermochemical results of the first simulation identified that the stoichiometric assumption (Equation 2) provided accurate data, as compared to an industry standard (Gordon & McBride, 1996) and published literature (Yamada & Nisioka, 1965). The thermochemical criteria used to determine accuracy, included the chamber temperature and mole fraction of the products.

The Industry standard (Gordon & McBride, 1996) used is the National Aeronautics and Space Administration's (NASA's) Chemical Equilibrium with Applications (CEA) program, which has been publicly available in various forms since 1967. Figure 5 provides a comparison between CEA and the masters project (MP). The thermochemical deviations noted between CEA and MP are 0.0% on average.

The thermochemical results pertaining to reaction equilibria were also in agreement with a physical understanding of the process. Minimization of Gibbs free energy, which coincides with maximization of Entropy for the reaction (Atkins, 1999; Levine, 1995; McQuarrie & Rock, 1991), would occur when the aqueous hydrogen peroxide decomposes fully into gaseous (more chaotic) products. Additionally, the decomposition temperature (Figure 4) was substantially below 2300K, which is an approximate point that products tend to dissociate further (Course Notes, SJSU Advanced Space Propulsion, 1999). Thus, the heat of reaction is based solely upon the heats of formation of hydrogen peroxide, water, and oxygen, in their respective states.

The accuracy obtained through the simplified stoichiometric assumption – including concentration effects – eliminated the need for calculating equilibria through usage of reaction rates, and the consideration of all reaction steps.

HYDROGEN PEROXIDE MONOPROPELLANT THRUSTER
COMPARISON - NASA's CEA vs. MP (Student Masters Project)

Run	Pc (psia)	Pe (psia)	Weight Percentage H2O2	Pressure Ratio Pc/Pe	MP Mole Fract H2O(vapor)	MP Mole Fract O2(gas)	CEA Mole Fract H2O(vapor)	CEA Mole Fract O2(gas)	Difference Product Mole Fract
1	300	14.7	0.70	20.4	0.7835	0.2165	0.7835	0.2165	0.0%
2	300	14.7	0.78	20.4	0.7540	0.2460	0.7540	0.2460	0.0%
3	300	14.7	0.87	20.4	0.7194	0.2806	0.7194	0.2806	0.0%
4	300	14.7	0.95	20.4	0.6874	0.3126	0.6874	0.3126	0.0%
5	300	14.7	0.98	20.4	0.6750	0.3250	0.6750	0.3250	0.0%
6	200	14.7	0.70	13.6	0.7835	0.2165	0.7835	0.2165	0.0%
7	200	14.7	0.98	13.6	0.6750	0.3250	0.6750	0.3250	0.0%
8	200	5.0	0.70	40.0	0.7835	0.2165	0.7835	0.2165	0.0%
9	200	5.0	0.98	40.0	0.6750	0.3250	0.6750	0.3250	0.0%
10	250	2.5	0.70	100.0	0.7835	0.2165	0.7835	0.2165	0.0%
11	250	2.5	0.98	100.0	0.6750	0.3250	0.6750	0.3250	0.0%

Run	MP Tc	CEA Tc	Difference Tc	MP Ae/At	CEA Ae/At	Difference Ae/At	MP Isp	CEA Isp	Difference Isp
1	537.0	536.0	0.2%	3.147	3.124	0.7%	96.70	96.76	-0.1%
2	736.7	735.2	0.2%	3.187	3.167	0.6%	112.68	113.04	-0.3%
3	951.3	956.3	-0.5%	3.246	3.228	0.6%	127.44	128.50	-0.8%
4	1151.3	1151.9	-0.1%	3.271	3.282	-0.3%	139.17	140.49	-0.9%
5	1224.7	1225.5	-0.1%	3.284	3.301	-0.5%	143.18	144.66	-1.0%
6	537.0	536.0	0.2%	2.439	2.429	0.4%	92.00	92.08	-0.1%
7	1224.7	1225.5	-0.1%	2.527	2.548	-0.9%	135.97	137.33	-1.0%
8	537.0	536.0	0.2%	4.890	4.835	1.1%	103.15	103.17	0.0%
9	1224.7	1225.5	-0.1%	5.166	5.149	0.3%	153.15	154.75	-1.0%
10	537.0	536.0	0.2%	9.132	8.973	1.7%	109.92	109.86	0.1%
11	1224.7	1225.5	-0.1%	9.814	9.610	2.1%	163.78	165.36	-1.0%
AVERAGE			0.0%			0.5%			-0.6%

Figure 5 NASA's CEA and Masters Project Results Comparison

The effect of hydrogen peroxide concentration on the mole fraction of the products was analyzed per Figure 6. As the concentration of hydrogen peroxide increases over water, the amount of O_2 in the products increases proportionally. This coincides with the balanced reaction (Equation 2) described within the *Method* section.

