

Three-dimensional diagrams for burning rate and temperature sensitivity as a function of pressure and temperature for a 5-ATZ/Sr(NO₃)₂ mixture

Kazuo Hasue^{*†} and Makoto Matsukawa^{**}

^{*}Department of Applied Chemistry, School of Applied Sciences, National Defense Academy (ret.)
1-10-20, Hashirimizu, Yokosuka, Kanagawa 239-8686, JAPAN

[†]Corresponding author : khasue@hotmail.com

^{**}The Kure Ammunition Storehouse and Maintenance Depot, Japan Maritime Self-Defense Force,
Kirikushi, Etajima, Etajima, Hiroshima 737-2123, JAPAN

Received : July 16, 2015 Accepted : May 11, 2016

Abstract

The burning rate of propellants is affected by pressure and temperature. The relation between the burning rate and pressure has been well-studied. However, the effect of the initial temperature on the burning rate has not been investigated quantitatively except in the authors' reports. In this study, the burning rate of 5-amino-1H-tetrazole and strontium nitrate mixtures was examined and an equation for the burning rate as a function of pressure and temperature was obtained. In general, the burning rates predicted by the regression equation were in good agreement with the observed values. The temperature sensitivities were also predicted using the regression equation and compared with the observed values and good agreement was found between the predicted and observed values.

Keywords : 5-amino-1H-tetrazole, strontium nitrate, burning rate, temperature sensitivity, regression analysis

1. Introduction

To obtain the burning rate is the principal objective of the combustion study of energetic materials. The factors that affect the burning rate of propellants are pressure and temperature. There has been a considerable amount of research on the effect of pressure on the burning rates of rocket propellants, and the relation between the burning rate and pressure was found to be described by Vieille's law.

However, the effect of the initial temperature on the burning rate has only been partially studied in terms of the temperature sensitivity of rocket propellants⁽¹⁻¹⁰⁾ and airbag gas generating agents^(11,12). In these studies, the relation between the initial temperature and the burning rate has not reported quantitatively, therefore an attempt to obtain the burning rate at any temperature and pressure can not be accomplished. To obtain a temperature sensitivity-pressure diagram, an equation in differential form of the burning rate and initial temperature is required. In previous studies, References

5,6,11, and 12 adopted a second-order polynomial equation and probably References 2,7, and 10 adopted it too. In most reports, the burning rates were observed at three different initial temperatures. A second-order polynomial equation has been adopted for the burning rate and initial temperature equation because it gives a better correlation coefficient than the first-order equation. However, the second-order polynomial equation has a possibility to give the minimum or maximum values within the range of study and the higher or lower values when it is extrapolated to higher or lower temperatures. Therefore, the first-order equation would be a better choice for the burning rate and initial temperature equation.

Authors have reported equations of burning rate as a function of pressure and temperature for 1H-tetrazole (1 HT)/ammonium nitrate (AN) mixtures⁽³⁾, phase stabilized ammonium nitrate/1H-tetrazole mixture⁽⁴⁾, bis(1H-tetrazolyl) amine ammonium salt / phase stabilized ammonium nitrate mixture⁽⁵⁾, 1H-tetrazole/CuO/additive mixtures⁽⁶⁾, guanidine nitrate/strontium nitrate/basic

copper nitrate mixture¹⁷). From these equations, the burning rate can be estimated at any temperature and pressure. In these reports, authors have adopted the first-order equation for the burning rate and initial temperature equation.

It is desirable for an airbag to maintain the time required for inflation, regardless of low or high temperature conditions in winter and summer. If the temperature sensitivity of the burning rate is large, then the rate of airbag inflation would change with temperature, which is undesirable for an airbag used under fluctuating temperature conditions; therefore, it is desirable for the temperature sensitivity to be low.

In this study, 5-amino-1H-tetrazole (5-ATZ) was selected as a fuel because it is one of the energetic tetrazoles¹⁸ and has high nitrogen content. Strontium nitrate $\text{Sr}(\text{NO}_3)_2$ (SrN) was selected as an oxidizer. The 5-ATZ/SrN mixture is one of the gas generating agents in practical application¹⁹. The purpose of this paper is to study the effect of initial temperature on the burning rate and deduce the temperature sensitivity from measured burning rate results.

