A Computational Method for Determining the Equilibrium Composition and Product Temperature in a LH$_2$/LOX Combustor

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Introduction

The Generalized Fluid System Simulation Package [2] (GFSSP) is a general-purpose computer program developed at NASA/MSFC for analyzing steady state and transient flow rates, pressures, temperatures, and concentrations in a complex flow network. The code can handle compressible and incompressible flows as well as phase change and mixture thermodynamics. The program which was developed out of need for an easy to use system level simulation tool for complex flow networks, has been used for the following purposes to name a few: Space Shuttle Main Engine (SSME) High Pressure Oxidizer Turbopump Secondary Flow Circuits, Axial Thrust Balance of the Fastrac Engine Turbopump, Pressurized Propellant Feed System for the Propulsion Test Article at Stennis Space Center, X-34 Main Propulsion System, X-33 Reaction Control System and Thermal Protection System, and International Space Station Environmental Control and Life Support System design. There has been an increasing demand for implementing a combustion simulation capability into GFSSP in order to increase its system level simulation capability of a propulsion system starting from the propellant tanks up to the thruster nozzle for spacecraft as well as launch vehicles.

The present work was undertaken for addressing this need. In what follows, the model used for combustion of liquid hydrogen (LH₂) with liquid oxygen (LOX) using chemical equilibrium assumption, and the novel computational method developed for determining the equilibrium composition and temperature of the combustion products by application of the first and second laws of thermodynamics will be described. The modular FORTRAN code developed as a subroutine that can be incorporated into any flow network code with little effort has been successfully implemented in GFSSP as the preliminary runs indicate. The code provides capability of modeling the heat transfer rate to the coolants for parametric analysis in system design.

Theoretical Model

The current investigation considers the problem of combustion of LH₂ with LOX in a combustor with the assumption of $H_2O$, $H_2$, $O_2$, $OH$, $H$, and $O$ constituting the products of combustion. The schematic diagram of the problem is depicted in Figure 1.

![Schematic diagram of the combustion chamber.](image)

The problem is solved by using chemical equilibrium assumption for steady flow case by applying the first and second laws of thermodynamics [4]. An equivalent approach of using chemical equilibrium is the minimization of Gibbs free energy, which has been used in codes like CEA [1,5]. For given inlet conditions and exit pressure, the resulting equations, which turn out to be coupled, non-linear, algebraic equations, are solved simultaneously. Three cases are
considered; (a) stoichiometric case, (b) fuel rich case, and (c) oxygen rich case, for all possible environments.

**Stoichiometric Case:**
The chemistry mechanism used for this case is given by a set of reactions as follows

\[
\begin{align*}
2H_2 & + O_2 \Leftrightarrow 2H_2O \\
H_2 & \Leftrightarrow 2H \\
O_2 & \Leftrightarrow 2O \\
2H_2O & \Leftrightarrow H_2 + 2OH
\end{align*}
\]

and the changes in each specie in the form of fractions \( a, b, c, \) and \( d \) can be expressed as

\[
\begin{align*}
2H_2 & + O_2 \Leftrightarrow 2H_2O \\
-2a & -a +2a \\
H_2 & \Leftrightarrow 2H \\
-b & +2b \\
O_2 & \Leftrightarrow 2O \\
-c & +2c \\
2H_2O & \Leftrightarrow H_2 + 2OH \\
-2d & +d +2d
\end{align*}
\]

which result in the following overall reaction

\[
2H_2 + O_2 \rightarrow (2a-2d)H_2O + (2-2a-b+d)H_2 + (1-a-c)O_2
\]

\[(2d)OH + (2b)H + (2c)O\]

