

Combustion mechanism of tetra-ol glycidyl azide polymer

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Abstract

Tetra-ol glycidyl azide polymer (GAP) is one of the best candidates for the solid fuel of gas hybrid rocket system because of self-combustibility, better mechanical property and high heat of formation, and comprehensive understanding of combustion phenomena is indispensable for such an application. Combustion model of GAP, which is one-dimensional three-phase mode combustion model, was developed by Beckstead et al. and they applied it to tri-ol GAP successfully. We have applied this model to tetra-ol GAP as an initial attempt, and numerical simulation showed that maximum temperatures in the gas phase exceeded those of experimental results significantly, and calculated burning rates were much higher than strand burner data, thus, modification of the model taking account of combustion incompleteness was found to be necessary. Modifications of combustion model were made taking the residue analysis results into account as *Blow Off Mechanism*. Simulated final temperature in the gas phase and burning rate are lowered effectively and coincide well with experimental data adjusting kinetic parameters.

Keywords: Tetra-ol glycidyl azide polymer, Combustion modeling, Residue behavior, Beckstead's model, Gas hybrid rocket.

1. Introduction

GAP (poly (3-nitratoethyl-3-methyloxetane)) is one of the most prospective High Energy Materials (HEMs) having high heat of formation, high density, excellent hazard properties. NOF Corporation developed a tetra-ol GAP prepolymer (Fig.1), which needs no cross linking agent and less curative comparing to conventional di-ol GAP, thus, having higher energy density and better mechanical property which makes this material favorable to hybrid rocket fuels.

GAP combustion models were studied by Davidson and Beckstead¹⁾. Their combustion model integrates experimental results of several researchers, however not all the pieces fit together because of differences in experiments, experimental error, and interpretation of results. Consequently they suggested that the information (such

as final flame temperature, final combustion products, surface temperature, temperature profile, and so on) of GAP need to be clarified. A three-phase steady state one-dimensional numerical model of GAP, which was extended from previous model, was made by Puduppakkam and Beckstead^{2), 3)}. Point of modification was that the

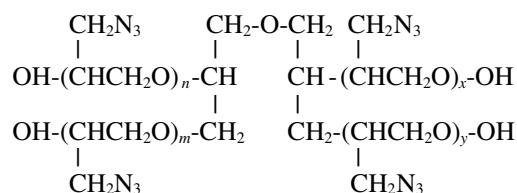


Fig. 1 Structure of Tetra-ol GAP prepolymer.

step ($C_2H_2 \Rightarrow CH_4 + C(S)$) was employed to increase the pressure dependence of burning rate, and therefore the calculated burning rates had a moderate pressure exponent (~ 0.4). Their model predicted a combustion process with a large condensed phase heat release and high surface temperatures and low flame temperatures, and the composition of the GAP hexamethylene di-isocyanate (HMDI) sample was found to have a large influence on the burning rate. They concluded experimental conclusions have been validated using the model in the process. Combustion models of GAP related propellants have been studied by Yang et al.⁴⁾ and their works give lots of important information as for GAP combustion.

Combustion model of tri-ol GAP was developed by Beckstead successfully as mentioned above. We tried to simulate tetra-ol GAP combustion characteristics using Beckstead's model with the same reaction rate constants, however, this attempt was not successful. Burning surface temperature, gas phase final temperature, and burning rate are significantly higher than experimental results. Thus, modification of the model taking account of combustion incompleteness was found to be necessary.

In the previous study⁵⁾ the significance of combustion incompleteness of GAP was stressed. The existence of carbonaceous residues was reported by Kubota and Sonobe and Lengelle⁶⁾. Then Tang et al.⁷⁾ found large amount of fine yellow powder by direct photograph observation and they suggest that the hot condensable gases from the GAP surface were rapidly quenched by the cold ambient gas and as a result were condensed into powder. Arisawa and Bill⁸⁾ observed GAP oligomers from surface during thermal decomposition by Fourier Transform infrared Spectrometer (FTIR). The oligomers are the lower molecular weight fractions of GAP and vaporize during pyrolysis. Thus, Tang et al. concluded oligomers seem to form the fine powder. Consideration of combustion incompleteness including the detailed analysis of combustion residues is indispensable for the establishment of the combustion model of GAP, however, such a study has never been conducted.