Based on the burning rate equation obtained, three-dimensional diagrams of the burning rate and temperature sensitivity were made. Without complicated calculations, the burning rate and the temperature sensitivity can be predicted at any pressure and temperature within the range of study.

2. Experimental

2.1 Materials

5-ATZ (Fujimoto Chemicals Co., Ltd.) and SrN (Kanto Chemicals Co. Inc.) were dried in a vacuum and sieved. The particle sizes of 5-ATZ and SrN were in the range of 150-300 and 75-149 μm , respectively. 5-ATZ and SrN particles were mixed at a stoichiometric ratio (36.48/63.52 wt %) for 30 min at 80 rpm using a rotary mixer (S-3, Tsutsui Scientific Instruments Co. Ltd.).

2.2 Burning rate

One and a half grams of the stoichiometric 5-ATZ/SrN mixture was compressed at approximately 300 MPa for 3 min to form cylindrical pellets (diameter 10 mm, length 9 mm). The side of the cylindrical pellet was coated with epoxy resin to assure cigarette-like burning. Combustion tests were performed using a pressure and temperature controlled chimney-type strand burner with optical windows (TDK-15011, Tohata Denshi Co. Ltd.), under a N_2 atmosphere in the range of 1-6 MPa. Figure 1 shows the schematic diagram of the strand burner. The initial temperatures (T_i) were 243, 298, and 343 K. Ignition of the pellet was carried out with an electrically heated nichrome wire (diameter 0.6 mm) by means of a regulated DC power supply (QP035-20R, Takasago Ltd.). The pressure in the chamber was measured with a strain-gauge pressure transducer (PG-100KU, Kyowa Electronic Instruments Co. Ltd.). After amplification through a direct-current amplifier (CDV-230C, Kyowa Electronic Instruments Co. Ltd.), the data was recorded using a digital data recorder (GR-3000, Keyence Corp.). The burning rates (r) were deduced from the duration of the recorded pressure increase. The pressure began to increase as soon as the sample started to burn and stopped increasing when combustion ceased. The average internal pressure (P) was calculated by averaging the pressures at the start and the end of combustion. The highest pressure difference was approximately 0.1 MPa for the arithmetic mean value of 5 MPa.

In this study, there are three significant figures. However, in all calculations, three significant figures plus one digit were employed to avoid introducing a new calculation error by rounding off²⁰. Therefore, the values in all equations and tables are four digits.

2.3 Temperature sensitivity

The dependency of the burning rate on the initial temperature can be expressed as the temperature sensitivity, which is one of the important parameters for

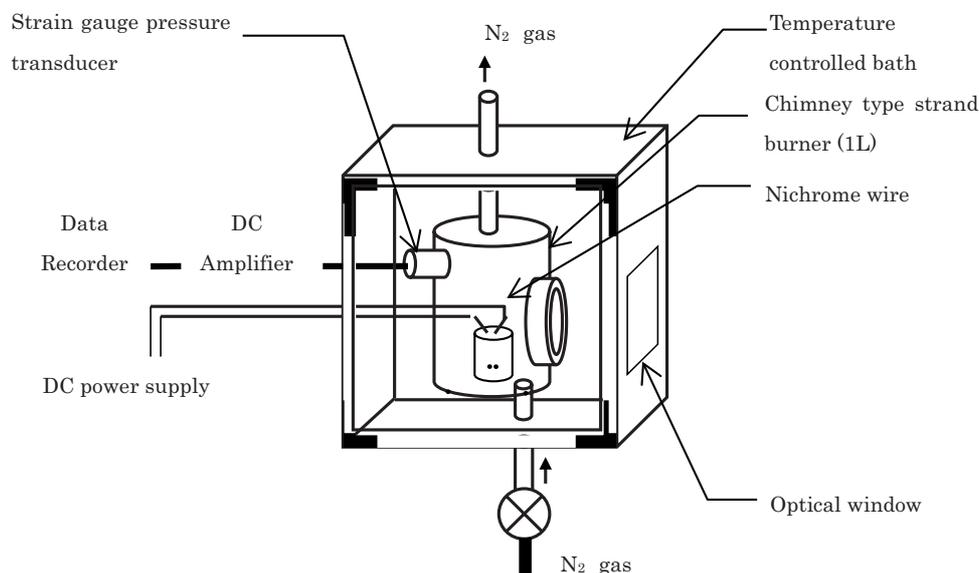


Figure 1 Schematic diagram of pressure and temperature controlled test chamber with optical window.