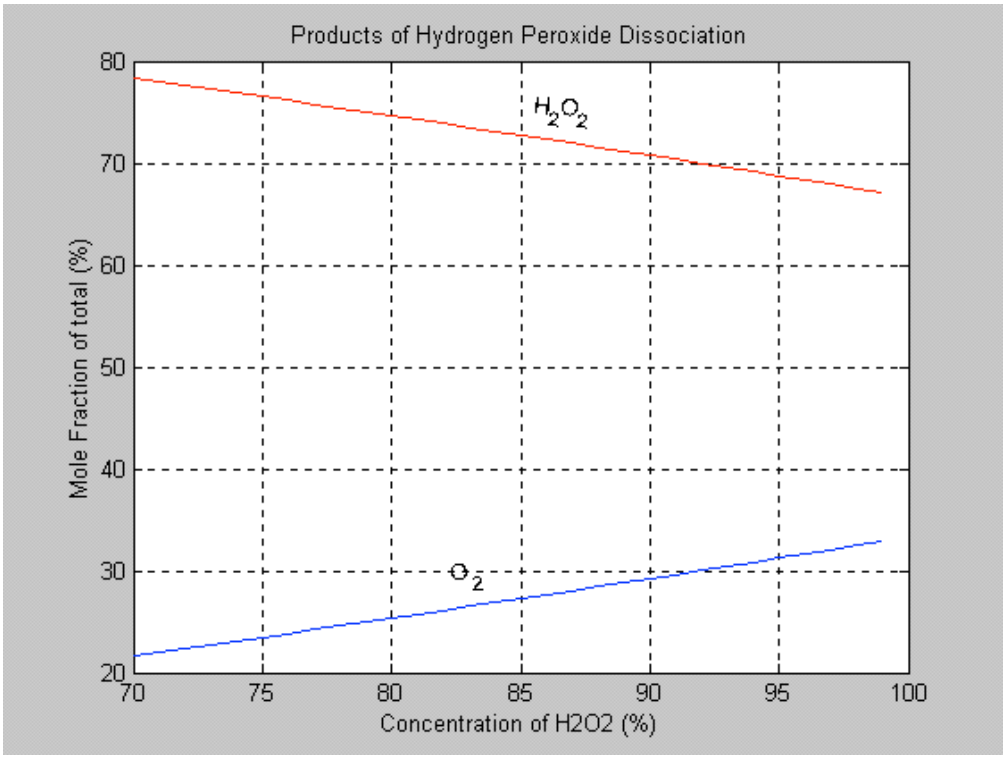

Figure 6 Hydrogen Peroxide Reaction Products

The amount of heat released in the reaction was analyzed through observation of the chamber temperature. A survey of the chamber temperature versus hydrogen peroxide concentration is provided within Figure 7. The chamber temperature is representative of the temperature of the products, assuming adiabatic conditions. The results of Figure 7 correlate well with a similar figure (low resolution, hand drawn data points) published within Yamada and Nisioka (1965).

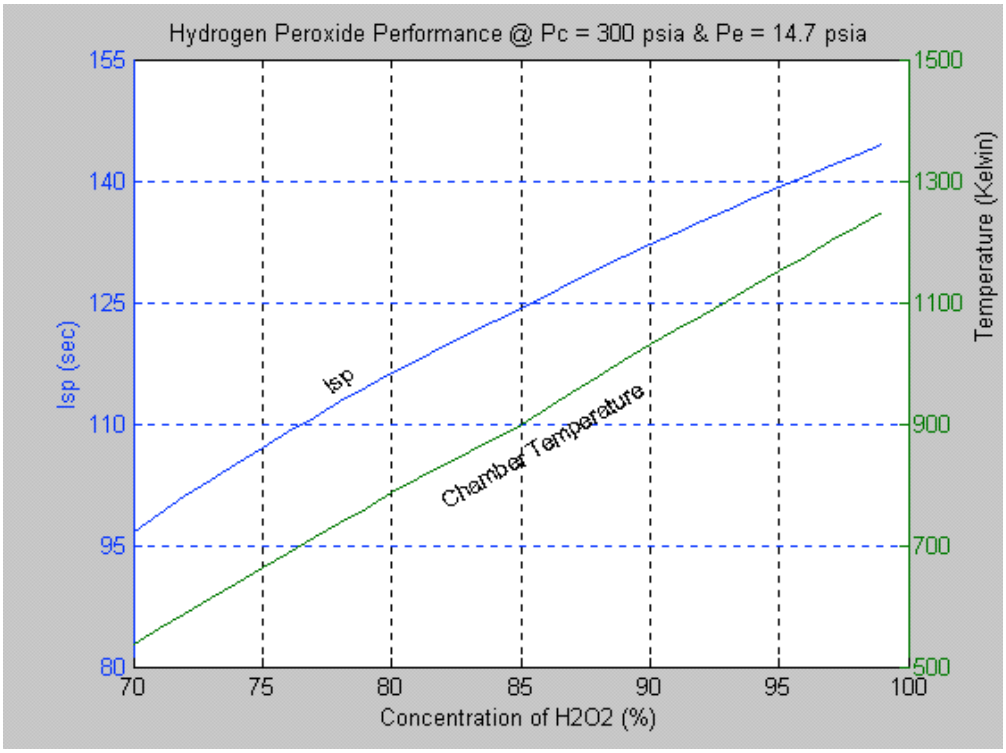

Figure 7 Concentration Effects on Hydrogen Peroxide Performance

Theoretical Rocket Performance

Within the limits of hydrogen peroxide concentrations of 70% to 98%, the simulation results were found to be accurate versus an Industry Standard (Gordon & McBride, 1996; Figure 5) and published literature (Quintana, 1999; Table 1).

