Solid Propellant Burning Equilibrium Ingredients Calculation Based on Temperature Iteration

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Abstract. Aiming at shortcomings of depending on experiences and inferior computation accuracy brought by using linear interpolation to calculate fixed pressure burning temperature, a new method using iteration was put forward. Moreover, the optimization model to calculate equilibrium ingredients was formulated based on the new method, and sequential quadric programming method rather than Lagrange multiplier was used to compute the model. At last, a numerical example was given to validate the method in this paper. Results make show that more perfect outcomes can be achieved through the method in this paper than classical method.

1. Introduction

Equilibrium ingredients and burning temperature of propellant is necessary data for ignition engine design, inner ballistic computation and performance evaluation of solid rocket motor, at present there are three classical methods to calculate equilibrium ingredients and burning temperature of propellant, which are gradual approximation method, minimum G-free energy method and Brinkley method [1]. Burning temperature must be certain beforehand in all of above-mentioned method, however burning temperature is also unknown. Therefore, a simple linear interpolation method was frequently adopted to calculate burning temperature based two presupposed temperatures in all of above-mentioned method. In this way, analyst’s experiences and the two preselected temperatures would have remarkable influences on computation accuracy. To solve this problem, a new method to calculate burning temperature was put forward in this paper, which linear interpolation was substituted by iteration. Furthermore, the equilibrium ingredients optimization model was set up based on minimum G-free energy and the iteration method. Finally, the method in this paper was used to calculate equilibrium ingredients and burning temperature of a given solid propellant components.

2. Fixed pressure burning temperature calculation

The principle of solving fixed pressure burning temperature of $T_i$ is that solid propellant’s total enthalpy of $I_p$ must be equal to burning products total enthalpy of $I_m$, namely

$$
\sum_{i=1}^{N} \left[ H_{j_{i}}^{T_{i}} + c_i (T_i - T_s) \right] q_i = \sum_{i=1}^{N} \left( H_{j_{i-298}}^{\theta} + \int_{T_i}^{T_s} C_{j_{i}} dT \right) n_i
$$

Where $T_i$ is initial temperature of propellant, K. $T_s$ is benchmark temperature, which is commonly 298K. $c_i$ is specific heat of the $i$-th component of propellant, which varies hardly with temperature, J/(kg.K). $q_i$ is mass percentage of the $i$-th component of propellant.
\( H_{j}^{T} \) is standard creation enthalpy of the \( i \)-th component of propellant, which can be found in reference [2].

\( n_{i} \) is molar number of the \( i \)-th burning equilibrium ingredient.

\( H_{i-298}^{0} \) is standard creation enthalpy of the \( i \)-th burning equilibrium ingredient.

\( C_{pi} \) is fixed pressure specific heat of the \( i \)-th burning outcome, which is function of temperature and can be calculated through reference [3].

2.1. The method of classic linear interpolate

In the method of calculating burning temperature by classic linear interpolate, two temperatures were presumed firstly. Then burning ingredients and their total enthalpy could be obtained when propellant burning at the two presumed temperatures. If total enthalpy of burning ingredients was linear function of temperature between two presumed temperatures, using interpolate could easily get the fixed pressure temperature based on conversation of energy. The process can be figured by Fig.1.

![Fig.1 method of linear interpolation to calculate fixed pressure burning temperature](image)

Obviously, the two presumed temperatures are vital to computation accuracy in this method. If analysts had abundant experiences, the presumed two temperatures would approximate true fixed pressure burning temperature and computation error of linear interpolate would be little. Otherwise, linear interpolate would bring non-ignorable errors. Even though for proficient analysts, it was also difficult to presume appropriate temperatures when facing a new type of propellant. Therefore, it is necessary to find new method to solve burning temperature.

