Development of a Chemical Oxidizer Tank Model for Hybrid Rocket Engines

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Abstract

This paper documents a numerical model, developed for the McGill Rocket Team based on classical chemical thermodynamics coupled with the Trebble-Bishnoi equation of state, to solve for the oxidizer tank conditions (pressure, temperature, mole flowrate and liquid/vapour equilibrium) during the operation of a hybrid rocket. This model is modular and can be coupled to fluid mechanics and combustion chamber models for a more detailed analysis of a hybrid rocket engine.

1 Introduction

A hybrid rocket engine is a type of rocket engine that uses a liquid or gaseous oxidizer with a solid fuel. One of the McGill Rocket Team's goals, for the 2017-2018 IREC competition, is to build a hybrid rocket. Such an endeavour will also require mathematical modelling along with empirical testing to optimize performance. The development of a mathematical model of a hybrid rocket engine requires, among other things, a model of the oxidizer tank. These values are crucial for estimating the engine burn time, the oxidizer mass required and the combustion chamber inlet conditions.

The objective of this paper is to describe a numerical model of the oxidizer tank during operation that is robust, accurate, modular, and easy to maintain in MATLAB. Although similar models have previously been developed [2, 1, 7], they generally have a few issues, such as being specific to a single kind of oxidizer, not allowing for the modelling of additional pressurants such as helium, not using gas models that are as accurate as desired, or not being modular enough to be able to couple to models of other parts of the hybrid engine. This model should be documented in sufficient detail here such that future members should be able to understand its working from consulting this document and easily make changes to the MATLAB code or the model. This model is particularly useful for modelling nitrous oxide (N_2O) given the typical launch conditions at IREC but can be used with other oxidizers as well, depending on the operating temperature of the rocket.

2 Some Basic Theory

The thermodynamic properties and equilibrium states of all chemical systems (i.e. gases and liquids) can be determined using equations that relate the state variables of the system: pressure, temperature, specific volume and composition (if dealing with chemical mixtures). Such equations are called **equations of state**. The simplest equation of state is known as the **ideal gas law**:

$$P\hat{V} = RT \tag{1}$$

Where the hat on the V denotes *specific volume*, or volume per mole of substance. From the equation of state, it then becomes possible to calculate other thermodynamic properties from state functions, such as the internal energy U, enthalpy H, Gibbs free energy G and entropy S. For liquid/vapour mixtures, the ideal gas law is often paired with **Raoult's law**, which states that the partial pressure of a gas is proportional to its vapour pressure and its mole fraction:

$$P_i = P_i^* x_i \tag{2}$$

Where P_i denotes the partial pressure of component i in the mixture, and P_i^* and x_i are the vapour pressure and mole fraction, respectively.

The ideal gas law is very simple and easy to use, but at elevated pressures, at lower temperatures or with chemical mixtures, substantial inaccuracies begin to appear. The solution is to add a corrective term Z, which is called the **compressibility factor**.

$$P\hat{V} = ZRT \tag{3}$$

Many equations of state (but not all) are focused on finding values for Z given the chemical properties of the system. In a similar fashion, pressure alone becomes inadequate for describing vapour/liquid equilibria, and is replaced by a term $f(T, P, x, Z)$ that more accurately reflects the chemical dynamics of the system, called **fugacity**.

$$f_i = f_i^* x_i \tag{4}$$

Fugacity and pressure are related with the dimensionless **fugacity coefficient**.

$$\phi = \frac{f}{P} \tag{5}$$

What chemical properties are used in equations of state? The most important one is the substance's **critical point**. This is the point where the liquid and vapour phases of the chemical species become indistinguishable, i.e. the heat of vaporization becomes 0. Above their critical point, chemicals behave like gases — regardless of pressure. It turns out that different chemicals behave similarly depending on how "close" to criticality they are. As the critical point can be easily experimentally determined, that makes it a good way to predict the properties of various liquids and gases under a variety of conditions. The temperature, vapor pressure, specific volume and compressibility factor at the critical point are called the critical temperature T_c, critical pressure P_c, critical volume V_c and critical compressibility Z_c, respectively.

Another frequently used parameter is the **acentric factor** ω, which accounts for the non-sphericity of molecules. This is also easily experimentally determined, and for many chemicals, the acentric factor has been tabulated.

One note on nomenclature: This document uses the terms "gas" and "vapour", but they are generally **not interchangeable**. "Gas" refers to the entirety of the gaseous phase while "vapour" refers exclusively to the oxidizer that is in the gas phase. If the tank contents consist solely of pure oxidizer, then vapour and gas may be used interchangeably.

3 Liquid Phase Model

Our objective is to determine the following variables at any given point in time:

1. T, the temperature of the oxidizer. The tank is assumed to be in thermal equilibrium, so there is no temperature gradient throughout the process.

2. P, the tank pressure.
3. n_l, the number of moles of liquid oxidizer.
4. n_g, the number of moles of gaseous oxidizer.

The model begins by first making a few assumptions:

- The tank walls are adiabatic (i.e. no heat loss during operation).
- The liquid is pure oxidizer, while the gas can be a mixture of oxidizer and pressurant (this assumption can be removed in the future, with some relatively minor changes).
- The liquid/vapour system reach equilibrium instantaneously.

This leaves us with 4 key constraints:

1. Conservation of energy
2. Conservation of mass
3. Fixed volume
4. Equilibrium constraint

Applying these constraints leaves us with a system of ordinary differential equations, which can be solved simultaneously in order to find the temperature, pressure, moles of gas and moles of liquid at every point in time. The differential equations resulting from each constraint are shown in the following sections.