Table 1 Results Comparison of Theoretical Rocket Performance

Parameter	Reference* Value	Computer Sim Value	Deviation
H2O2 Concentration	90%	90%	0%
Pressure Ratio, P_c/P_e	undefined	30.6	N/A
Chamber Temp	1029 K	1029 K	0 K
Specific Impulse, Isp	138 sec	138 sec	0 sec

* Reference: Quintana, 1999

The deviation of specific impulse (Isp) that exists between CEA and MP (Figure 5) is less than 1% on average. NASA's CEA program and the masters project computer program were extensively reviewed for differences in calculation. Each program utilizes a different method of solution, and are inherently complex. The deviation is primarily attributed to (1) use of constants for unit conversions, and (2) reference data for the enthalpy of products. In regards to the later observance, NASA CEA and MP use different source data for the enthalpy of products. Source data for MP are detailed within Appendix 2. Source data of CEA is provided within Gordon and McBride (1996).

Appendix 3 provides sample output from the NASA CEA program.

Theoretical rocket performance was evaluated for various concentrations of hydrogen peroxide rocket propellant. Figure 7 describes the anticipated performance of ground based (exit pressure, P_e = 14.7 psia) thruster tests, given a chamber pressure (P_c) of 300 psia.

Figure 8 examines the effects of chamber pressure on thruster performance. The results of Figure 8 identifies that at a chamber pressure of 450 psia, the Isp approaches 150 seconds. According to published literature (Sercel, 2000; Yamada & Nisioka, 1965), the specific impulse of hydrogen peroxide is commonly quoted as 150 seconds.

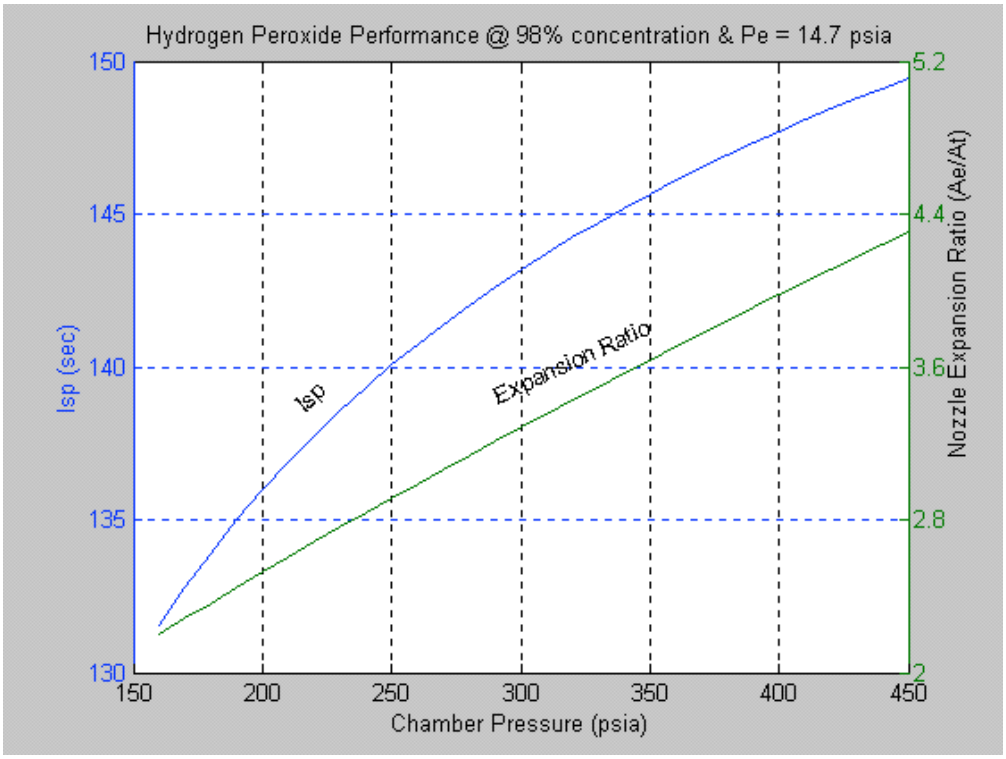

Figure 8 Chamber Pressure Effect on Hydrogen Peroxide Performance

Preliminary Thruster Design

Computer simulation accuracy was determined by comparing the output to NASA's CEA program (Figure 5) and published literature (Haag, 1998; Table 2). Dimensional and performance data of an actual hydrogen peroxide thruster was provided by Haag (1998). After scaling the thrust to match the observed results, the throat diameter exhibited direct correlation with the computer simulation.

Table 2 Results Comparison of Preliminary Thruster Design

Parameter	Reference* Value	Computer Sim Value	Deviation
Mass Flow Rate	4.9 g/sec	4.9 g/sec	0.0 g/sec
Throat Diameter	1.5 mm	1.5 mm	0.0 mm
Chamber Temp	961 Kelvin	1005 Kelvin	44 Kelvin

* Reference: Haag, 1998

The differences in chamber temperature results of Table 2 are attributed to the measurement devices and heat transfer loss (non-adiabatic).