2.2. Iteration method to solve burning temperature

In practice, calculating burning temperature is to solve the following equation

\[
f(T) = \sum_{i=1}^{m} \left[ H_{j}^{T} + c_{i}(T_{i} - T_{o}) \right] \cdot q_{i} - \sum_{i=1}^{N} \left( H_{i-298}^{0} + \int_{T_{i}}^{T_{o}} C_{pi} dT \right) \cdot n_{i} = 0 \quad (2)
\]

Here, the formula (2) is a higher nonlinear equation with regard to \( T_{e} \), because \( C_{pi} \) and \( n_{i} \) are all function of \( T_{e} \), and there are no visible function between \( n_{i} \) and \( T_{e} \). The equation can’t be solved by analytical method; it can only be solved by iteration. However, iteration based on gradient is not advisable because of no visible function between \( n_{i} \) and \( T_{e} \). We can use secant method [4] to solve the equation. So, the iteration formation to calculate \( T_{e} \) can be expressed as following

\[
T_{k+1} = T_{k} - \frac{f(T_{k})(T_{k} - T_{k+1})}{f(T_{k}) - f(T_{k+1})} \quad (3)
\]

When absolute value of difference between \( I_{p} \) and \( I_{m} \) is less than \( \varepsilon_{2} \), where \( \varepsilon_{2} \) denotes iteration accuracy and is a given small decimal fraction.

3. Equilibrium ingredients calculation based on temperature iteration

Now, there are three classical methods to calculate equilibrium ingredients and burning temperature of propellant, which are gradual approximation method, minimum G-free energy method and Brinkley
method. Gradual approximation method is simplest among three methods, but this method isn’t suitable for thermodynamics calculation with complex ingredients. Minimum G-free energy method has explicit physics meanings, this method considers equilibrium ingredients are ingredients which minimize G-free energy of burning products, so the problem of calculating equilibrium ingredients is transferred to minimum optimization of G-free energy. The number of equations to be solved in Brinkley method is fewest, but Brinkley method is most complicated among three methods, the method demands to input a good many coefficient matrix, which easily creates mistake, and linearization in solving equations will bring calculation errors. So, the minimum G-free energy method would be used to calculate equilibrium ingredients in this paper. In this way, we can set up following optimization model to calculate equilibrium ingredients.

\[
\min \Phi = \sum_{i=1}^{N} (-Y_i^c n_i) + \sum_{i=1}^{N} \left( -Y_i + \ln n_i + \ln p_e - \ln n_e \right) \cdot n_i \tag{4a}
\]

s.t.

\[
\begin{align*}
N_k &= \sum_{i=1}^{N} A_{ki} \cdot n_i \\
n_i &\geq 0 \\
(k &= 1, 2, \ldots, m) \\
(i &= 1, 2, \ldots, N) 
\end{align*}
\]

Where \( \Phi = G / RT \), \( G \) is G-free energy.

\( Y_i^c = -G_{Tc}^\theta / RT \), \( G_{Tc}^\theta \) is standard molar G-free energy of agglomerate, which can be calculated through reference [3].

\( Y_i = -G_{ni}^\theta / RT \), \( G_{ni}^\theta \) is standard molar G-free energy of gas, which can be calculated through reference [3].

\( A_{ki} \) is molar number of the \( k \)-th element contained in one mole of the \( i \)-th burning ingredient.

\( m \) is the number of propellant element.

\( N_k \) is molar number of element in assumed chemical formula.

It is noted that \( \ln n_i \) was involved in formula (4a), but \( n_i \) could be zero, it would bring calculation difficulty. To avoid the problem, we can make \( n_i \) greater than \( \varepsilon_1 \) (a given small decimal fraction) in the process of optimization, namely

\[ n_i \geq \varepsilon_1 \quad i = 1, 2, \ldots, N \]

If result of \( n_i \) was less than \( \xi \), where, \( \xi \) is another given small decimal fraction and greater than \( \varepsilon_1 \), \( n_i \) should be zero, namely this burning ingredient didn’t exist.

In engineering, Lagrange multiplier was usually used to solve above optimization model. In this way, \( n_i \) could be less than zero in the process of optimization, which can make optimization calculation terminate. In this paper, Lagrange multiplier was substituted by SQP (Sequence Quadratic Programming) to solve the optimization model.