3.1 Conservation of Energy

Assuming the tank is adiabatic, the only source of energy loss is the enthalpy of the molecules leaving the tank through the outlet. As the tank volume does not change, we consider only the internal energy of its contents:

$$\frac{d}{dt}(n_t\hat{U}_t) = -\dot{n}\hat{H}_l \tag{6}$$

$$n_tU_t = n_{tank}U_{tank} + n_gU_g + n_lU_l \tag{7}$$

It is possible to split the internal energy and enthalpy into two values: the **ideal** value and the **excess** value, which is simply defined as the difference between the ideal value and the real value.

$$H = H^* + H_{excess} \tag{8}$$

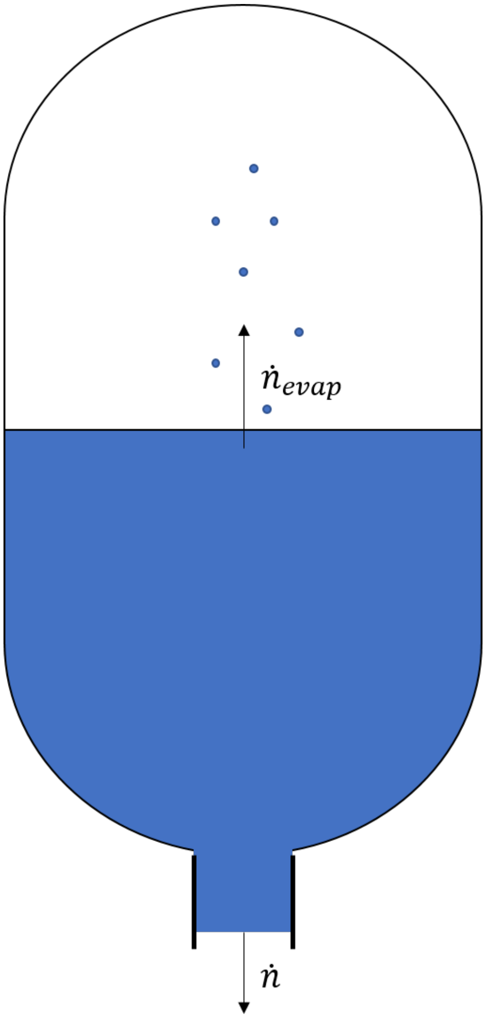

Figure 1: A sketch of the oxidizer tank during operation. The liquid oxidizer is on the bottom, and as the pressure drops, some of the oxidizer will vaporize to repressurize the tank.

The fundamental relation between internal energy U and enthalpy H is:

$$U = H - PV = H - ZRT \tag{9}$$

By taking the derivative with respect to time, combining with equations 8 and 9 and separating the partial derivatives, we obtain:

$$X\frac{dT}{dt} + W\frac{dP}{dt} + Y\frac{dn_l}{dt} + \Gamma\frac{dn_g}{dt} = 0 \tag{10}$$

These terms can be further split into the liquid and vapour derivatives:

$$X = L_T + V_T \tag{11}$$

$$W = L_P + V_P \tag{12}$$

$$Y = L_n - \hat{H}_{l,excess} \tag{13}$$

$$\Gamma = V_n + \Delta\hat{H}_v - \hat{H}_{l,excess} \tag{14}$$

L_T is given by:

$$L_T = n_l\left[\hat{C}^*_{p,l} + \frac{\partial\hat{H}_{l,excess}}{\partial Z_l}\frac{\partial Z_l}{\partial T} + \frac{\partial\hat{H}_{l,excess}}{\partial T} - R\left(Z_l + T\frac{\partial Z_l}{\partial T}\right)\right] \tag{15}$$

All of the values in this equation can be calculated. The specific heat $\hat{C}^*_{p,l}$ can be determined using tabulated correlations for a variety of substances, while the derivatives can be determined using any kind of slope finding algorithm, such as Richardson extrapolation. The remaining liquid and vapour derivatives are listed in the appendix.

3.2 Conservation of Mass

The only location where mass is flowing out of(and hopefully not into) the tank is at the outlet. The change in the number of moles leaving the tank is therefore a function of the pressure difference between the combustion chamber and the tank, as well as possibly the specific volume, density, and specific heat ratios. This function will be denoted as K.

$$\frac{dn_g}{dt} + \frac{dn_l}{dt} = -K(\Delta P) \tag{16}$$

3.3 Fixed Volume

The volume of the tank is constant. This is an additional constraint, because as the liquid empties, the empty space must be filled out by the gas, leading to a drop in pressure and an equilibrium shift.

$$V = n_g\hat{V}_g + n_l\hat{V}_l \tag{17}$$

Replacing the V terms with the expression $\frac{ZRT}{P}$, we obtain:

$$P = \frac{RT}{V}(n_g Z_g + n_l Z_l) \tag{18}$$

Taking the time derivative of this expression, we obtain the following:

$$\eta\frac{dT}{dt} + \gamma\frac{dP}{dt} + Z_l\frac{dn_l}{dt} + \delta\frac{dn_v}{dt} = 0 \tag{19}$$

Where

$$\eta = n_g\frac{\partial Z_g}{\partial T} + n_l\frac{\partial Z_l}{\partial T} + \frac{1}{T}(Z_g n_g + Z_l n_l) \tag{20}$$

$$\gamma = n_g\frac{\partial Z_g}{\partial P} + n_l\frac{\partial Z_l}{\partial P} - \frac{V}{RT} \tag{21}$$

$$\delta = (1-y)\frac{\partial Z_g}{\partial y} + Z_g \tag{22}$$

3.4 Equilibrium Constraint

At chemical equilibrium, the fugacity coefficients must be equal:

$$\phi_l = y\phi_v \tag{23}$$

Since the system is at equilibrium at the beginning of the process, and is assumed to stay at equilibrium, these values must stay the same throughout, i.e. the difference betyween the liquid and vapour fugacities remains 0 over time. Knowing that $y = \frac{n_g}{n_v}$, and taking the derivative with respect to time, we obtain:

$$\frac{d}{dt}(n_g\phi_l - n_v\phi_v) = 0 \tag{24}$$

By expanding the partial derivatives and converting to the standard form of the differential equation, we have:

$$\Theta\frac{dT}{dt} + \Lambda\frac{dP}{dt} + \Psi\frac{dn_g}{dt} = 0 \tag{25}$$