energetic materials. Variation of the burning rate per unit of temperature change at a constant pressure is called the temperature sensitivity of burning rate at a constant pressure (σ_p)²¹, which can be expressed as

$$\sigma_p = \frac{(r_1 - r_0)}{r \cdot (T_1 - T_0)} \quad (1)$$

where r_0 and r_1 are the burning rates at temperatures T_0 and T_1 , respectively, and r is the average burning rate between T_0 and T_1 . The unit of σ_p is K^{-1} .

Equation 1 can be rewritten in differential form

$$\sigma_p = \left(\frac{\partial \ln r}{\partial T_i} \right)_p \quad (2)$$

where σ_p can be obtained from Equation 2 by determining the relationship between r and T_i . A correlation equation between r and T_i was determined; in this study, a linear equation for T_i (Equation 3):

$$r = b_1(P) \cdot T_i + b_0(P) \quad (3)$$

where $b_1(P)$ and $b_0(P)$ are functions of pressure.

3. Results and discussion

3.1 Observed burning rate

The burning rates of energetic materials generally follow Vieille's law, given by $r = a \cdot P^n$, where a is a constant that depends on the chemical composition and an initial propellant temperature, and n is the pressure exponent of the burning rate²¹.

The results of the burning rate tests for the 5-ATZ/SrN are presented in Figure 2 for T_i of 243, 298, and 343K. The observed burning rates (r_{obs}) are seen to follow Vieille's law, as indicated by the dashed lines in Figure 2.

3.2 Equation for burning rate as a function of pressure and temperature

The fitting results for the Vieille's law, $r = a \cdot P^n$, are summarized in Table 1. The correlation coefficients of the

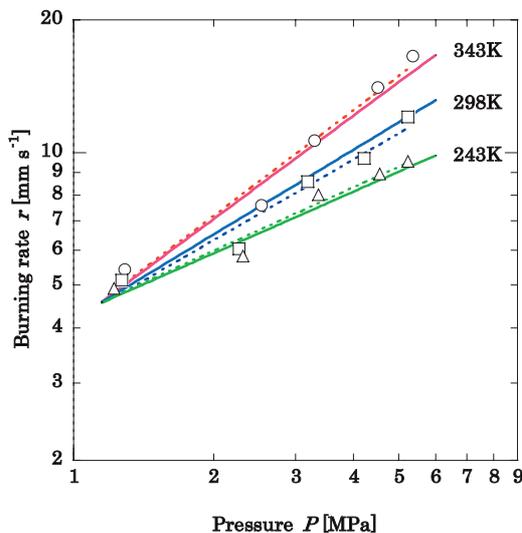


Figure 2 Burning rate for the 5-ATZ/SrN mixture at each initial temperature. Dashed line : Observed Solid line : Predicted by Equation 4

Table 1 The values for a and n of the 5-ATZ/SrN mixture.

Initial temperature [K]	a [mm s ⁻¹ MPa ⁻¹]	n [-]	Correlation coefficient
343	4.131	0.7976	0.9899
298	4.143	0.6093	0.9810
243	4.291	0.4795	0.9840

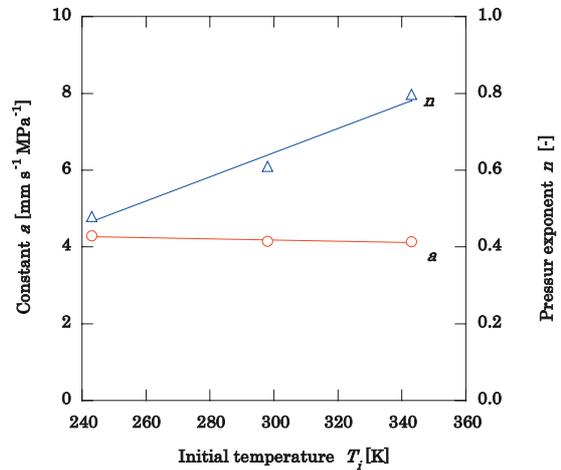


Figure 3 Relation between a , n and initial temperature for the 5-ATZ/SrN mixture.