The residues were found to be composed of soot (black powder), high viscosity residue (HVR), and yellow powder, and the mass fractions of residues are measured as a function of pressure. At 1 MPa, gas phase products are only 60 %, however, it increases to 91 % at 10 MPa. These data along with the results by means of SEM and IR help the understanding of degradation process of GAP. Combustion model, which consists of three regimes: the solid phase region, two-phase (gas and liquid) region and gas phase region has been modified. The behavior of HVR based upon experimental results was entrained in model. *Blow Off Mechanism* was added in residue behavior, and full kinetics chemistry was employed even in the bubbles at two-phase region. With this modification, final temperature in the gas phase decreases and burning rate was lowered effectively. The rapid temperature increase and final temperature were well simulated numerically, and calculated burning rate coincided with measured well at all pressures. This development of tetra-ol GAP combus-

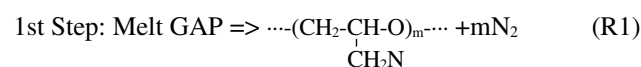
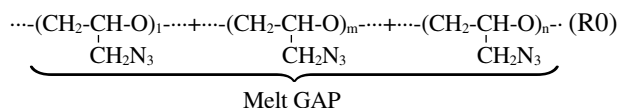
tion model taking account of *Blow Off Mechanism* is the main of this study.

2. Combustion model of tetra-ol GAP

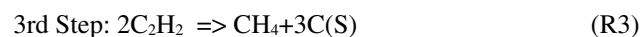
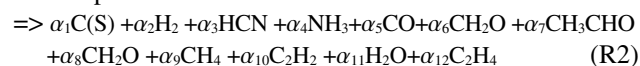
We adopted the combustion model of Beckstead^{1)~3)}. In this model, as shown in Fig.2, three regimes: the solid phase region, two-phase (gas and liquid) region, and gas phase region are considered. Melting step, which considered to be the degradation of polymer backbone based on the IR result mentioned above, and two gas generative reactions R1 and R2 are included in the two-phase region.

Melting Step:

Cured GAP \Rightarrow



2nd Step:



R1 is N_2 liberation step from azide groups with large heat release, which is universally considered to be the first chemical step in the GAP combustion. The polymeric fragments are defined to degrade further to gaseous species as in R2. In the current study, R3 which was employed in Beckstead's model is also employed as a source for soot formation. Gas phase full kinetics with 64 chemical species, 443 elemental reactions based on Yetter's RDX mechanism⁹⁾, GRI-mech 3.0¹⁰⁾, and Acetaldehyde pyrolysis mechanism^{11), 12)} is employed in this study. The detailed whole set of the kinetics scheme can be downloaded at the author web site¹³⁾. Gas phase reactions are composed of R3 and this full kinetics scheme, and this set is used in both of bubbles in two-phase region and gas phase. Equations used in this model are identical with those in Ref.14 except those for evaporation and reactions between gas and liquid. These equations were solved numerically by using a modified version of PREMIX¹⁴⁾ code based on CHEMKIN¹⁵⁾.

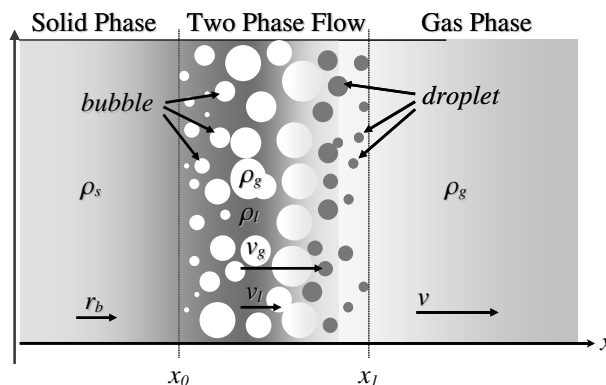


Fig. 2 Physical image of GAP combustion.