Where

$$\Theta = n_g\left(\frac{\partial \phi_l}{\partial Z_l}\frac{\partial Z_l}{\partial T} + \frac{\partial \phi_l}{\partial T}\right) - n_v\left(\frac{\partial \phi_v}{\partial Z_v}\frac{\partial Z_v}{\partial T} + \frac{\partial \phi_v}{\partial T}\right) \tag{26}$$

$$\Lambda = n_g\left(\frac{\partial \phi_l}{\partial Z_l}\frac{\partial Z_l}{\partial P} + \frac{\partial \phi_l}{\partial P}\right) - n_v\left(\frac{\partial \phi_v}{\partial Z_v}\frac{\partial Z_v}{\partial P} + \frac{\partial \phi_v}{\partial P}\right) \tag{27}$$

$$\Psi = \psi_l - \phi_v - y(1-y)\left(\frac{\partial \phi_v}{\partial Z_v}\frac{\partial Z_v}{\partial y} + \frac{\partial \phi_v}{\partial y}\right) \tag{28}$$

3.5 Solution Matrix

Combining the four derived differential equations, we obtain the system of equations needed to solve for T, P, n_l and n_g:

$$\begin{bmatrix} W & X & Y & \Gamma \\ 0 & 0 & 1 & 1 \\ \eta & \gamma & Z_l & \delta \\ \Theta & \Lambda & 0 & \Psi \end{bmatrix} \begin{bmatrix} \frac{dT}{dt} \\ \frac{dP}{dt} \\ \frac{dn_l}{dt} \\ \frac{dn_v}{dt} \end{bmatrix} = \begin{bmatrix} 0 \\ -K \\ 0 \\ 0 \end{bmatrix} \tag{29}$$

4 Pure Gas Phase Model

Once the liquid has been completely emptied, or if the nitrous begins at above the critical temperature, then the gas will empty from the tank. Because the system is no longer in a liquid/vapour equilibrium, the physics are significantly simpler. Some additional assumptions will be made here:

- The oxidizer and pressurant, if any, are **homogeneously mixed**.
- The flow can be modeled as **isentropic**, i.e. no energy loss.
- The **same equations** governing the flow of the liquid can be applied to the flow of the gas.

With these assumptions in mind, the next step is to set up the equations. We first note the equation governing flow:

$$\frac{dn_g}{dt} = \frac{1}{M}\frac{dm}{dt} = -K(\Delta P) \tag{30}$$

Where M and m denote the average molar weight and the total mass of the tank, respectively. For isentropic expansion, the temperature, pressure, and density of an **ideal** gas can be described with the following relations:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{\rho_2}{\rho_1}\right)^{\gamma-1} \tag{31}$$

Where ρ and γ denote the density and the heat capacity ratio of the gas, respectively. The subscripts 1 and 2 can be used to denote the state of the gas at two different points in time. Obviously, the gas is unlikely to be behaving ideally, and so the compressibility factors must be included. First, for a real gas, the pressure can be related to the density, temperature and compressibility with the following equation:

$$P = \frac{1}{M} Z \rho R T \tag{32}$$

Noting that $\rho = m/V$, it is possible to obtain the following with some basic algebra and canceling out V, R and M, all constants:

$$\frac{P_2}{P_1} = \frac{T_2/(Z_1 m_1)}{T_1/(Z_2 m_2)} \tag{33}$$

Substituting back into (31) and simplifying,

$$\frac{T_2}{T_1} = \left(\frac{Z_1 m_1}{Z_2 m_2}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{\rho_2}{\rho_1}\right)^{\gamma-1} \tag{34}$$

This means that it is possible to relate the change in mass, known from the flow equation (30), to the pressure, temperature and density simultaneously (Remember that $m_2 = m_1 + \frac{\Delta m}{\Delta t}$)!

The only remaining question is how to calculate Z, as it is dependent on P. The easiest way is to use iteration, by first guessing the value of Z. This will allow us to calculate P and T based on (34). We use these values to recalculate Z in (32). If the resulting value is higher than our guess, then Z is incremented slightly. If it is lower, then Z is decremented. This process is repeated until convergence is achieved.

The initial guess can be provided by the Trebble-Bishnoi equation of state, which will give the compressibility, pressure, oxidizer amount, and temperature at the beginning of the process (it could also be used to calculate the emptying process, but using a simple iteration loop is much more computationally efficient).

5 The Trebble-Bishnoi Equation of State

The Trebble-Bishnoi equation of state (TB-EOS) is a 4-parameter cubic equation of state of the form

$$P = \frac{RT}{V-b} - \frac{a(T)}{V^2 + (b+c)V - (bc - d^2)} \tag{35}$$

where a, b, c and d are parameters that depend on the chemical properties of the system [4, 3]. In cubic form, the TB-EOS can be written as:

$$\begin{aligned} 0 = Z^3 + (C-1)Z^2 + (A - 2BC - B - C - B^2 - D^2)Z \\ + [B^2C + BC - AB + D^2(B+1)] \end{aligned} \tag{36}$$

where:

$$A = \frac{aP}{R^2T^2} \tag{37}$$

$$B = \frac{bP}{RT} \tag{38}$$

$$C = \frac{cP}{RT} \tag{39}$$

$$D = \frac{dP}{RT} \tag{40}$$

The largest and smallest solutions to this polynomial give the compressibility of the gas and liquid phases respectively, while the middle root is discarded.

5.1 Determining the Parameters

The first parameter, a, is a function of T and is obtained by first calculating its value at the critical point, a_c:

$$a_c = 0.45724 \frac{R^2T_c^2}{P_c} \tag{41}$$

Afterwards, for a given temperature, a is given by:

$$a(T, \omega) = a_c \cdot \alpha(T_r, q_1) \tag{42}$$

$$\alpha = \exp[q_1(1 - T_r)] \tag{43}$$

$$T_r = T/T_c \tag{44}$$

$$q_1 = \begin{cases} 0.66208 + 4.63961\omega + 7.45183\omega^2 & \text{for } \omega < -0.10 \\ -0.31913 & \text{for } \omega < 0.35 \text{ and } T_r \leq 1.0 \\ 0.35 + 0.7924\omega + 0.1875\omega^2 - 28.93(0.3 - Z_c)^2 & \text{for } -0.10 \leq \omega \leq 0.40 \\ 0.32 + 0.9424\omega - 28.93(0.3 - Z_c)^2 & \text{for } \omega > 0.40 \end{cases}$$