equation for the mixture were in the range of 0.9810-0.9899 (0.974 at the 0.001 significance level²²) and, consequently, the data correlate well according to the equation.

A regression analysis was conducted to derive an equation for obtaining a and n at any T_i . The relations between a and T_i , and n and T_i are shown in Figure 3. The coefficient a decreased slightly as T_i increased. The correlation coefficient was 0.9227. As the result of this tendency, the calculated burning rate of 343 K was lower than that of 243 K at 1MPa.

The pressure exponent n increased as T_i increased. The correlation coefficient was 0.9867.

It was found by a regression analysis that the predicted burning rate (r_{pre}) can be expressed as $r_{pre} = a_{reg} P^{n_{reg}}$, where a_{reg} and n_{reg} are a and n for Vieille's law, respectively. The value of a_{reg} can be expressed as $4.673 - 0.001644 \times T_i$ and n_{reg} can be expressed as $-0.3000 + 0.003152 \times T_i$.

Therefore, the burning rate can be expressed as

$$r_{pre} = (4.673 - 0.001644 \times T_i) \times P^{(-0.3000 + 0.003152 \times T_i)} \quad (4)$$

The burning rate can be predicted from Equation 4 for any T_i and pressure within the range of study. The observed and predicted burning rates are represented in Figure 2 as dashed lines and solid lines, respectively. There is relatively good agreement between r_{pre} and r_{obs} for a wide range of T_i and P .

A three-dimensional diagram of the burning rate predicted from Equation 4 in the range of 240-350 K and 1-6 MPa is shown in Figure 4. Without a complicated calculation, the burning rate at any conditions can be estimated by using the three-dimensional diagram. It is

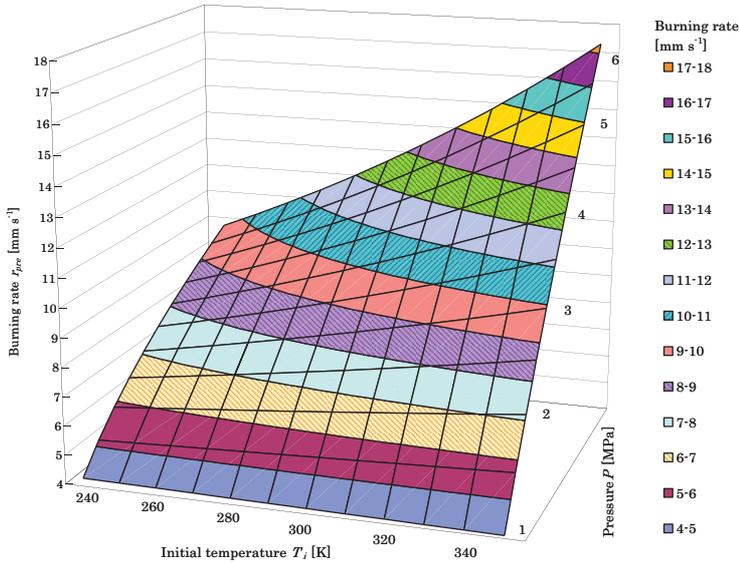


Figure 4 Three-dimensional diagram for burning rate as a function of pressure and temperature for the 5-ATZ/SrN mixture.

found that the effect of pressure increase on the burning rate is more evident at the higher initial temperature. Gas-generating agents for air bags generally require a burning rate of at least $10 \text{ mm}\cdot\text{s}^{-1}$ or more at 7 MPa ²³. According to Figure 4, the composition gives $10 \text{ mm}\cdot\text{s}^{-1}$ at pressure as low as 3 MPa .