It is noted that burning temperature must be known when we use SQP to solve the optimization model, but burning temperature is also parameter to be solved. So, we must integrate formula (4) with the new method in section 2.2 to calculate equilibrium ingredients. The step of calculation can be expressed as following.

1. Input initial datum of propellant;
2. Calculate assumed chemical formula and total enthalpy of propellant;
3. Assume two initial burning temperatures \( (T_0, T_1) \);
4. Use SQP to solve formula (4), get burning ingredients at \( T_0, T_1 \);
5. Calculate total enthalpy of burning ingredients at \( T_0, T_1 \);
(6) If $|I_p - I_m| \leq \varepsilon_2$, transfer to (9). Otherwise calculate a new burning temperature $T_{k+1}$ according to formula (3);
(7) Use SQP to solve formula (4), get burning ingredients at $T_{k+1}$;
(8) Calculate total enthalpy of burning ingredients at $T_{k+1}$, and transfer to (6);
(9) Terminate, and output results.

4. Example

Assume solid propellant’s components were showed in Tab.1; please calculate its equilibrium ingredients and burning temperature when the propellant burns at pressure of 6.08Mpa. ($T_i$ is 298K.)

| Number | Component  | Mass percent | Standard creation enthalpy (KJ/mol) |
|--------|------------|--------------|-------------------------------------|
| 1      | NH$_4$ClO$_4$ | 68%          | -291.56                             |
| 2      | Al         | 15.5%        | 0                                   |
| 3      | CaCO$_3$   | 3.5%         | -1211.66                            |
| 4      | C$_{22}H_{44}O_{61}$ | 13% | -14001.83                        |

Via calculation, we can achieve that assumed chemical formula and total enthalpy of the propellant are respectively $Ca_{0.3497}Al_{5.74}C_{7.38}H_{37.26}O_{26.152}N_{5.7875}Cl_{5.7875}$ and $-6.0935 \times 10^5$cal.

Assume burning products include fifteen types of ingredients, which are CaO (s), Al$_2$O$_3$ (s), CO, H$_2$, H$_2$O, N$_2$, HCl, CO$_2$, H, AlOCl, Cl, HO, NO, CHO and O, their G-free energy can be calculated through reference 3. Here, $\varepsilon_1$, $\varepsilon_2$ and $\xi$ are respectively $10^{-5}$, $10^{-4}$ and $10^{-4}$. We can achieve that fixed burning temperature is 3634.5 K and equilibrium ingredients are shown in Tab.2.

| burning ingredient | the number of moore | burning ingredient | the number of moore |
|--------------------|---------------------|--------------------|---------------------|
| CaO (s)            | 0.3497              | H                  | 0.5486              |
| Al$_2$O$_3$ (s)    | 2.7392              | AlOCl              | 0.2665              |
| CO                 | 6.4232              | Cl                 | 0.2735              |
| H$_2$              | 6.9687              | HO                 | 0.3413              |
| H$_2$O             | 8.5868              | NO                 | 0.0333              |
| N$_2$              | 2.8772              | CHO                | 0.0134              |
| HCl                | 5.2478              | O                  | 0.0155              |
| CO$_2$             | 0.9524              |                    |                     |

From tab.2 we can see that relative error between total enthalpy of burning ingredients achieved by the method in this paper and total enthalpy of propellant is only $6.56 \times 10^{-6}$. So, the method in this paper can be used to calculate equilibrium ingredients and fixed burning temperature of solid propellant.

5. Conclusions

We can obtain following conclusions via above analysis.
(1) Compare to classic linear interpolate, iteration has no special requirements on initial assumed burning temperature, which don’t rely on analyst’s experiences, and can get high calculation accuracy.
(2) When solving equilibrium ingredients optimization model, SQP avoids the problem brought by Lagrange multiplier, and is more effective method.

References
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