The value of b is determined in a similar manner:

$$b_c = 0.07780\frac{RT_c}{P_c} \tag{45}$$

$$b = b_c \cdot \beta(T_r, \omega) \tag{46}$$

$$\beta = \begin{cases} 1.0 + q_2(1 - T_r + \ln T_r) & \text{for } T_r \leq 1.0 \\ 1.0 & \text{for } T_r > 1.0 \end{cases}$$

$$q_2 = \begin{cases} 0 & \text{for } \omega < -0.0423 \\ 0.05246 + 1.15058\omega - 1.99348\omega^2 & \\ +1.59490\omega^3 - 1.39267\omega^4 & \text{for } -0.0423 \leq \omega \leq 0.30 \\ 0.17959 + 0.23471\omega & \text{for } \omega > 0.30 \end{cases}$$

c is found using the following relations:

$$C_c - 1 = -3\zeta_c \tag{47}$$

$$\zeta_c = 1.075 Z_c \tag{48}$$

$$C_c = \frac{cP_c}{RT_c} \tag{49}$$

Finally, the value of d is obtained from a table, or in certain cases calculated from a generalized correlation:

$$d = 0.341 V_c - 0.005 \tag{50}$$

Where V_c is in units of m^3/kmol.

5.2 Extension to Mixtures

When applied to fluid mixtures, the TB-EOS must include some additional terms to account for the interactions between different mixture components [5]. There are now 3 different types of parameters: a_i, the parameter for the *pure* substance i in the mixture, a_ij, the value of a that accounts for the interaction between component i and component j, and a_m, the value of a for the *overall mixture.* a_i and a_j are calculated as done normally with a pure substance. Afterwards, the interaction parameters are defined as:

$$a_{ij} = (a_i a_j)^{1/2}(1 - K_{a_{ij}}) \tag{51}$$

$$b_{ij} = \frac{b_i + b_j}{2}(1 - K_{b_{ij}}) \tag{52}$$

$$c_{ij} = \frac{c_i + c_j}{2}(1 - K_{c_{ij}}) \tag{53}$$

$$d_{ij} = \frac{d_i + d_j}{2}(1 - K_{d_{ij}}) \tag{54}$$

Where K denotes an interaction constant between components for that specific parameter. Generally, K can be considered to be equal to 0, unless specified otherwise. The mixture parameters are:

$$a_m = \sum_{i=1}^{i=n}\sum_{j=1}^{j=n} x_i x_j a_{ij} \tag{55}$$

$$b_m = \sum_{i=1}^{i=n}\sum_{j=1}^{j=n} x_i x_j b_{ij} \tag{56}$$

$$c_m = \sum_{i=1}^{i=n}\sum_{j=1}^{j=n} x_i x_j c_{ij} \tag{57}$$

$$d_m = \sum_{i=1}^{i=n}\sum_{j=1}^{j=n} x_i x_j d_{ij} \tag{58}$$

Once the mixture parameters are determined, calculation of the TB-EOS proceeds as usual, except using the mixture parameters rather than the pure parameters for the calculations.

5.3 Enthalpy and Fugacity

Once the state variables of the system are known for a given instant, we can then calculate the enthalpy H and fugacity f. These are essential for the energy balance and chemical equilibrium equations. For the TB-EOS, we begin by calculating the values of three variables: τ, θ and λ [6]:

$$\tau = 1 + \frac{6c}{b} + \frac{c^2}{b^2} + \frac{4d^2}{b^2} \tag{59}$$

The values of the two other variables depend on the sign of τ. If τ is positive:

$$\theta = \sqrt{\tau} \tag{60}$$

$$u = 1 + \frac{c}{b} \tag{61}$$

$$\lambda = \ln \left| \frac{2Z + B(u - \theta)}{2Z + B(u + \theta)} \right| \tag{62}$$

If τ is negative:

$$\theta = \sqrt{-\tau} \tag{63}$$

$$\lambda = -2 \arctan \left(\frac{2Z + uB}{B\theta} - \pi \right) \tag{64}$$

Afterwards, the enthalpy is:

$$\begin{aligned} H - H^* = H_{excess} = {} & RT(Z-1) + \frac{\lambda}{b\theta}(a - \frac{\partial a}{\partial T}) \\ & + \frac{\partial b}{\partial T}\left(\frac{-RT}{V-b} + \frac{a}{b^2\tau}\left[\frac{V(2c+b) - bc + c^2 - 2d^2}{\delta} + \frac{(3c+b)\lambda}{b\theta} \right] \right) \end{aligned} \tag{65}$$

where:

$$\delta = V^2 + (b+c)V - (bc + d^2) \tag{66}$$

The fugacity is:

$$\ln \left| \frac{f}{P} \right| = Z - 1 - \ln|Z - B| + \frac{A}{B\theta}\lambda \tag{67}$$

For mixtures, the enthalpy equation is identical, except the mixture parameters, denoted with the subscript m, are used instead of the pure substance values. The fugacity equation is slightly more complex, although quite similar:

$$\begin{aligned}\ln|\frac{f_i}{x_j P}| = \frac{b_d}{b_m}(Z-1) - \ln|Z-B_m| \\ + \frac{A_m\lambda}{B_m\theta}\left[\frac{(a_d/n)}{a_m} - \frac{b_d}{b_m} - \frac{n\theta_d}{\theta}\right] \\ - \frac{A_m}{B_m\theta}\left[\frac{ZB_m n\theta_d + 0.5B_m^2(un\theta_d - \theta nu_d)}{Z^2 + (B_m + C_m)Z - (B_m C_m + D_m^2)}\right]\end{aligned} \tag{68}$$

Where

$$n\theta_d = \frac{-1}{2\theta b_m^2}\left[6b_m c_d - 6b_d c_m + 2c_m c_d + 8d_m d_d - \frac{b_d}{b_m}(2c_m^2 + 8d_m^2)\right] \tag{69}$$

$$nu_d = \frac{c_d}{b_m} - \frac{b_d c_m}{b_m^2} \tag{70}$$

$$a_d = \frac{\partial}{\partial n_i}(a_m n^2) - 2\sum_{j=1}^{j=n} n_j a_{ij} \tag{71}$$

$$b_d = \frac{\partial}{\partial n_i}(b_m n) = 2\sum_{j=1}^{j=n} x_j b_{ij} - b_m \tag{72}$$

$$c_d = \frac{\partial}{\partial n_i}(c_m n) = 2\sum_{j=1}^{j=n} x_j c_{ij} - c_m \tag{73}$$

$$d_d = \frac{\partial}{\partial n_i}(d_m n) = 2\sum_{j=1}^{j=n} x_j d_{ij} - d_m \tag{74}$$

For more information on how these equations are obtained, consult the appendix.