Final Output

The culmination of the three major stages of the computer program (thermochemistry, theoretical rocket performance, and preliminary thruster design) provided the tools necessary to develop a thruster.

Example output based upon the requirements of Table 3a, are provided within Tables 3b through Table 3e.

Table 3a Example Thruster Requirements

Parameter	Description	Value
P_c	Chamber Pressure	250 psia
P_e	Exit Pressure	14.7 psia
$\%H_2O_2$	Concentration of H_2O_2	85 %
Catalyst	Silver Mesh	40-40 (samarium oxide coated)
T	Design thrust	10 lbf (44 N)

Table 3b Theoretical Rocket Performance

Isp	Theoretical Specific Impulse	121 sec
Tc	Chamber Temperature	898 K
c*	Characteristic Velocity	876 m/sec
C_F	Coefficient of Thrust	1.361
$\dot{m}$	Mass flow rate	37 gram/sec
ε	Expansion Ratio	2.887

Table 3c Nozzle Dimensions Based Upon Theoretical Performance

Parameter	Description	Reference Figure	Value
A_e	Exit Area of Nozzle	Figure 2	0.5415 cm^2
A_t	Throat Area	Figure 2	0.1876 cm^2
α	Nozzle Half-angle	Figure 2	12º

Table 3d Chamber Dimensions Based Upon Chosen Configuration

Parameter	Description	Reference Figure	Value
β	Nozzle Half-angle	Figure 6	55º
A_c	Chamber cross-section area	Figure 6	3.151 cm^2

Table 3e Predicted Thruster Performance

Parameter	Description	Reference	Value
λ	Nozzle Correction Factor	Hill (1992)	0.989
ζ_V	Est. Velocity Correction Factor	Sutton (2001)	0.96
ζ_d	Est. Discharge Correction Factor	Sutton (2001)	1.00
ζ_F	Est. Thrust Correction Factor	Sutton (2001)	0.96
T	Predicted Thrust		9.5 lbf (41.8 N)
Isp	Predicted Isp		115 sec

The empirically derived values of L_i, L_c (Figure 6) were not included in the program output. The values are to be determined through experiment, with consideration of the previously addressed limitations (see *Method* section).

The computer simulation did not address the external dimensions of the thruster, as they are dependant upon thruster design and assembly. The thruster walls must be of the appropriate materials to withstand the applied temperatures and pressures (Sutton, 2001; Huzel & Huang, 1992).. Reactivity of materials with hydrogen peroxide must also be considered (Pottinger, 2001; Whitehead, 1998; Bruce, 2001).

Optimization

As detailed within the report, further enhancement to the computer program is possible. Enhancement would be achievable through optimization to one or all of the three major stages of the program (*Thermochemistry, Theoretical Rocket Performance*, and *Preliminary Thruster Design*).

Optimization to the thermochemical portion of the computer program, are summarized below:

- Heat Transfer - the program assumes an adiabatic reaction, which is not representative of actual conditions.
    - Optimization may be added to the model by accounting for heat transfer to the catalyst support structure and the walls of the thruster.
- Chemical Reactants – the chemical reaction did not account for reactants beyond hydrogen peroxide and water.
    - If significant levels of contaminate are present within the propellant, feed system, or chamber, it would be optimal to model the effects of these impurities.
- Reaction Products – the products of dissociation were gaseous oxygen and water. In a more rigorous sense, negligible traces of additional compounds or elements would be present.
    - At high concentrations (> 90%) of hydrogen peroxide aqueous solutions, the dissociation would also result in a negligible amount of OH, and other gaseous products. An optimal model would account for all products.
    - During the reaction through the catalyst, the entirety of hydrogen peroxide will not dissociate. The completeness of dissociation is dependant upon the catalyst and operational conditions. An optimal model would account for incomplete dissociation.

Optimization to the theoretical rocket performance stage of the computer program, are summarized below:

- Frozen Flow – the computer model assumes frozen flow conditions.
    - The actual conditions of the thruster may experience further dissociation or re-association of the products. Additionally, the water vapor may condense within the flow region of the nozzle, for low concentration (<85%) hydrogen peroxide and low exit pressures. An optimal model would eliminate the frozen flow assumption.
- Heterogeneous Working Substance – impurities within the exhaust gases would affect the average exhaust velocity of the engine.
    - It would be optimal to account for all impurities and the effect to average exhaust velocity and momentum.

Optimization to the preliminary thruster design stage of the computer program primarily concerns the catalyst pack. Additional areas of thruster design optimization (e.g., bell shaped nozzle) are adequately addressed within Sutton (2001), Huzel and Huang (1992), and Hill (1992).

The catalyst is paramount to hydrogen peroxide thruster design. An optimal catalyst configuration (Bowker, 1998; Rusek, 1995; Rusek & Anderson, 1998; Whitehead, 1998; Davis & McCormick, 1960; Sellers, Brown, & Paul, 1998) should seek the following seven items:

1. High product yield per unit time
2. Minimal pressure drop
3. Low temperature engine starts, pulsed or steady state
4. Structurally capable for all loads - CTE mismatches, etc.