The individual mole fractions of species in the products can be expressed in terms of fractions \( a, b, c, \) and \( d \) in the following form

\[
\begin{align*}
z_{H_2O} &= \frac{2a-2d}{3-a+b+c+d} \\
z_{H_2} &= \frac{2-2a-b+d}{3-a+b+c+d} \\
z_{O_2} &= \frac{1-a-c}{3-a+b+c+d} \\
z_{OH} &= \frac{2d}{3-a+b+c+d} \\
z_{H} &= \frac{2b}{3-a+b+c+d} \\
z_{O} &= \frac{2c}{3-a+b+c+d}
\end{align*}
\]

and the application of second law with chemical equilibrium assumption yields

\[
K_1 = \frac{z_{H_2O}^2}{z_{H_2} \cdot z_{O_2}} \left( \frac{P}{P_o} \right)^{-1} \\
K_2 = \frac{z_{H}^2}{z_{H_2}} \left( \frac{P}{P_o} \right)
\]

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\[ K_3 = \frac{z_O^2}{z_{O_2}} \left( \frac{P}{P_o} \right) \]

\[ K_4 = \frac{z_{H_2} \cdot z_{OH}^2}{z_{H_2O}} \left( \frac{P}{P_o} \right) \]

and the first law of thermodynamics in the absence of work is expressed as

\[
\dot{Q}_{\text{cv.}} + (\dot{n}_{H_2})_r (\Delta H_{H_2})_r + (\dot{n}_{O_2})_r (\Delta H_{O_2})_r = (\dot{n}_{H_2O})_p (\bar{H}_{f_{H_2O}}^o + \Delta \bar{H}_{H_2O})_p + (\dot{n}_{H_2})_p (\Delta \bar{H}_{H_2})_p
\]

\[
+ (\dot{n}_{O_2})_p (\Delta \bar{H}_{O_2})_p + (\dot{n}_{OH})_p (\bar{H}_{f_{OH}}^o + \Delta \bar{H}_{OH})_p
\]

\[
+ (\dot{n}_H)_p (\bar{H}_{f_{H}}^o + \Delta \bar{H}_{H})_p + (\dot{n}_O)_p (\bar{H}_{f_{O}}^o + \Delta \bar{H}_{O})_p
\]

where the number of moles per unit time, \( \dot{n}_i \), for any specie \( i \), can also be expressed in terms of the fractions \( a, b, c, \) and \( d \) can be expressed as

\[
(\dot{n}_{H_2O})_p = \frac{(2a - 2d)}{3}(\dot{n}_{\text{tot}})_r
\]

\[
(\dot{n}_{H_2})_p = \frac{(2 - 2a - b + d)}{3}(\dot{n}_{\text{tot}})_r
\]

\[
(\dot{n}_{O_2})_p = \frac{(1 - a - c)}{3}(\dot{n}_{\text{tot}})_r
\]

\[
(\dot{n}_{OH})_p = \frac{2d}{3}(\dot{n}_{\text{tot}})_r
\]

\[
(\dot{n}_H)_p = \frac{2b}{3}(\dot{n}_{\text{tot}})_r
\]

\[
(\dot{n}_O)_p = \frac{2c}{3}(\dot{n}_{\text{tot}})_r
\]

where \( (\dot{n}_{\text{tot}})_r = (\dot{n}_{H_2})_r + (\dot{n}_{O_2})_r \), \( (\dot{n}_{H_2})_r = \frac{\dot{m}_{H_2}}{MW_{H_2}} \), \( (\dot{n}_{O_2})_r = \frac{\dot{m}_{O_2}}{MW_{O_2}} \), and

\[
(\dot{n}_{\text{tot}})_p = \frac{(3 - a + b + c + d)}{3}(\dot{n}_{\text{tot}})_r.
\]

The five equations to be solved simultaneously can be written in the following form after some manipulations

\[
f_1 = \frac{(a - 2d)^2 (3 - a + b + c + d)}{(2 - 2a - b + d)^2 (1 - a - c)} \left( \frac{P}{P_o} \right) - K_1 = 0
\]

\[
f_2 = \frac{(2b)^2}{(3 - a + b + c + d)(2 - 2a - b + d)} \left( \frac{P}{P_o} \right) - K_2 = 0
\]

\[
f_3 = \frac{(2c)^2}{(3 - a + b + c + d)(1 - a - c)} \left( \frac{P}{P_o} \right) - K_3 = 0
\]

\[
f_4 = \frac{(2 - 2a - b + d)^2}{(2a - 2d)^2 (3 - a + b + c + d)} \left( \frac{P}{P_o} \right) - K_4 = 0
\]