6 Initial Conditions

How are the initial conditions for the differential equations determined? At the beginning of the burn, it is presumed that we know the temperature of the tank (easily measured) and the mass of oxidizer/pressurant loaded into the tank, but not the pressure nor what portion of the oxidizer has evaporated. Therefore, the TB-EOS is used to determine the pressure and the relative amounts of liquid and gaseous oxidizer, in a separate MATLAB script.

6.1 Constraints and Objective Functions

The relevant constraints to consider are conservation of mass, fixed volume, and chemical equilibrium. Since the tank can exchange heat with its surroundings conservation of energy is not applicable here.

$$n_{oxidizer} = n_v + n_l \tag{75}$$

$$n_g = n_v + n_{pressurant} \tag{76}$$

$$\phi_l = y\phi_v \tag{77}$$

$$V = n_g\hat{V_g} + n_l\hat{V_l} \tag{78}$$

As we know the total mass of oxidizer in the tank, knowing n_v also give us n_l from (75). This leaves two unknowns: P and n_v. We can therefore define two **objective functions** by rearranging (77) and (78):

$$\mathbf{F}_1(P, n_v) = (n_v + n_{pressurant})\phi_l - n_v\phi_v \tag{79}$$

$$\mathbf{F}_2(P, n_v) = (n_v + n_{pressurant})Z_g + (n_{oxidizer} - n_v)Z_l - \frac{PV}{RT} \tag{80}$$

The system is at equilibrium when both $\mathbf{F}_1$ and $\mathbf{F}_2$ are equal to 0.

6.2 Solution Method

To find the initial conditions, an initial guess is generated using Raoult's law:

$$n_v = \frac{y n_{pressurant}}{1-y} \tag{81}$$

$$P = \frac{P^*_{oxidizer}(T)}{y} \tag{82}$$

The pure vapor pressure P^* can be found for various substances using tabulated correlations.

Next, the compressibility factors $Z_l(T, P)$, $Z_g(T, P, y)$ and fugacity coefficients ϕ_l, ϕ_v are calculated using the TB-EOS. $\mathbf{F}_1$ and $\mathbf{F}_2$ can then be evaluated. To converge towards 0, Newton-Raphson's method for nonlinear systems is applied:

$$\begin{pmatrix} n_v \\ P \end{pmatrix}_{k+1} = \begin{pmatrix} n_v \\ P \end{pmatrix}_k - \mathbf{J^{-1}} \begin{bmatrix} \mathbf{F}_1 \\ \mathbf{F}_2 \end{bmatrix}_k \tag{83}$$

Where $\mathbf{J}$ is the Jacobian of the objective function vector. The error is then calculated:

$$||\delta_{k+1}|| = \sqrt{\left(n_v\big|_{k+1} - n_v\big|_k\right)^2 + \left(P\big|_{k+1} - P\big|_k\right)^2} \tag{84}$$

$$||\mathbf{F}|| = \sqrt{\mathbf{F}_1^2 + \mathbf{F}_2^2} \tag{85}$$

$$\text{norm} = \max(||\delta_{k+1}||, ||\mathbf{F}||) \tag{86}$$

We set an arbitrary tolerance tol, which is the maximum acceptable error. If norm < tol, the solution has converged. If norm > tol, we recalculate y based on the new value of n_v:

$$y|_{k+1} = \frac{n_v|_{k+1}}{n_v|_{k+1} + n_{pressurant}} \tag{87}$$

We recalculate the compressibility factors Z_g and Z_l and repeat the steps until convergence is achieved.

7 Structure of Program

The overall structure of the MATLAB program is as follows:

1. Input physical parameters, temperature, mass of oxidizer/pressurant.
2. Run initial conditions script.
3. Check if oxidizer is supercritical. If so, skip the liquid script and run the gas script.
4. Calculate all parameters in TB-EOS.
5. Calculate all required derivatives either analytically or using Richardson extrapolation.
6. Solve next step of Runge-Kutta algorithm.
7. Iterate 3-5 until the liquid is emptied.
8. Switch to gaseous model until gas is empty.