5. Maintains phase without melting of fusing
6. High total throughput capability
7. Maintains consistent performance over life

Depending upon the mission criteria, additional areas of consideration may arise.

CONCLUSION

What was learned

As detailed within the introduction, the report was performed for fulfillment of the requirements for a Masters Degree in Aerospace Engineering at San Jose State University. The primary goal of the report was to demonstrate that the student was capable of applying the theoretical concepts from coursework. The student achieved this goal by (1) supporting coursework material with extensive research on chemical propellants, (2) creating a computer program that used raw chemical information to generate a preliminary thruster design, and (3) employing various means to validate results.

As desired by the student whom completed the project, an enhanced understanding of physical chemistry (rates of reaction, heat of reaction, equilibria, catalysis, etc.) was obtained by characterizing chemical rocket propellants.

The exercise of researching and applying thruster development techniques was enriching to the student. With development of the report, the student obtained the tools to begin fabrication of a monopropellant rocket engine. Such engines would be test articles that would lead to more complex and efficient thrusters.

Recommended Future Work

Several areas for optimization were previously described. Efforts that would resolve the recommended optimization(s) would be ideal for future work. This includes, but is not limited to, advances in computer modeling of heat transfer, chemical reactions, and multiphase flow.

In addition to the advances in computer modeling, the gathering of empirical data would be worthy of pursuing. Implementation of the preliminary thruster design that was provided within this report would allow for enhanced modeling of items such as correction factors, completeness of dissociation, and heat transmissibility.

Beyond the scope of this report, additional areas of research regarding hydrogen peroxide are growing. Example areas of study include hybrid systems for launch vehicles (Markopoulos, 2001), hypergolic fuel combinations (Frolik, 2000), and small satellite propulsion systems (Keith, 1998; Whitehead, 1998). Further research could also explore the use of hydrogen peroxide for interplanetary missions.

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APPENDIX 1

Fundamental Progress of Computer Program through stages.

Stage 1 - Determine Heat of Reaction

$$\Delta_R H = \sum \upsilon \Delta_f H$$

Stage 2 – Determine Heat Available for Raising Temperature of Products

$$Q_{avail} = -\Delta_R H$$

Stage 3 – Determine Chamber Temperature through iterative process

$$Q_{avail} \text{ ---> } T_c$$

Stage 4 – Calculate Average Molecular Weight of Products

$$M_{avg} = \frac{\sum n_p M_p}{\sum n_p}$$

Stage 5 – Calculate Average Specific Heat

$$Cp_{avg} = \frac{\sum n_p Cp_p}{\sum n_p}$$

Stage 6 – Calculate Specific Heat Ratio

$$\gamma = \frac{Cp_{avg}}{Cp_{avg} - R}$$

Stage 7 – Calculate Exhaust Velocity from Thermodynamic criteria

$$V_2 = \sqrt{\frac{2\gamma}{\gamma - 1} RTc \left[1 - \left(\frac{p_e}{p_c} \right)^{(\gamma-1)/\gamma} \right]}$$

Stage 8 – Calculate the Thrust Coefficient from Thermodynamic criteria

$$C_F = \sqrt{\frac{2\gamma^2}{\gamma-1}\left(\frac{2}{\gamma+1}\right)^{\left(\gamma+1/\gamma-1\right)}\left[1-\left(\frac{p_e}{p_c}\right)^{(\gamma-1)/\gamma}\right]}$$

Stage 9 – Calculate the Characteristic Velocity from Thermodynamic criteria

$$c^* = \frac{\sqrt{\gamma RT_c}}{\gamma\sqrt{\left(\frac{2}{\gamma+1}\right)^{\left(\gamma+1/\gamma-1\right)}}}$$

Stage 10 – Calculate Ideal Specific Impulse

$$Isp = V_2/g$$

Stage 11- Determine Chamber parameters from Thermodynamic information

$\dot{m} = F_T/V_2$, mass flow rate

$\mathrm{V_t} = \sqrt{\left(\frac{2}{\gamma+1}\right)\gamma RT_c}$, throat velocity

$\widetilde{V}_c = \frac{RT_c}{P_c}$, specific volume entering nozzle

$\widetilde{V}_t = \widetilde{V}_c\left(\frac{\gamma+1}{2}\right)^{\left(1/\gamma-1\right)}$, specific volume at throat

$\widetilde{V}_e = \widetilde{V}_c\left(\frac{P_c}{P_e}\right)^{\left(1/\gamma\right)}$, specific volume of nozzle exit

Stage 12 – Determine Nozzle Dimensions based upon theoretical propellant performance