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\[ f_s = \dot{Q}_{\text{c,r}} + (\dot{n}_{H_2})_r (\Delta H_{H_2})_r + (\dot{n}_{O_2})_r (\Delta H_{O_2})_r - (\dot{n}_{H_2O})_p (\Delta H_{H_2O})_p \]
\[-(\dot{n}_{H_2})_p (\Delta H_{H_2})_p - (\dot{n}_{O_2})_p (\Delta H_{O_2})_p - (\dot{n}_{OH})_p (\Delta H_{OH})_p \]
\[-(\dot{n}_H)_p (\Delta H_H)_p - (\dot{n}_O)_p (\Delta H_O)_p = 0 \] (5)

The corresponding equations have been developed for the fuel rich case and oxygen rich case.

**Fuel rich case (FRC)**

The chemistry mechanism for this case uses the following reactions

\[ xH_2 + yO_2 \leftrightarrow 2yH_2O + (x - 2y)H_2 \quad \text{for } x > 2y \]

\[ H_2 \leftrightarrow 2H \]

\[ O_2 \leftrightarrow 2O \]

\[ 2H_2O \leftrightarrow H_2 + 2OH \]

and the changes in each specie in the form of fractions \( a \), \( b \), \( c \), and \( d \) can be expressed as

\[ xH_2 + yO_2 \leftrightarrow 2yH_2O + (x - 2y)H_2 \]

\[ -2ya \quad -ya \quad +2ya \quad + (x - 2y)a \]

\[ H_2 \leftrightarrow 2H \]

\[ -b \quad +2b \]

\[ O_2 \leftrightarrow 2O \]

\[ -c \quad +2c \]

\[ 2H_2O \leftrightarrow H_2 + 2OH \]

\[ -2d \quad +d \quad +2d \]

The overall reaction is given by

\[ xH_2 + yO_2 \rightarrow (2ya - 2d)H_2O + [x(1+a) - 4ya - b + d]H_2 \]

\[ + (y - ya - c)O_2 + (2d)OH + (2b)H + (2c)O \]

Individual mole fractions are given as

\[ z_{H,O} = \frac{(2ya - 2d)}{x(1+a) + y - 3ya + b + c + d} \]

\[ z_{H_2} = \frac{x(1+a) - 4ya - b + d}{x(1+a) + y - 3ya + b + c + d} \]

\[ z_{O_2} = \frac{y - ya - c}{x(1+a) + y - 3ya + b + c + d} \]

\[ z_{OH} = \frac{2d}{x(1+a) + y - 3ya + b + c + d} \]

\[ z_{H} = \frac{2b}{x(1+a) + y - 3ya + b + c + d} \]

\[ z_{O} = \frac{2c}{x(1+a) + y - 3ya + b + c + d} \]

With equilibrium constants given in terms of the mole fractions of products

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The five coupled, non-linear algebraic equations for this case become

\[
f_1 = \frac{(2ya - 2d)^y [x(1 + a) + y - 3ya + b + c + d]^y}{[x(1 + a) - 4ya - b + d]^y} \left( \frac{P}{P_o} \right)^{-y} - K_1 = 0 \tag{1*}
\]

\[
f_2 = \frac{(2b)^2}{[x(1 + a) + y - 3ya + b + c + d]} \left( \frac{P}{P_o} \right) - K_2 = 0 \tag{2*}
\]

\[
f_3 = \frac{(2c)^2}{[x(1 + a) + y - 3ya + b + c + d]} \left( \frac{P}{P_o} \right) - K_3 = 0 \tag{3*}
\]

\[
f_4 = \frac{x(1 + a) - 4ya - b + d}{(2ya - 2d)^2 [x(1 + a) + y - 3ya + b + c + d]} \left( \frac{P}{P_o} \right) - K_4 = 0 \tag{4*}
\]

\[
f_5 = \dot{Q}_{cx} + (\dot{n}_{H_2})_r (\Delta \overline{\bar{H}}_{H_2})_r + (\dot{n}_{O_2})_r (\Delta \overline{\bar{O}}_{O_2})_r - (\dot{n}_{H_2O})_p (\overline{\bar{H}}_{H_2O})_p + (\Delta \overline{\bar{H}}_{H_2O})_p
\]