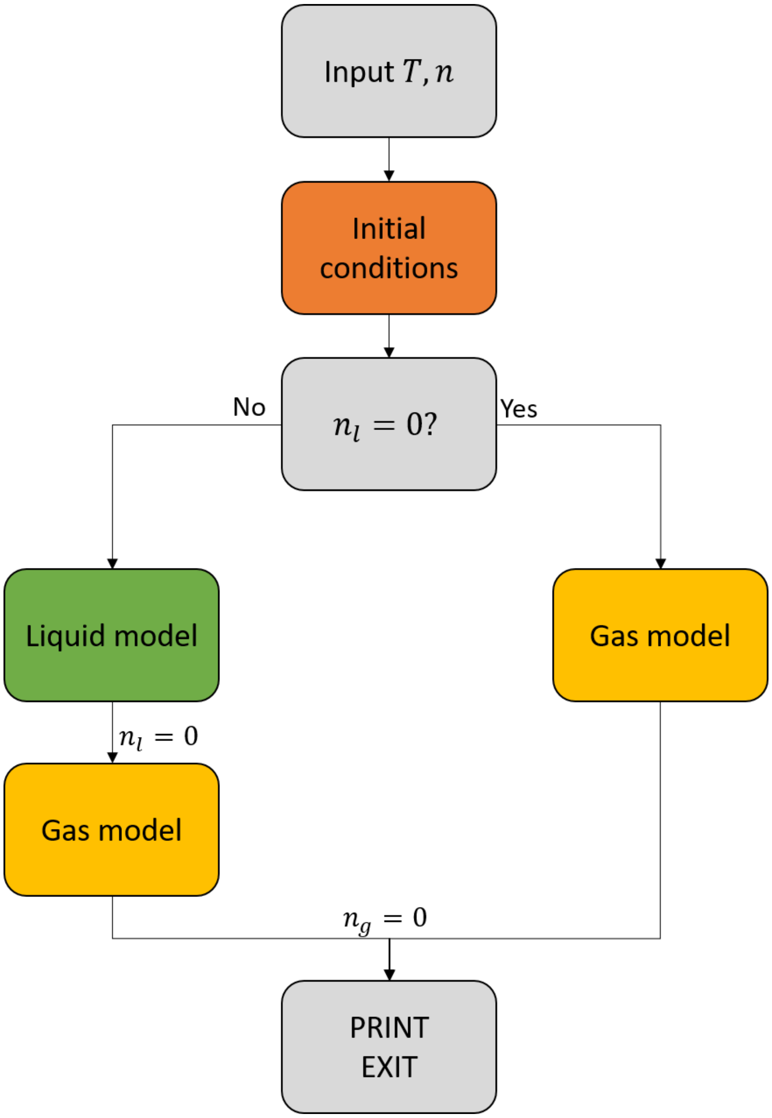

Figure 2: Overall structure of model.

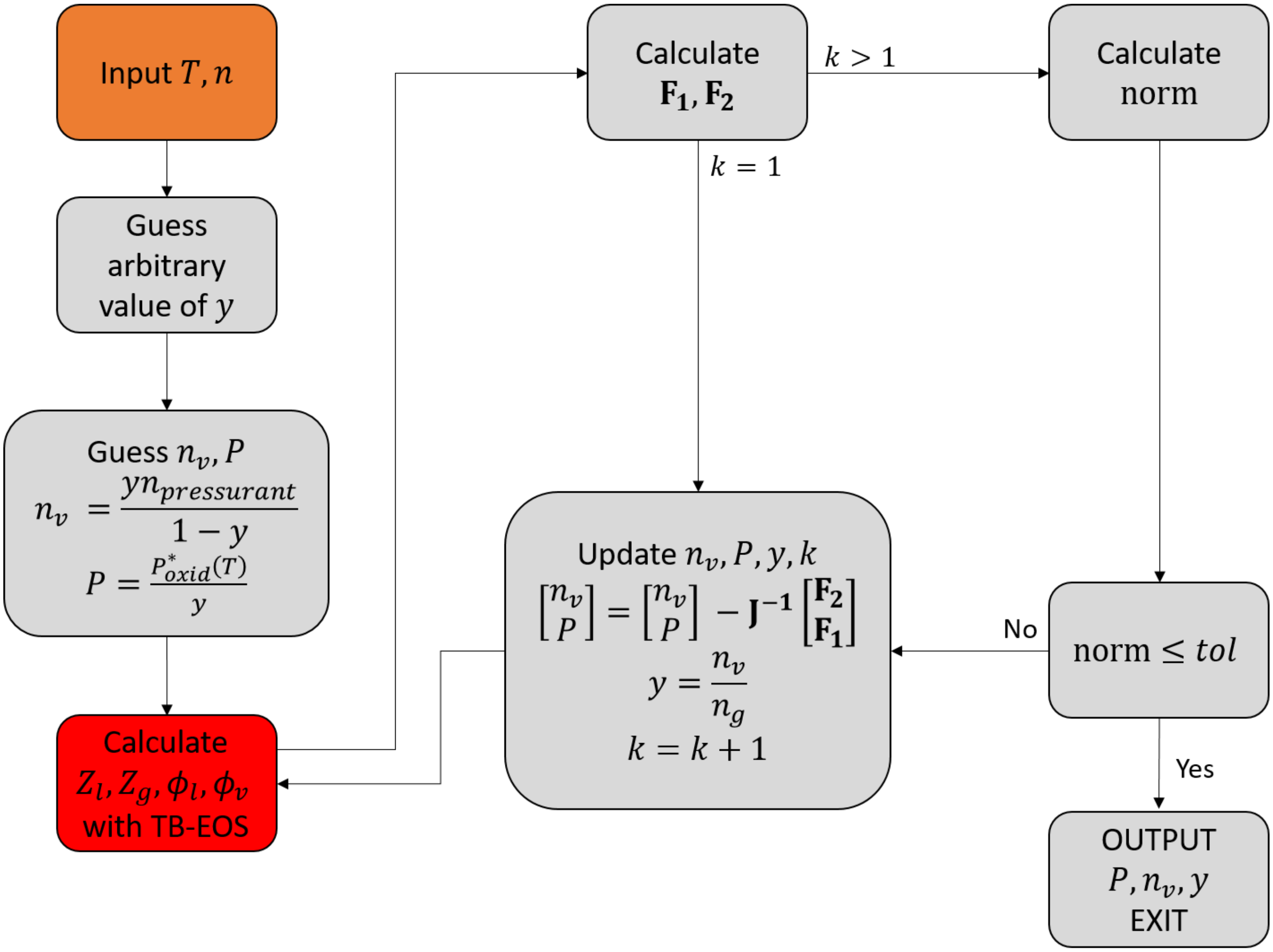

Figure 3: Structure of initial condition script.