$A_t = \frac{\dot{m}\widetilde{V}_t}{V_t}$, area of throat

$$A_e = \frac{\dot{m}\tilde{V}_e}{V_2}, \text{ area of exit}$$

$$\varepsilon = {A_e}/{A_t}, \text{ nozzle expansion ratio}$$

Stage 13 – Determine catalyst cross sectional area

$$A_c = \frac{\dot{m}g}{\kappa}$$

Stage 14 – Determine the Nozzle Correction Factor

$$\lambda = \frac{1}{2}(1+\cos\alpha)$$

Stage 15 – Calculate predicted performance

$$T = \lambda \zeta_F F_T, \text{ predicted thrust}$$

$$\zeta_d = \frac{\zeta_F}{\zeta_V}, \text{ discharge correction factor}$$

$$\dot{m} = \zeta_d \dot{m}_i, \text{ mass flow rate}$$

$$Isp = \frac{T}{\dot{m}g}, \text{ predicted specific impulse}$$

APPENDIX 2

Matlab® Computer Program

```
% Version 4.0 of program for Masters Project
% Project title: Thermochemical analysis of Hydrogen Peroxide
%                Monopropellant with design optimization for
%                rocket engines in low thrust applications
%

% Written by Tony Robles, March 4, 2002
% Aerospace Engineering
% San Jose State University
%



% Textbook Resources
%
% References:
% (A) Sutton, Rocket Propulsion Elements, 7th Ed.
% (B) Hill, Mechanics and Thermodynamics of Propulsion, 2nd Ed.
% (C) Atkins, Physical Chemistry, 6th Ed.
% (D) Levine, Physical Chemistry, 2nd Ed.
% (E) McQuarrie & Rock, General Chemistry, 3rd Ed.

% Technical Papers/Sources
%
% References:
% (F) Enthalpy tables by Hirschfelder, Curtis, McClure, and
%     Osborn "Thermodynamic Properties of Propellant Gases",
%     OSRD Report #547
% (G) McCormick, Design of Catalyst Packs for the Decomposition
%     of Hydrogen Peroxide, 1960 American Rocket Society



% Beginning of Computer Program
%


clear all

% Constants
%

g = 9.81; % Acceleration of gavity, m/sec^2
```

```
% Design Parameters
%

Thrust = 44; %Thrust in newtons, N
Pc = 250; % Chamber Pressure, psia
Pe = 14.7; % Exit Pressure, psia
PH2O2 = 0.85; % Percentage/Concentration of Hydrogen Peroxide


% Properties of chemical constituents
% ** References (C),(D),&(E)
%

% Hydrogen Peroxide
M_a = 34.015; %Molecular weight, grams/mole
DfH_a = -187.78; %Heat of Formation, kJ/mol

% Water
M_b = 18.015; %Molecular weight, grams/mole
DfH_b = -285.83; %Heat of Formation of water (liquid), kJ/mol

% Water Vapor
M_c = 18.015; %Molecular weight, grams/mole
DfH_c = -241.82; %Heat of Formation of water (vapor), kJ/mol

% Oxygen
M_d = 31.999; %Molecular weight, grams/mole
DfH_d = 0; %Heat of Formation, kJ/mol


% Enthalpy of Products versus Temperature, Ref. (F)

Temp = [300:100:2000];
Enthalpy_H2O = [0.000,0.811,1.641,2.496,3.380,4.292,5.234,...
      6.208,7.211,8.247,9.312,10.399,11.519,12.660,...
      13.821,15.006,16.206,17.424]; %kcal/kg-mol
Enthalpy_O2 = [0.000,.721,1.447,2.203,2.931,3.778,4.954,...
      5.421,6.278,7.135,7.990,8.847,9.704,10.592,11.481,...
      12.369,13.257,14.146]; %kcal/kg-mol


% Governing Reaction (for all cases, except H2O2 = 100%)
% ** References (C),(D),&(E)
%

% a H2O2(l) + b H2O(l) --> c H2O(g) + d O2(g)
```

```
b = 1; % number of moles of H2O(l)

rho_a = 1442.5*(1000)/(100^3); % Density of Hydrogen Peroxide
rho_b = 1; % Density of Water, gram/cc

Mass_H2O = b*M_b;
Mass_H2O2 = (PH2O2/(1-PH2O2))*Mass_H2O;
ofratio = (Mass_H2O2)/(Mass_H2O);

a = Mass_H2O2/M_a; % number of moles of H2O2(l)
c = a + b; % number of moles of H2O(g)
d = (a*2+b-c)/2; % number of moles of O2


% Determination of Heat of Reaction using simple principles
%

% (1) Calculation of the Heat of Reaction at STP
% ** References (C)&(D)
%

DrHo = ((c*DfH_c + d*DfH_d) - (a*DfH_a + b*DfH_b))/a; %kJ/mol


% (2) Heat available for the reaction
% ** Reference (B)
%

Q_avail = - DrHo; %kJ/mol


% (3) Determine the chamber temperature, based upon the Heat
% available to raise the products from standard temperature
% ** Reference (B)
%

[z,N] = size(Temp);

for  i = 1:N
  Q(i) = (c/a)*Enthalpy_H2O(i) + (d/a)*Enthalpy_O2(i);
  % Enthalpy in units of kcal/kg-mol
  Q(i) = Q(i) * 4.184; %kJ/mol
  if Q(i) < Q_avail
    LowLim = Q(i);
    z = i;
```

```