Table 1 Parameters in Beckstead's model.

Heat release of R1		352 kJkg ⁻¹
Pre-exponential Factor		Activation Energy
R1	0.1 × 10 ¹⁶	163 kJmol ⁻¹
R2	0.3 × 10 ¹⁰	126 kJmol ⁻¹
R3	0.2 × 10 ¹¹	21 kJmol ⁻¹

Table 2 Tetra-ol GAP physical properties.

Density (kgm ⁻³)	1290
Heat capacity (kJkg ⁻¹ K ⁻¹)	3.3
Thermal conductivity (Jm ⁻¹ s ⁻¹ K ⁻¹)	2.17 × 10 ⁻²

Both of the two-phase region and the gas phase region are solved simultaneously, which is different from Beckstead's numerical procedure. Burning rate, temperature profile, and chemical species profiles were numerically simulated with this model using kinetic parameters proposed by Beckstead²⁾ (Table 1), and physical properties of tetra-ol GAP (Table 2). Heat of formation of tetra-ol GAP is higher than tri-ol GAP approximately 1.5 time to twice (the detail is classified). Figure 3 shows the comparison of (a) temperature profile at 1 MPa and 5 MPa, (b) surface temperature and gas phase final temperature, and (c) linear burning rate between the experimental results and the numerical simulations. Temperature profiles were measured with ϕ 2.5 μ m S-type fine thermocouple embedded in GAP sample^{17), 18)}. Pressure range was from 1 to 10 MPa and initial temperature was 293 K. As shown in Fig.3 (a) and (b), gas phase final temperature and surface temperature exceed those of experimental results significantly, and therefore, calculated burning rates are much higher than the experimental results with strand burner (Fig.3(c)). Further, steep temperature increase just in front of the burning surface, which is probably due to azide group decomposition, is not simulated well (Fig.3(a)). We think that these inconsistencies are due to the combustion incompleteness, and the modification of the combustion model taking account of the incompleteness is necessary.

Combustion residues were analyzed in this study and their behaviors are characterized in the physical image shown in Fig.4. Burning surface of GAP was observed by means of a medium speed camera at 500 fps. The surface is covered by melt, and a lot of bubbles are popping out there. Black particles (soot) are formed very quickly at the melt surface, and stick to melt for a while and then, are released to the gas phase with the same order of gas velocity. Spherical droplets residue observed in SEM photographs can not be identified in the video images because their diameters are very small, however, may depart from burning surface and fly away at gas phase velocity as well as soot particles because of their smaller size and mass than soots. These droplets are considered as polymeric HVR, and degrade to yellow powder at higher pressures, probably having oligomeric structure.

In the previous model, HVR droplets remain in the gas phase nearby the melt surface, and they are consumed