\[
- (\dot{n}_{H_2})_p (\Delta \overline{\bar{H}}_{H_2})_p - (\dot{n}_{O_2})_p (\Delta \overline{\bar{O}}_{O_2})_p - (\dot{n}_{H_2O})_p (\overline{\bar{H}}_{H_2O})_p + (\Delta \overline{\bar{H}}_{H_2O})_p
\]

\[
- (\dot{n}_{H_2})_p (\overline{\bar{H}}_{f_{2H}} + \Delta \overline{\bar{H}}_{H_2})_p - (\dot{n}_{O_2})_p (\overline{\bar{O}}_{f_{2H}} + \Delta \overline{\bar{O}}_{O_2})_p = 0 \tag{5*}
\]

where the number of moles per unit time, \( \dot{n}_i \), for any specie \( i \), are expressed in terms of the fractions \( a, b, c \), and \( d \) accordingly.

**Oxygen rich case (ORC)**

The chemistry mechanism for this case uses the following reactions

\[ xH_2 + yO_2 \leftrightarrow xH_2O + (y-x)O_2 \quad \text{for } x < y \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2 )</td>
<td>( 2H )</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>( 2O )</td>
</tr>
<tr>
<td>( 2H_2O )</td>
<td>( H_2 + 2OH )</td>
</tr>
</tbody>
</table>

and the changes in each specie in the form of fractions \( a, b, c \), and \( d \) can be expressed as
The overall reaction is given by

\[ x \text{H}_2 + y \text{O}_2 \iff x \text{H}_2\text{O} + (y - \frac{x}{2})\text{O}_2 \]

\[-xa - \frac{x}{2}a + xa + (y - \frac{x}{2})a \]

\[ H_2 \iff 2H \quad -b + 2b \]

\[ O_2 \iff 2O \quad -c + 2c \]

\[ 2\text{H}_2\text{O} \iff \text{H}_2 + 2\text{OH} \quad -2d + d + 2d \]

The overall reaction is given by

\[ x \text{H}_2 + y \text{O}_2 \rightarrow (xa - 2d)\text{H}_2\text{O} + [x(1-a) - b + d]H_2 \]

\[ + [y - (y - x)a - c]O_2 + (2d)\text{OH} + (2b)H + (2c)O \]

Individual mole fractions are given as

\[ z_{\text{H}_2\text{O}} = \frac{(xa - 2d)}{x + y + (y-x)a + b + c + d} \]

\[ z_{H_2} = \frac{x(1-a) - b + d}{x + y + (y-x)a + b + c + d} \]

\[ z_{O_2} = \frac{y + (y - x)a - c}{x + y + (y-x)a + b + c + d} \]

\[ z_{\text{OH}} = \frac{2d}{x + y + (y-x)a + b + c + d} \]

\[ z_O = \frac{2c}{x + y + (y-x)a + b + c + d} \]

With equilibrium constants given in terms of the mole fractions of products

\[ K_1 = \frac{z_{\text{H}_2\text{O}}^x}{z_{H_2}^{1/2} z_{O_2}^{1/2}} \left( \frac{P}{P_o} \right)^{-x/2} \]

\[ K_2 = \frac{z_{H_2}^x}{z_{H_2}^{1/2}} \left( \frac{P}{P_o} \right) \]

\[ K_3 = \frac{z_{O_2}^2}{z_{O_2}} \left( \frac{P}{P_o} \right) \]

\[ K_4 = \frac{z_{\text{H}_2\text{O}}^2 z_{\text{OH}}^2}{z_{\text{H}_2\text{O}}^{1/2} z_{\text{OH}}^{1/2}} \left( \frac{P}{P_o} \right)^{-1} \]