  end
end

UpperLim = Q(z+1);
T_low = Temp(z);
T_high = Temp(z+1);

Tc = ((Q_avail - LowLim)/(UpperLim - LowLim)) * ...
   (T_high - T_low) + T_low; %Kelvin


% (4) Calculate the average molecular weight of the Products
% ** References (A)&(B)
%

Sum_nM = c*M_c +  d*M_d;
Sum_n = c + d;

M = Sum_nM/Sum_n;


% (5) Calculate the average specific heat of the Products,
%  Cp = dH/dT
% ** References (A),(B),&(C)

frac = (Tc - T_low)/(T_high - T_low);
DH_H2O = (frac*(Enthalpy_H2O(z+1) - Enthalpy_H2O(z)) + ...
   Enthalpy_H2O(z)) * 4184; %J/mol
DH_O2 = (frac*(Enthalpy_O2(z+1) - Enthalpy_O2(z)) + ...
   Enthalpy_O2(z)) * 4184; %J/mol

Cp_H2O = DH_H2O/(Tc - 298);
Cp_O2 = DH_O2/(Tc - 298);

Cp = (c*Cp_H2O + d*Cp_O2)/Sum_n; %J/K-mol


% (6) Calculate the specific heat ratio
% References (C),(D),&(E)
%

R = 8.31451; % Universal gas constant, J/K-mol
gamma = Cp/(Cp-R);


% (*) Summarize the values of steps #1 through #6
```

```
%

Tc
M;
Cp;
gamma;
P1 = Pc;
P2 = Pe;
molfracH2O = c/(c+d);
molfracO2 = d/(c+d);

R = 8314.51/M; % gas constant, J/kg-K


% Steps (7) thru (10) are based upon the quasi-1D flow
% model with the following additional assumptions: isentropic
% nozzle expansion, perfect gas law, adiabatic chamber and
% nozzle walls, frozen flow, and no appreciable friction or
% boundary layer affects
% ** Reference (A)
%

% (7) Calculate the exhaust velocity
%

V2 = sqrt( (2*gamma/(gamma-1)) * R * Tc * (1-(P2/P1)^...
   ((gamma-1)/gamma))); % exit velocity, m/sec

% (8) Calculate the thrust coefficient
%

Cf = sqrt( (2*gamma/(gamma-1)) * gamma * ((2/(gamma+1))^...
   ((gamma+1)/(gamma-1)))*(1-(P2/P1)^((gamma-1)/gamma)))

% (9) Calculate the characteristic velocity
%

cstar = sqrt(gamma*R*Tc)/(gamma*sqrt((2/(gamma+1))^...
   ((gamma+1)/(gamma-1)))) %m/sec

% (10) Calculate the Isp
%

Isp = V2/g %sec
```

```
% (11) Determination of thruster P,V,T parameters, using
% thermodynamic data
% ** Reference (A) & (B)
%

m_dot = Thrust/V2 % mass flow rate, kg/sec

Pc = Pc*6894.757; % Pressure in Pascal, Pa
Pt = Pc*(2/(gamma+1))^(gamma/(gamma-1)); % Throat pressure, Pa

Tt = 2*Tc/(gamma+1); % Throat temperature, degrees Kelvin
T2 = Tc*(P2/P1)^((gamma-1)/gamma); % Exit temperature, deg Kelvin

Vt = sqrt((2/(gamma+1))*gamma*R*Tc); % Throat velocity, m/sec

% Method of Volumes, per Ref. (A)

Volm1 = R*Tc/Pc; % Specific volume of entrance to nozzle, m^3/kg
Volmt = Volm1*((gamma+1)/2)^(1/(gamma-1)); % throat, m^3/kg
Volme = Volm1*(P1/P2)^(1/gamma); % exit, m^3/kg


% (12) Calculate Nozzle expansion ratio and nozzle length
% ** Reference (A)
%

At = (m_dot*Volmt/Vt)*(100/1)^2 % Throat Area, cm^2
Ae = (m_dot*Volme/V2)*(100/1)^2 % Exit Area, cm^2
Dt = sqrt(4*At/pi) % Throat Diameter, cm
De = sqrt(4*Ae/pi); % Exit Diameter, cm
exp_ratio = Ae/At % expansion ratio

% Per Reference (A), p. 78, half-angle is optimal between
% 12 and 18 degrees, but may be lower. Mass increases with
% nozzle length. If mass is not an issue, then smaller half-
% angles may be used.
%

alpha = 12; % half-angle, degrees
alpha_rad = pi*alpha/180; %radians

L_cone = ((De/2)-(Dt/2))/tan(alpha_rad);


% Steps (13) includes Calculations based upon empirical data
%
```

```
% (13) Determine chamber diameter, assuming silver mesh catalyst
% ** Reference (G)
%

Throughput = m_dot * 2.2046 * 60; %lb/min
Loading_Factor = 10;

Pack_Area = Throughput/Loading_Factor %Catalyst Pack Area, in^2
Catpack_Dia = 2*2.54*sqrt(Pack_Area/pi); %Catalyst Diameter, cm


% (14) Determine the Nozzle Correction Factor
% ** Reference (A)&(B)
%

lambda = (1 + cos(alpha_rad))/2;


% (15) Modelling of Losses and Predicted Performance
% References (A)&(B)
%

zeta_v = 0.96; % Estimated velocity correction factor
Thrust_Efficiency = 0.96; % Estimated thrust correction factor
zeta_d = Thrust_Efficiency/zeta_v; % Estimated discharge correction factor

Predicted_Thrust = lambda*Thrust_Efficiency*Thrust %Newtons
Adjusted_mdot = zeta_d*m_dot; % mass flow rate, kg/sec
Predicted_Isp = Predicted_Thrust/(Adjusted_mdot*g) %seconds
```