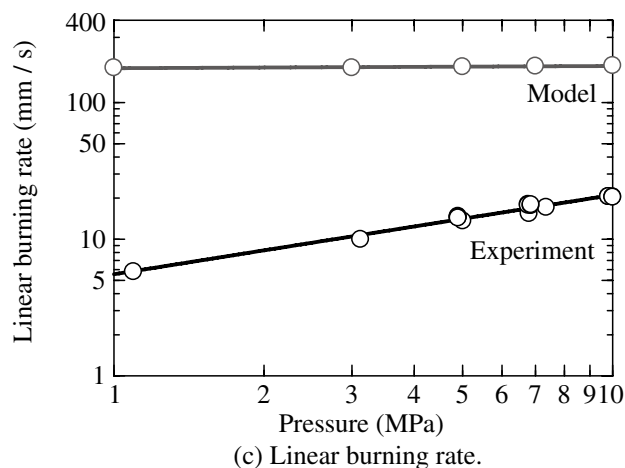
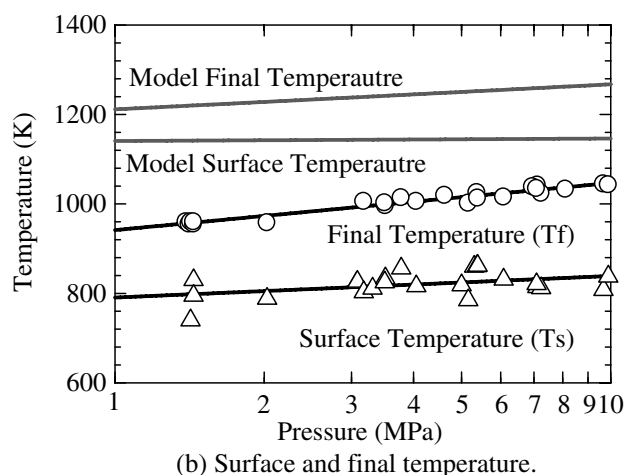
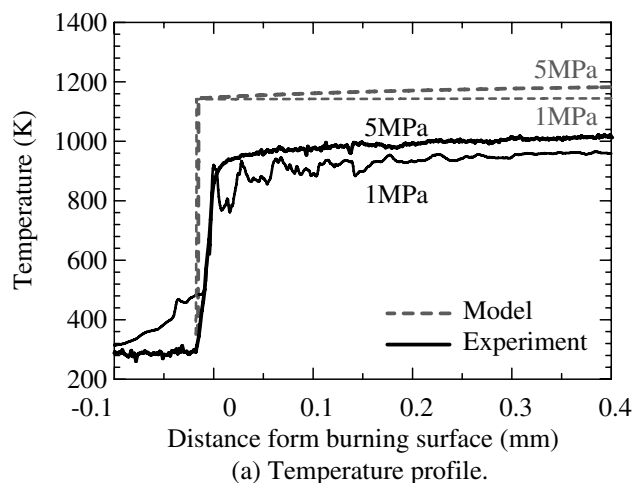


Fig. 3 Comparison of previous numerical simulation and experimental results.

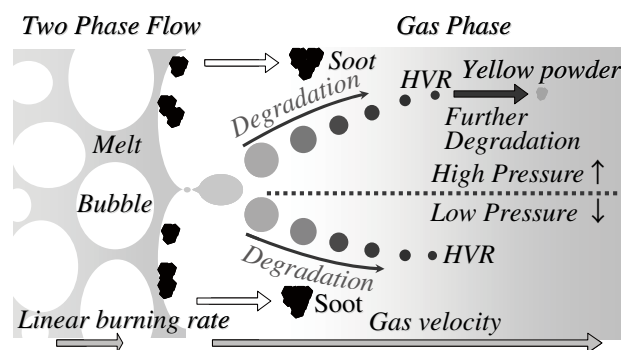
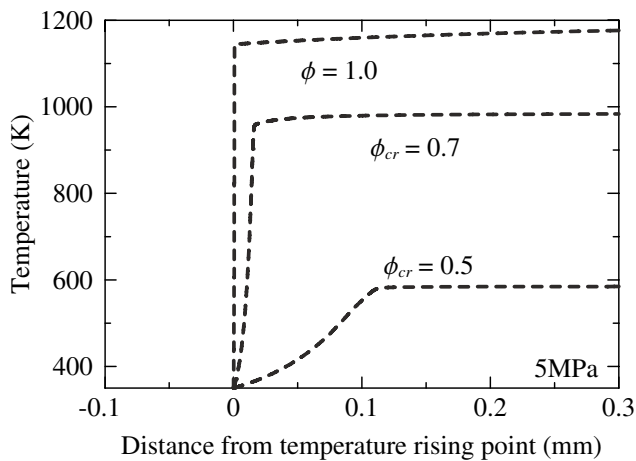
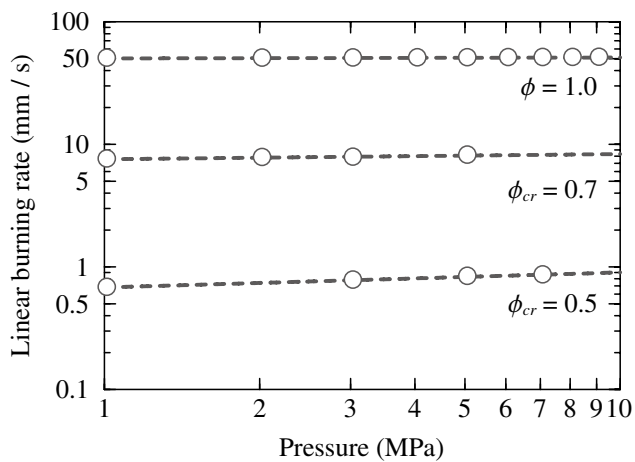