The five coupled, non-linear algebraic equations for this case become

\[ f_1 = \frac{(xa - 2d)^x [x + y + (y-x)a + b + c + d]^{x/2}}{[x(1-a) - b + d]^x [y + (y-x)a - c]^{x/2}} \left( \frac{P}{P_o} \right)^{-x/2} - K_1 = 0 \quad (1**) \]

\[ f_2 = \frac{(2b)^2}{[x + y + (y-x)a + b + c + d] x(1-a) - b + d} \left( \frac{P}{P_o} \right) - K_2 = 0 \quad (2**) \]
\[
f_3 = \frac{(2c)^2}{[x + y + (y-x)a + b + c + d][y + (y-x)a - c]} \left( \frac{P}{P_o} \right) - K_3 = 0
\]

\[
f_4 = \frac{[x(1-a) - b + d](2d)^2}{(xa - 2d)^2 [x + y + (y-x)a + b + c + d]} \left( \frac{P}{P_o} \right) - K_4 = 0
\]

\[
f_5 = \dot{Q}_{c,x} + (\dot{n}_{H_2})_x + (\dot{n}_{O_2})_x - (\dot{n}_{H_2O})_p (\overline{h}^o_{f,x} + \Delta \overline{h}_{H_2O})_p
\]
\[
- (\dot{n}_{H_2})_p (\Delta \overline{h}_{H_2})_p - (\dot{n}_{O_2})_p (\Delta \overline{h}_{O_2})_p - (\dot{n}_{H_2O})_p (\overline{h}^o_{f,x} + \Delta \overline{h}_{H_2O})_p = 0
\]

where the number of moles per unit time, \( \dot{n}_i \), for any specie \( i \), are expressed in terms of the fractions \( a, b, c, \) and \( d \) accordingly.

**Solution Method**

It should be noted that whichever of the three cases is under consideration, the set of equations to be solved will be equations 1-5, or 1*-5*, or 1**-5**. In these equations the chemical equilibrium constants \( K_1, K_2, K_3, \) and \( K_4 \) as well as all the \( \Delta \overline{h}_i \) terms for the reactants and products are all functions of temperature. These functions have been correlated with least squares method with third or fourth order polynomials in three ranges of temperature from \( 0^\circ R \) up to \( 10000^\circ R \).

**Newton-Raphson Solution Scheme:**

The application of the Newton-Raphson method involves the following 7 steps [3]:

1. Develop the governing equations. The equations have to be in the following form:

\[
f_1(x_1, x_2, x_3, x_4, x_5) = 0
\]

\[
f_2(x_1, x_2, x_3, x_4, x_5) = 0
\]

\[
f_3(x_1, x_2, x_3, x_4, x_5) = 0
\]

\[
f_4(x_1, x_2, x_3, x_4, x_5) = 0
\]

\[
f_5(x_1, x_2, x_3, x_4, x_5) = 0
\]

Note that equations 1-5, 1*-5*, and 1**-5** are already in this form with \( a, b, c, d \) and \( T \) corresponding to \( x_1, x_2, x_3, x_4, \) and \( x_5 \) respectively.

2. Guess a solution for the equations:

Guess \( x_1^*, x_2^*, x_3^*, x_4^*, x_5^* \) as an initial solution for the governing equations.

3. Calculate the residual of each equation.

When the guessed solutions are substituted into equations (6a-6e), the right hand sides of the equations, which are not zero, are the residuals.

\[
f_1(x_1^*, x_2^*, x_3^*, x_4^*, x_5^*) = R_1
\]

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\[ f_2(x_1^*, x_2^*, x_3^*, x_4^*, x_5^*) = R_2 \]  \hfill (7b)
\[ f_3(x_1^*, x_2^*, x_3^*, x_4^*, x_5^*) = R_3 \]  \hfill (7c)
\[ f_4(x_1^*, x_2^*, x_3^*, x_4^*, x_5^*) = R_4 \]  \hfill (7d)
\[ f_5(x_1^*, x_2^*, x_3^*, x_4^*, x_5^*) = R_5 \]  \hfill (7e)

The intent of the solution scheme is to correct \( x_1, x_2, x_3, x_4, \) and \( x_5 \) with a set of corrections \( x_1^*, x_2^*, x_3^*, x_4^*, \) and \( x_5^* \) such that \( R_1, R_2, R_3, R_4, \) and \( R_5 \) are zero.