APPENDIX 3

```
*****************************************************************************

        NASA-GLENN CHEMICAL EQUILIBRIUM PROGRAM CEA, OCTOBER 17, 2000
                    BY  BONNIE MCBRIDE AND SANFORD GORDON
      REFS: NASA RP-1311, PART I, 1994 AND NASA RP-1311, PART II, 1996

 *****************************************************************************

 #  Run 11: (Refer to Figure 5 of report)
 #  (a)  Rocket problem with infinite-area combustor (rocket iac by default).
 #  (b)  The fuel is H2O(L) at 298.17 K; the oxidant is H2O2(L) at 298.17 K.
 #  Both are in thermo.lib so that the enthalpies and "exploded" formulas
 #  do not need to be given.
 #  (c)  The oxidant-to-fuel ratio is 49.0(o/f=49.000).
 #  (d)  The chamber pressure is 250.0 psia (p,psi=250.0).
 #  (e)  Calculations are with equilibrium chemistry only (equilibrium).
 #  (f)  For exit points there is one pressure ratios (pi/p=100),

       problem  rocket  equilibrium  froz  o/f=49.000
 case=11  p,psi=250.0 pi/p=100.00
       reactants
 fuel = H2O(L)  wt% 100.   t(k) 298.17
 oxid = H2O2(L)  wt% 100.   t(k) 298.17
       output  siunits
       end
              THEORETICAL ROCKET PERFORMANCE ASSUMING EQUILIBRIUM
           COMPOSITION DURING EXPANSION FROM INFINITE AREA COMBUSTOR

                   CHAMBER   THROAT     EXIT
 Pinf/P              1.0000   1.8099   100.00
 P, BAR              17.237   9.5237  0.17237
 T, K               1225.45  1085.76   431.15
 RHO, KG/CU M    3.8164 0 2.3800 0 1.0847-1
 M, (1/n)            22.560   22.560   22.560
 Cp, KJ/(KG)(K)      1.8373   1.7767   1.4716
 GAMMAs              1.2510   1.2617   1.3341

 PERFORMANCE PARAMETERS

 Ae/At                       1.0000   9.6104
 CSTAR, M/SEC                1019.3   1019.3
 CF                          0.6971   1.5916
 Isp, M/SEC                   710.6   1622.2

 MOLE FRACTIONS

 H2O              0.67501  0.67501  0.67502
 *OH              0.00001  0.00000  0.00000
 *O2              0.32498  0.32498  0.32498

  * THERMODYNAMIC PROPERTIES FITTED TO 20000.K

    PRODUCTS WHICH WERE CONSIDERED BUT WHOSE MOLE FRACTIONS
    WERE LESS THAN 5.000000E-06 FOR ALL ASSIGNED CONDITIONS

 *H              HO2             *H2             H2O2            *O
 O3              H2O(cr)         H2O(L)
```

APPENDIX 4

Additional Finding From the Literature Search

History of Hydrogen Peroxide

Hydrogen peroxide has a long and colorful history, contrary to its clear exhaust plume. Hydrogen peroxide was used on the X-15 experimental plane and the infamous V2 rocket of World War II (Stokes, 1998). However, its use faded with the generation of more powerful, yet more toxic, propellants (Keith, 1998). Revitalization of hydrogen peroxide as a rocket propellant was primarily because the dissociation products are water and oxygen. Non-toxic exhaust is optimal for such applications as on-board naval missiles (Minthorn, 1999). Other properties that make hydrogen peroxide desirable include a high specific weight, potential for low cost, and relatively lower toxicity in the liquid state compared to other propellants.

Handling

Hydrogen peroxide is considered a "green" propellant. However, being a green propellant does not preclude dangers in handling. Hydrogen peroxide reacts with organic material (wood, clothing, etc.) and may induce combustion at high concentrations. In addition, the PPM concentration of hydrogen peroxide vapor in the atmosphere is strictly limited for human exposure. Storage requirements are available from the manufacturer (e.g., FMC, etc.), Fiegenbaum et. al. (1998), Whitehead (1998), Pauls and McMahon (1999), and other sources. The Material Data Safety Sheets (MSDS) for the chemical should always be read prior to handling.

Performance

Hydrogen peroxide may be used effectively as a rocket propellant above 70% concentration (Whitehead, 1998). A more common rocket propellant grade, high test hydrogen peroxide (HTP), extends above 85% concentration (Bruce et. al., 2001; Frolov, 1998). The benefit of higher concentration is observed within the performance of the rocket engine as detailed within *Computer Analysis* section below. However, as the concentration increases, the dangers of storage and handling increase as well as the difficulty of manufacturing (Whitehead, 1998).