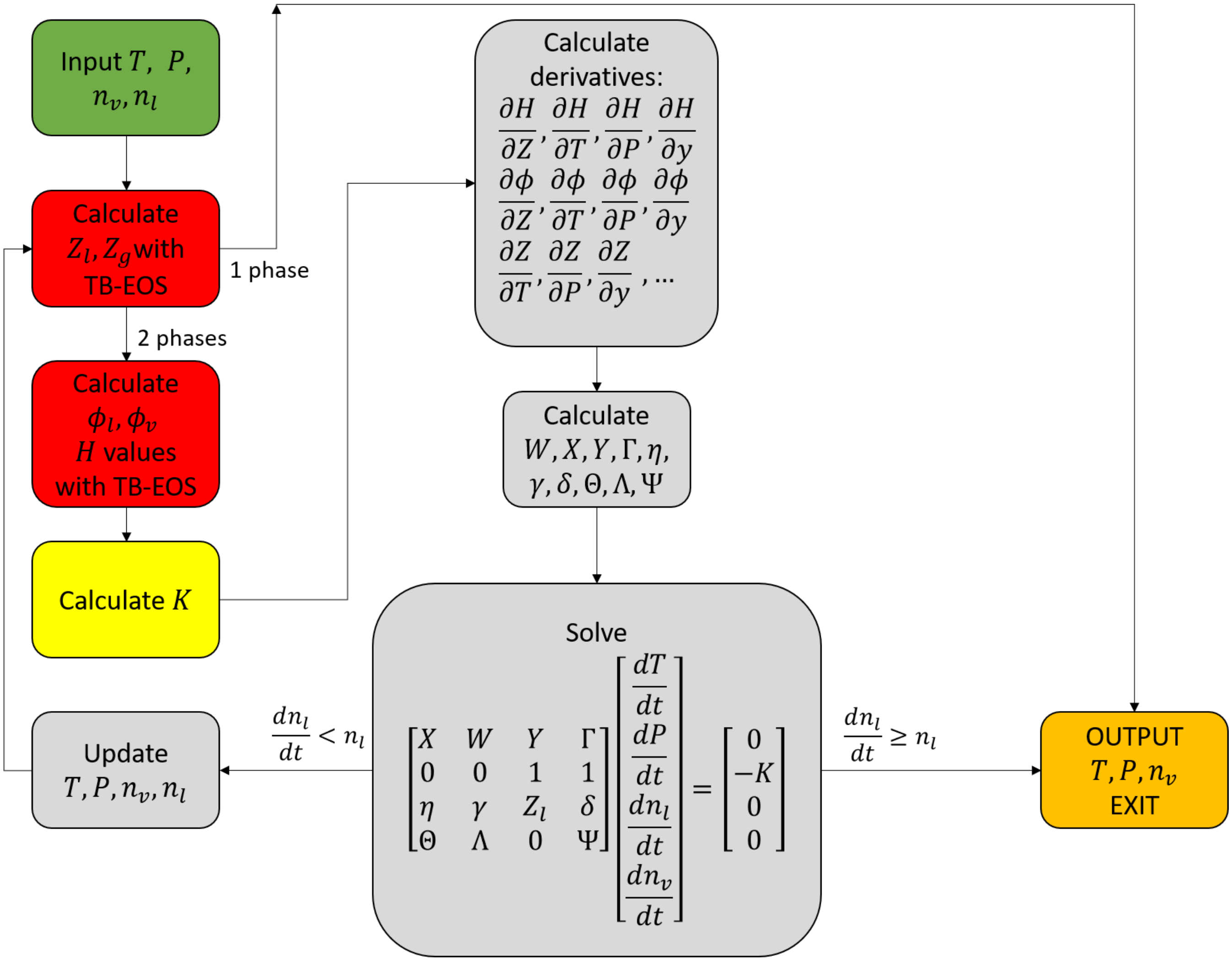

Figure 4: Structure of liquid flow model.

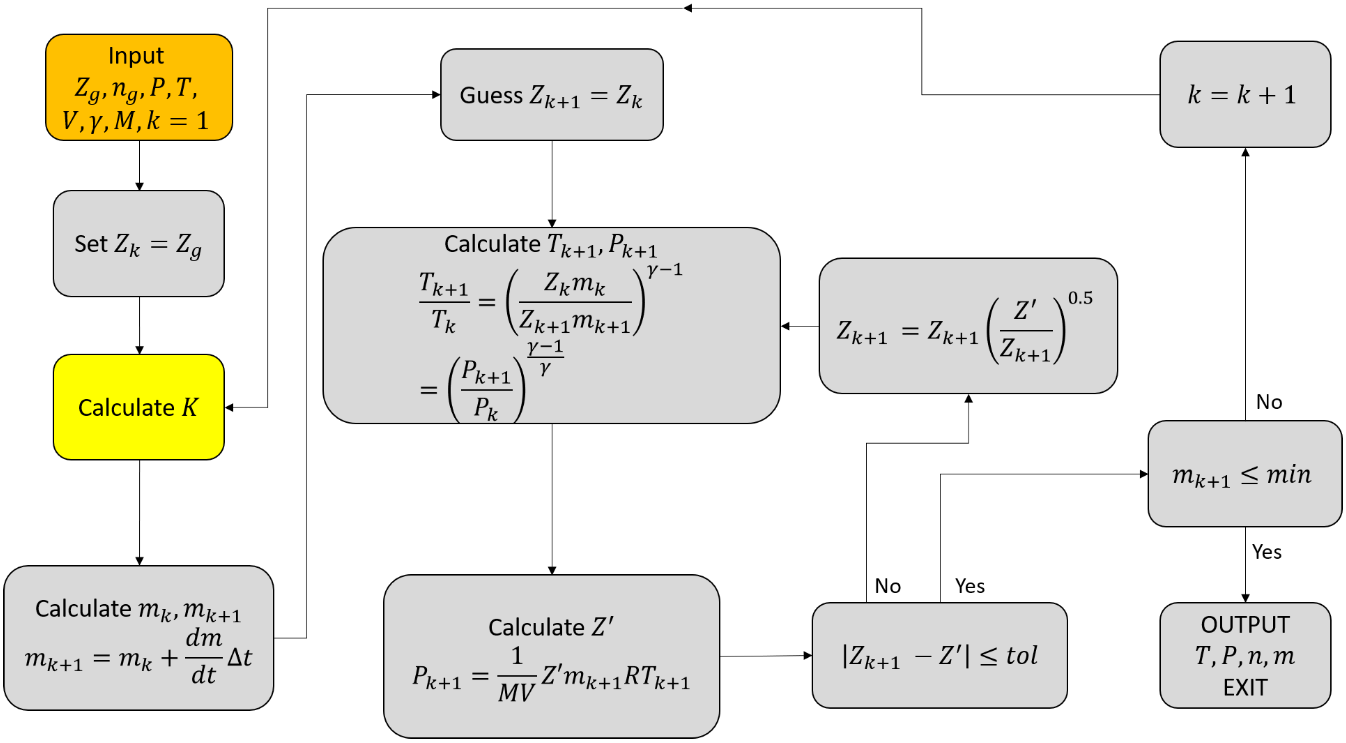

Figure 5: Structure of gas flow model.