3.3 Temperature sensitivity

The burning rate is dependent on pressure and temperature. The dependency of the burning rate on the pressure is expressed as Vieille's law. On the other hand, the dependency of the burning rate on the initial temperature can be expressed as the temperature sensitivity.

The burning rates from 1 to 6 MPa at each T_i were calculated by means of Vieille's law, $r = a \cdot P^n$, using values of a and n from Table 1. The calculated burning rate (r_{calc}) as a function of T_i at various pressures are indicated by crosses in Figure 5. The calculated burning rate r_{calc} increases with an increase in T_i except for a pressure of 1 MPa. The first-order equation was adopted to fit these r_{calc} data. The coefficients $b_1(P)$ and $b_0(P)$ of Equation 3 were determined for various pressures as shown in Table 2.

The temperature sensitivities of burning rate σ_p [computed from Equation 2] versus P from 1 to 6 MPa at various T_i are shown by dashed lines in Figure 6. The values of σ_p increased as P and decreased as T_i increased.

The energy balance equation at the burning surface is²⁴)

$$r = \frac{\lambda_g (dT/dx)_g}{\rho C_p (T_s - T_i - Q_s/C_p)} \quad (5)$$

where T_s is the surface temperature, λ_g is the heat conductivity, $(dT/dx)_g$ is the temperature gradient at T_s , ρ is the density, and Q_s is the heat of reaction at T_s .

The temperature sensitivity of burning rate σ_p can be expressed as follows²⁴)

$$\sigma_p = \left(\frac{\partial \ln \varphi}{\partial T_i} \right)_p + \frac{1 - (\partial T_s / \partial T_i)_p}{T_s - T_i - Q_s/C_p} \quad (6)$$

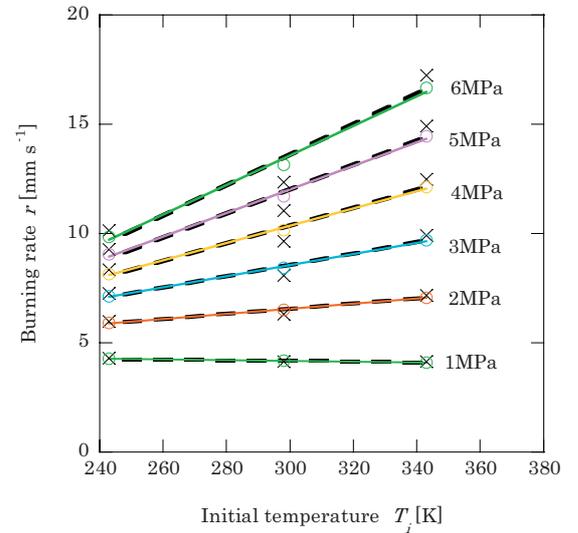


Figure 5 Burning rate as a function of initial temperature at various pressures for the 5-ATZ/SrN mixture. Dashed line and cross : Calculated Solid line and circle : Predicted

Table 2 Coefficients $b_1(P)$ and $b_0(P)$ of Equation 3 determined at various pressures of the 5-ATZ/SrN mixture.

Pressure [MPa]	$b_1(P)$	$b_0(P)$	$b_1(P)^*$	$b_0(P)^*$
1	-0.001644	4.673	-0.001644	4.673
2	0.01176	4.029	0.01157	3.083
3	0.02613	0.7265	0.02556	0.8897
4	0.04075	-1.853	0.03969	-1.550
5	0.05541	-4.580	0.05379	-4.117
6	-0.07003	7.394	0.06779	-6.757

* : Based on the predicted burning rates by means of Equation 4.