4. Develop a set of correction equations for all variables.
   First construct the matrix of influence coefficient:
   \[
   \begin{bmatrix}
   \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \frac{\partial f_1}{\partial x_3} & \frac{\partial f_1}{\partial x_4} & \frac{\partial f_1}{\partial x_5} \\
   \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \frac{\partial f_2}{\partial x_3} & \frac{\partial f_2}{\partial x_4} & \frac{\partial f_2}{\partial x_5} \\
   \frac{\partial f_3}{\partial x_1} & \frac{\partial f_3}{\partial x_2} & \frac{\partial f_3}{\partial x_3} & \frac{\partial f_3}{\partial x_4} & \frac{\partial f_3}{\partial x_5} \\
   \frac{\partial f_4}{\partial x_1} & \frac{\partial f_4}{\partial x_2} & \frac{\partial f_4}{\partial x_3} & \frac{\partial f_4}{\partial x_4} & \frac{\partial f_4}{\partial x_5} \\
   \frac{\partial f_5}{\partial x_1} & \frac{\partial f_5}{\partial x_2} & \frac{\partial f_5}{\partial x_3} & \frac{\partial f_5}{\partial x_4} & \frac{\partial f_5}{\partial x_5} \\
   \end{bmatrix}
   \]

   Then construct the set of simultaneous equations for corrections:

   \[
   \begin{bmatrix}
   \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \frac{\partial f_1}{\partial x_3} & \frac{\partial f_1}{\partial x_4} & \frac{\partial f_1}{\partial x_5} \\
   \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \frac{\partial f_2}{\partial x_3} & \frac{\partial f_2}{\partial x_4} & \frac{\partial f_2}{\partial x_5} \\
   \frac{\partial f_3}{\partial x_1} & \frac{\partial f_3}{\partial x_2} & \frac{\partial f_3}{\partial x_3} & \frac{\partial f_3}{\partial x_4} & \frac{\partial f_3}{\partial x_5} \\
   \frac{\partial f_4}{\partial x_1} & \frac{\partial f_4}{\partial x_2} & \frac{\partial f_4}{\partial x_3} & \frac{\partial f_4}{\partial x_4} & \frac{\partial f_4}{\partial x_5} \\
   \frac{\partial f_5}{\partial x_1} & \frac{\partial f_5}{\partial x_2} & \frac{\partial f_5}{\partial x_3} & \frac{\partial f_5}{\partial x_4} & \frac{\partial f_5}{\partial x_5} \\
   \end{bmatrix}
   \begin{bmatrix}
   x_1^* \\
   x_2^* \\
   x_3^* \\
   x_4^* \\
   x_5^* \\
   \end{bmatrix}
   =
   \begin{bmatrix}
   R_1 \\
   R_2 \\
   R_3 \\
   R_4 \\
   R_5 \\
   \end{bmatrix}
   \]

5. Solve for \( x_1^*, x_2^*, x_3^*, x_4^*, \) and \( x_5^* \) by solving the simultaneous equations.

6. Apply correction to each variable.

7. Iterate until corrections become smaller than a prescribed value.

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Subroutines EQNS, SIMUL, PARDIF, and GAUSSY as described in reference [3] were modified for the problem under investigation. EQNS provides the simultaneous equations to be solved; SIMUL performs the Newton-Raphson solution of equations in EQNS with application of PARDIF and GAUSSY appropriately; PARDIF extracts the partial derivatives; and GAUSSY solves the resulting set of linear simultaneous equations by Gauss elimination method.

**Conclusion**

A modular FORTRAN code was developed for applying the first and second laws of thermodynamics to the combustion of LH$_2$ with LOX. Chemical equilibrium assumption based on the minimization of Gibbs free energy was employed. Case studies were performed with stoichiometric, fuel-rich and oxygen-rich cases. All these yielded very good results compared with hand calculations. Preliminary runs also indicate successful integration of this modular code with GFSSP. This modular code enhances the capability of GFSSP in performing system level simulation of a complete propulsion system using LH$_2$/LOX, starting from the propellant tanks up to the thruster nozzle.

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**References**