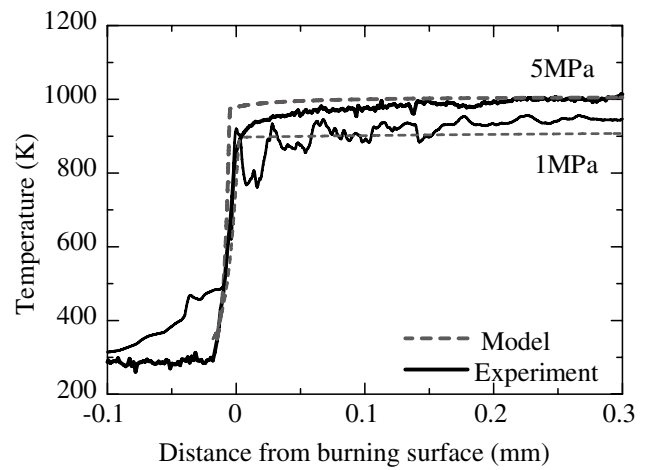
Fig. 4 Residues production process.



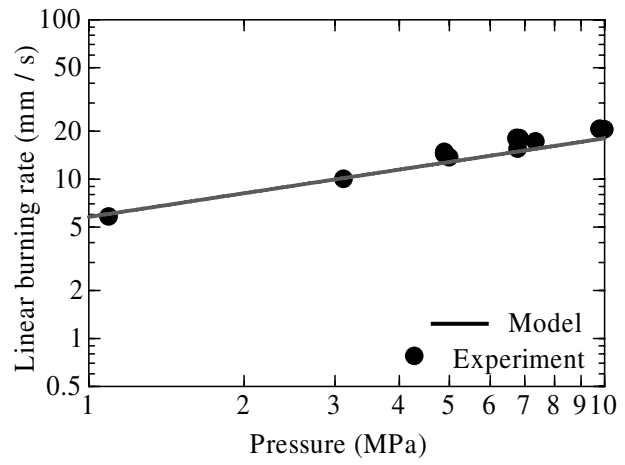
(a) Temperature profile.



(b) Linear burning rate.

Fig. 5 Effects of critical void fraction (ϕ_{cr}) on temperature profile and linear burning rate.

(a) Temperature profile.



(b) Linear burning rate.

Fig. 6 Comparison of numerical simulation and experimental results.

Table 3 Heat release of R1 and kinetic parameters of R1 and R2.

Heat release of R1		1507 kJkg ⁻¹
Pre-exponential Factor		Activation Energy
R1	0.9×10^{10}	163 kJmol ⁻¹
R2	0.1×10^9	126 kJmol ⁻¹

completely by chemical reaction, however, practically HVR is blown off from the burning surface to the gas phase by decomposed gases of GAP. It can be considered that HVR and soot carry the thermal enthalpy and HVR carry the chemical enthalpy away from the burning surface in this manner, and do not contribute to the burning rate. We consider this phenomenon would be the prime source for the large temperature and burning rate drops from the numerical simulations.