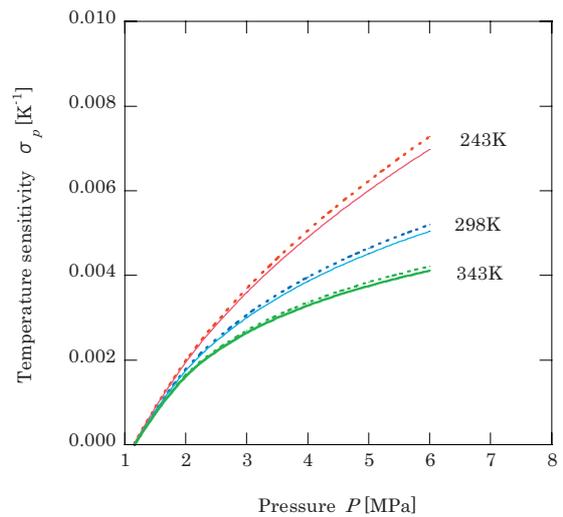


Figure 6 Temperature sensitivity and predicted temperature sensitivity for the 5-ATZ/SrN mixture. Dashed line : Observed Solid line : Predicted

where $\varphi = \lambda_g (dT/dx)_g$ and ρ , C_p , and Q_s are assumed to be independent on T_i . Assuming that Φ and Ψ are

$$\Phi = \left(\frac{\partial \ln \varphi}{\partial T_i} \right)_p \quad (7)$$

$$\Psi = \frac{1 - (\partial T_s / \partial T_i)_p}{T_s - T_i - Q_s / C_p} \quad (8)$$

then, σ_p can be expressed as follows

$$\sigma_p = \Phi + \Psi \quad (9)$$

Assuming $\varphi = \lambda_g (dT/dx)_g$ and T_s are also independent on T_i , then Φ is negligible and Equation 6 can be expressed as follows.

$$\sigma_p = \frac{1}{T_s - T_i - Q_s / C_p} \quad (10)$$

The surface temperature T_s generally increases with $P^{(2), (5), (10), (24)}$ then σ_p decreases with P . The temperature sensitivity σ_p decreases with an increase in P when Ψ is dominating. In other words, Ψ decreases with an increase in P . In contrast, in situations where σ_p increases with an increase in P when Φ is dominating. The equation also indicates a decrease in σ_p with decreasing T_i .

For ammonium perchlorate (AP) composite propellants, Φ increases with P and Ψ decreases with P , and σ_p increases with P , consequently Φ is dominating⁽¹⁰⁾. For tetrazole/AN systems, σ_p generally decreases with an increase in $P^{(11), (14), (15)}$ except IHT/AN and IHT/AN/CuO⁽³⁾, consequently Ψ is dominating.

In this study, σ_p increases with an increase in P , it is concluded that Φ is dominating.

The thickness of condensed phase reaction zone of AGAT/AN is reported to be approximately 0.2mm and Ψ is dominating⁽¹¹⁾ and that of 5-ATZ/SrN is approximately 0.05mm⁽²⁵⁾ and Φ is dominating as mentioned before. These results suggest that the thickness of the condensed phase reaction zone affects the value of Φ and Ψ . Since σ_p of 5-ATZ/SrN increases with P , Φ should increase with P , that is, the effect of the gas phase reaction would increase.

The predicted burning rate r_{pre} was obtained by using Equation 4 and then the coefficients $b_1(P)$ and $b_0(P)$ of Equation 3 were determined for various pressures as shown by solid lines in Figure 2. The predicted temperature sensitivity (σ_{pre}) are shown by solid lines in Figure 6. There is good agreement between σ_{pre} and σ_p .

3.4 Equation for temperature sensitivity as a function of pressure and temperature

An attempt was made to study the relationship of temperature sensitivity with P and T_i . The predicted temperature sensitivity (σ_{pre}) can be expressed by the following equation^{(5), (11), (14), (17)}.

$$\sigma_{pre} = A \cdot P^B \quad (11)$$

where $A = K_1 + K_2 \cdot T_i + K_3 \cdot T_i^2$ and $B = K_4 + K_5 \cdot T_i + K_6 \cdot T_i^2$. At various T_i , A and B were obtained for the solid lines in Figure 5; results are given in Table 3. Regression analyses were conducted for A and B as shown in Figure

Table 3 Values for variables A and B of $\sigma_{pre} = A \cdot P^B$ at each temperature.