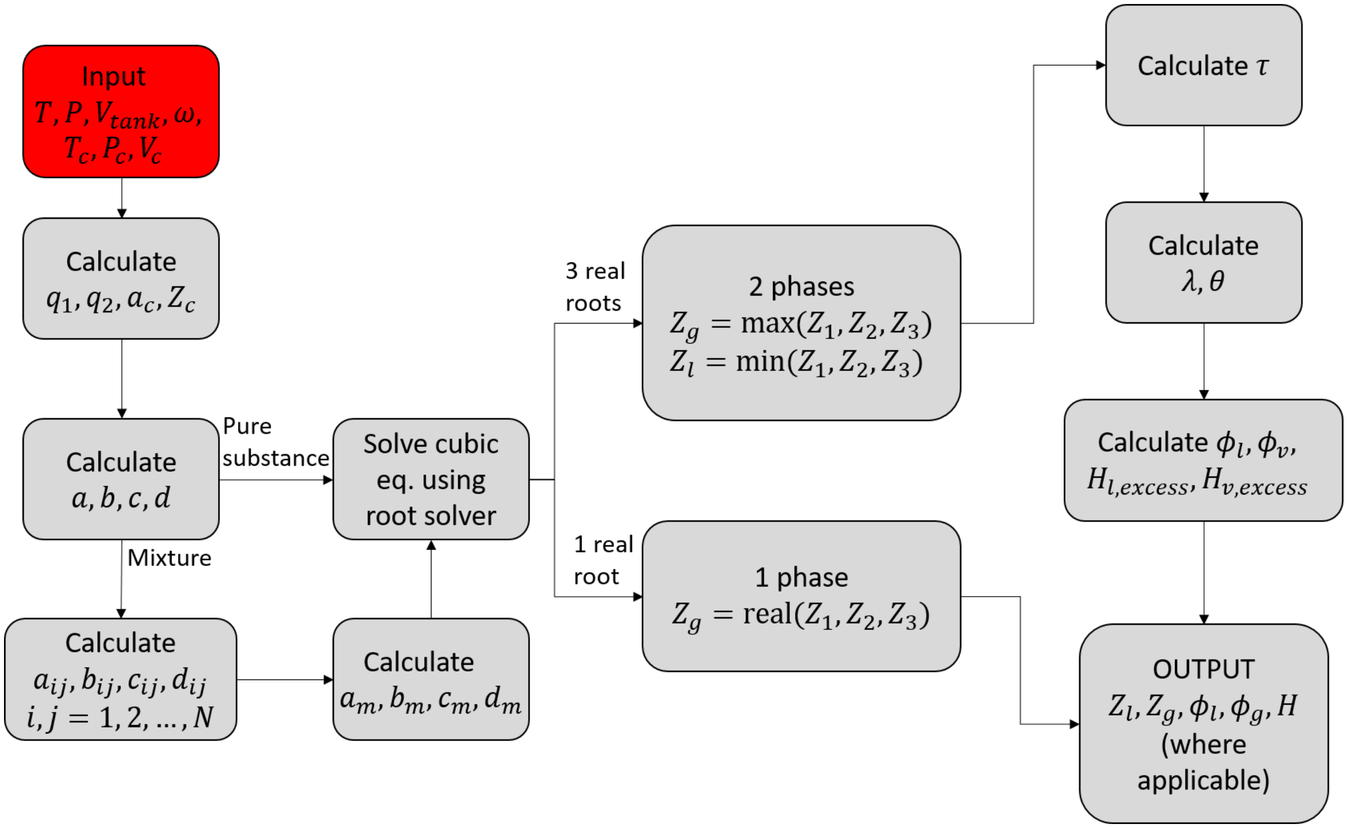

Figure 6: Structure of Trebble-Bishnoi equation of state solution.

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A Appendix

A.1 List of symbols

To be added later.

A.2 Energy Balance Equations

$$L_T = n_l\left[\hat{C}^*_{p,l} + \frac{\partial \hat{H}_{l,excess}}{\partial Z_l}\frac{\partial Z_l}{\partial T} + \frac{\partial \hat{H}_{l,excess}}{\partial T} - R\Big(Z_l + T\frac{\partial Z_l}{\partial T}\Big)\right] \tag{88}$$

$$V_T = \sum_{i=1}^{m} n_{g_i}\hat{C}_{g_i} + n_g\left[\frac{\partial \hat{H}_{g,excess}}{\partial Z_g}\frac{\partial Z_g}{\partial T} + \frac{\partial \hat{H}_{g,excess}}{\partial T} - R\Big(Z_g + T\frac{\partial Z_g}{\partial T}\Big)\right] \tag{89}$$

$$L_P = n_l\left[\frac{\partial \hat{H}_{l,excess}}{\partial Z_l}\frac{\partial Z_l}{\partial P} + \frac{\partial \hat{H}_{l,excess}}{\partial P} - RT\frac{\partial Z_l}{\partial P}\right] \tag{90}$$

$$V_P = n_g\left[\frac{\partial \hat{H}_{g,excess}}{\partial Z_g}\frac{\partial Z_g}{\partial P} + \frac{\partial \hat{H}_{g,excess}}{\partial P} - RT\frac{\partial Z_g}{\partial P}\right] \tag{91}$$

$$L_n = \hat{H}_{l,excess} - Z_l RT \tag{92}$$

$$V_n = \hat{H}_{g,excess} - Z_g RT + (1-y)\left[\frac{\partial \hat{H}_{g,excess}}{\partial Z_g}\frac{\partial Z_g}{\partial y} + \frac{\partial \hat{H}_{g,excess}}{\partial y} - RT\frac{\partial Z_g}{\partial y}\right] \tag{93}$$

$$\begin{aligned} X &= L_T + V_T \\ W &= L_P + V_P \\ Y &= L_n - \hat{H}_{l,excess} \\ \Gamma &= V_n + \Delta\hat{H}_v - \hat{H}_{l,excess} \end{aligned}$$

$$X\frac{dT}{dt} + W\frac{dP}{dt} + Y\frac{dn_l}{dt} + \Gamma\frac{dn_g}{dt} = 0$$

A.3 Derivation of Enthalpy and Fugacity

To be added later.