The distribution of void fraction (ϕ) was calculated with solving of equation in the simulation (see Fig.2), $\phi = 0$ at $x = x_0$ at the temperature of melting point of cured-GAP; between solid phase region and condensed phase region, and $\phi = 1$ at $x = x_j$; between condensed phase region and gas phase region. In the modified model in this study, it is assumed that at a critical void fraction (ϕ_{cr}), HVR droplets are blown off from burning surface and fly away to the gas

phase keeping the burning surface temperature. Figure 5 shows how this *Blow Off Mechanism* works effectively. Temperature profile and burning rate are significantly affected by ϕ_{cr} change.

In this simulation the heat release for breaking off N₂ from azide group, kinetic parameters of R1 and R2, and the critical void fraction are the parameters, and the data employed to adjust the residue mass fractions are summarized in Table 3. Numerical simulation well corresponds with the experimental residue mass fractions by adjusting critical void fraction as a function of pressure as shown in Table 4. The comparison of temperature profile at 5 MPa is shown in Fig.6 (a), and the rapid temperature increase and final temperature are well simulated. Figure 6 (b) is the comparison of burning rate. Calculated burning rate coincides with the experimental results very well at all pressures. The model still needs the improvements in con-

Table 4 Comparison of residue mass fraction.

<i>Experimental results</i>				<i>Numerical simulation</i>				
Pressure (MPa)	Gas (%)	HVR (%)	Soot and Yellow Powder (%)	Pressure (MPa)	Gas (%)	Residue (%)	C(S) (%)	ϕ_{cr}
1	59.6	31.4	9.0	1	60.2	34.4	5.4	0.66
3	66.4	26.9	6.7	3	64.5	30.4	5.1	0.70
5	75.4	18.4	5.7	5	75.1	20.1	4.8	0.80
7	80.1	14.8	5.1	7	79.3	16.0	4.7	0.84
10	91.1	5.3	3.6	10	90.7	5.0	4.3	0.95

densified phase chemistry, soot formation description, chemical reaction of HVR, interaction between HVR and gas phase, etc., however, the numerical simulation of residue mass fractions, temperature profiles, burning rate is satisfactory, which shows that the basis of this model employing *Blow Off Mechanism* is fairly adequate for GAP combustion.

3. Conclusions

The fundamental study to clarify the combustion mechanism of GAP is presented. One-dimensional three-phase mode combustion model of GAP based upon Beckstead's model has been constructed taking experimental observations into account. *Blow Off Mechanism* was added to account for the enthalpy losses by residues and full kinetics chemistry was entrained even in the bubbles at two-phase region. Product mass fractions, burning rate and temperature profile are numerically simulated well adjusting the kinetic parameters and the critical void fraction. This suggests that this combustion model with *Blow Off Mechanism* resolves the substance of the GAP combustion.

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Glycidyl azide polymer (GAP) の燃焼機構に関する研究

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高エネルギー物質Glycidyl Azide Polymer (GAP) の燃焼機構に関しては依然として不明な点が多い。本研究は、GAPの燃焼の3相一次元モデル化を、CHEMKINを利用した数値計算により確立することを目的としている。実験情報から、燃焼温度が断熱火炎温度より著しく低いこと、燃焼残渣の発生が認められている。特に低圧力域において多くの残渣が発生しており、これが燃焼表面から熱・化学エネルギーを持ち去り、GAPの不完全燃焼の要因となっていると推察される。本モデルでは燃焼残渣の挙動を取り入れたメカニズムを提案した。このメカニズムの導入により燃焼温度履歴と燃焼速度の圧力依存性のシミュレーションに成功した。

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