Temperature [K]	A	B
343	0.001209	0.6547
298	0.001214	0.7654
243	0.001156	0.9760

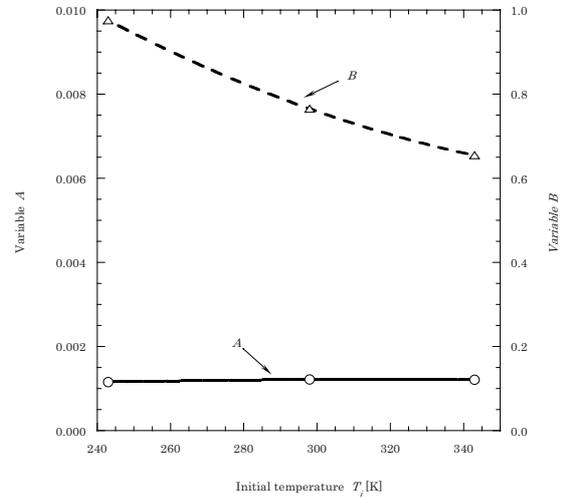


Figure 7 Regression analysis for variables A and B of $\sigma_{pre} = A \cdot P$.

7, and the obtained coefficients $K_1 - K_6$ are given in Table 4.

Therefore, σ_{pre} can be expressed as

$$\sigma_{pre} = (0.00004304 + 0.000007442 \times T_i - 0.0000001178 \times T_i^2) \times P^{(2.8995 - 0.01125 \times T_i + 0.00001371 \times T_i^2)} \quad (12)$$

A three-dimensional diagram for temperature sensitivity predicted from Equation 12 in the range of 240-350 K and 1-6MPa is shown in Figure 8. Without complicated calculations, σ_{pre} at any conditions can be estimated.

4. Conclusions

This study evaluated the possibility of predicting the burning rates of 5-amino-1H-tetrazole and strontium nitrate mixture at any initial temperature and pressure within the range of study.

An equation was obtained for the burning rate as a function of pressure and temperature after using a regression analysis to obtain the relation between the initial temperature and a or n in Vieille's law, as given by $r = aP^n$. In general, the predicted burning rates were in good agreement with the observed values.

A first-order equation was adopted for the burning rate and initial temperature equation.

The prediction of temperature sensitivity from the predicted burning rate, using a burning rate equation based on pressure and temperature is generally successful over a wide range of pressures and temperatures.

The temperature sensitivity increases with an increase in pressure and it suggests that the temperature sensitivity in the gas phase is dominating.

The three-dimensional diagrams of the burning rate and

Table 4 Values for coefficients K_1 through K_6 .

Sample	5-ATZ/SrN
K_1	4.304×10^{-5}
K_2	7.442×10^{-6}
K_3	-1.178×10^{-8}
K_4	2.900
K_5	-1.125×10^{-2}
K_6	1.371×10^{-5}

the temperature sensitivity are presented. Without complicated calculations, the burning rate and the temperature sensitivity can be predicted at any pressure and temperature.

References

- 1) R. L. Glick, *AIAA Journal*, 5, 586–587 (1967).
- 2) N. Kubota and A. Ishihara, *Proc. 20th Symposium (International) on Combustion*, 2035–2041, The Combustion Institute, Pittsburgh (1984).
- 3) N. S. Cohen and D. A. Flanigan, *AIAA Journal*, 23, 1538–1547 (1985).
- 4) N. Kubota and S. Miyazaki, *Propellants, Explos., Pyrotech.*, 12, 183–187 (1987).
- 5) A. S. Yang, I. H. Huang, W. H. Hsieh, and K. K. Kuo, *Combustion of Boron-Based Solid Propellants and Solid Fuels*, 412–426, Boca Raton : CRC Press (1993).
- 6) R. M. Salizzoni, W. H. Hsieh, and K. K. Kuo, *Combustion of Boron-Based Solid Propellants and Solid Fuels*, 438–452, Boca Raton : CRC Press (1993).
- 7) I. Aoki, *Kayaku Gakkaishi (Sci. Tech. Energetic Materials)*, 59, 36–43 (1998) (in Japanese).
- 8) A. I. Atwood, T. L. Boggs, P. O. Curran, and T. P. Parr, and D. M. Hanson-Parr, *J. Prop. Power*, 15, 748–752 (1999).
- 9) V. V. Kulkarni, A. R. Kulkarni, P. A. Phawade, and J. P. Agrawal, *Propellants, Explos., Pyrotech.*, 26, 125–129 (2001).
- 10) H. Bazaki, T. Kai, and T. Anan, *Kayaku Gakkaishi (Sci. Tech. Energetic Materials)*, 57, 153–159 (1996) (in Japanese).
- 11) Y. Miyata and K. Hasue, *J. Energ. Mater.*, 29, 26–45 (2011).
- 12) K. Yositate, K. Ihoh, S. Date, and K. Hasue, *Proc. 36th International Pyrotechnics Seminar, International Pyrotechnics Society*, 287–301, Rotterdam, Netherlands (2009).
- 13) K. Hasue and K. Yoshitake, *J. Energ. Mater.*, 31, 251–260 (2013).
- 14) K. Hasue, R. Miura, and K. Yoshitake, *Sci. Tech. Energetic Materials*, 74, 113–117 (2013).
- 15) K. Hasue, *J. Energ. Mater.*, 32, 199–206 (2014).
- 16) M. Matsukawa and K. Hasue, *ibid*, 32, 264–277 (2014).
- 17) K. Hasue and K. Yoshitake, *Sci. Tech. Energetic Materials*, 76, 8–13 (2015).
- 18) W. Abe, T. Ogura, Y. Miyata, K. Okamoto, S. Date, M. Kohga, and K. Hasue, *Sci. Tech. Energetic Materials*, 69, 183–190 (2008).
- 19) K. Ikeda, *Explosion*, 12, 77–80 (2002) (in Japanese).
- 20) H. Chihara and M. Sorai ed., “*Buturikagaku Jikkenhou 4th edition (Experiments of Physical Chemistry)*”, 287–288, Tokyo, Tokyokagakudojin (2000) (in Japanese).
- 21) N. Kubota, “*Propellants and Explosives - Thermochemical Aspects of Combustion*”, 53–54, Weinheim, WILEY-VC (2002).
- 22) “*Table of Critical Values for Pearson’s r*”, http://www.radford.edu/~jaspelme/statsbook/Chapterfiles/Table_of_Critical_Values_for_r.pdf (accessed: 20-September-2014) (online).
- 23) P. S. Khandhadia and S. P. Burns, US Patent 6306232B1 (2001).
- 24) N. Kubota ed., “*Puroperanto Handobukku (Propellant Handbook)*”, 257–258, Kayaku Gakkai (2005) (in Japanese).
- 25) K. Hasue, P. Boonyarat, Y. Miyata, and J. Takagi, *Kayaku Gakkaishi (Sci. Tech. Energetic Materials)*, 62, 168–174 (2001) (in Japanese).

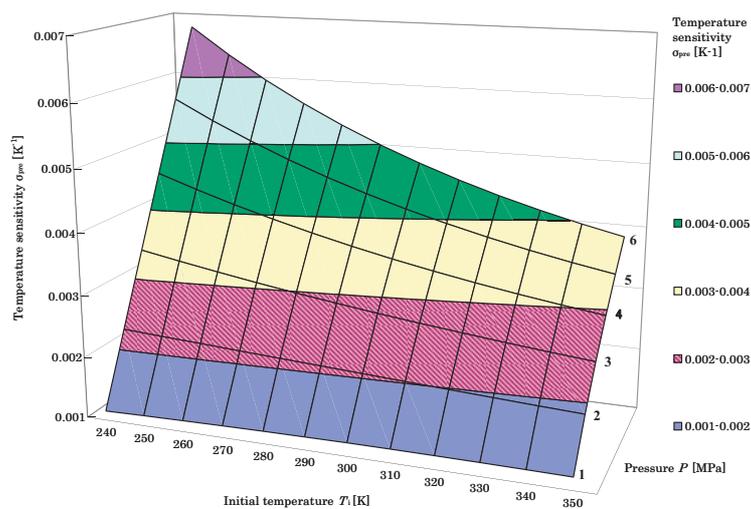


Figure 8 Three-dimensional diagram for temperature sensitivity as a function of pressure and initial temperature for the 5-ATZ/SrN mixture.