Article

Performance evaluation of gas generating agents based on 5-amino-1H-tetrazole /oxidizer mixtures by using closed vessel test

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Abstract

Gas generation behavior of gas generating agents have been examined for mixtures using of 5-amino-1H-tetrazole (5-ATZ) as a fuel component together with various types of oxidizers (lithium perchlorate $LiClO_4$ (LP), potassium perchlorate $KClO_4$ (KP), sodium nitrate $NaNO_3$ (SN), potassium nitrate KNO_3 (KN), strontium nitrate $Sr(NO_3)_2$ (SrN), and copper(II) oxide (CuO)), through deflagration test inside a closed 4 liter vessel. As a result, the degree of pressure gradients were in the order of LP > KP > SN > KN > SrN > CuO. Meanwhile, temperature gradients inside the vessel were in the same order. It was found that 5-ATZ/SN and 5-ATZ/KN mixtures' pressure gradients were larger and their generated gas temperature were lower than those of 5-ATZ/SrN mixture.

1. Introduction

Performance of gas generating agent is determined generally by the combination of fuel and oxidizer. The authors have been using 5-ATZ, a tetrazole compound which has been utilized for part of airbag gas generating agents as a fuel component, and mixing with various oxidizers, have been investigating on combustion characteristics of mixtures with improved performance, as compared to mixtures which have already been put into practical use. There are extensive studies [1-3] on gas generating agents related to 5-ATZ, and the authors also have already reported on the combustion characteristics of 5-ATZ/KP mixtures [4], 5-ATZ/SrN mixtures [5], 5-ATZ/KN mixtures[6], and 5-ATZ/SN mixtures [6]. In those papers, the samples were tested mainly by the chimney-type strand burner and the combustion characteristics, such as, the linear burning rate, the optimum mixing ratio which gave highest linear burning rate, the combustion products, and the tempreture profile in the vicinity of burning surface were examined.

The closed vessels such as 1 liter tank and 60 liter tank have been used to evaluate the the inflation of an actual airbag. In this study, the performance as a gas generating agents were studied by using a 4 liter closed vessel in which authors have expected the similar conditions as the other closed vessels. In order to acquire practical data for performance of gas generating agents, the 60 liter tank test is conducted in general, measuring the pressure-time history of each candidate material. However, the 60 liter tank test requires a relatively large amount of sample, so it is more convenient to employ a testing device that requires only a small amount of sample for each test, when screening test is to be conducted for each type of sample. The weight of samples tested in this study were 4g as compared to about 20 g [7] and about 40 g [8] for 60 liter tests. In this study, a restricted strand was burned within a closed vessel based on a chimney-type strand burner and the performance as a gas generating agents have been examined by observing the gas generation behavior. Since burning rate, amount of generated gas per unit mass, and volume of gas expansion due to an increase in temperature are considered in this experimental method, it would be possible to test the performance of the sample in a condition resembling the inflation of an actual airbag. The result has also been compared to the linear burning rate.

Table 1 Porosity of various 5-ATZ/oxidizer mixtures.

Sample	Density of oxidizer (g cm^{-3})	Composition (wt%)	Apparent density (g cm^{-3})	Theoretical maximum density (g cm^{-3})	Porosity (%)
5-ATZ / $LiClO_4$	2.428	47.7 / 52.3	1.81	1.88	3.49
5-ATZ / $KClO_4$	2.52	41.2 / 58.8	1.94	1.97	1.45
5-ATZ / $NaNO_3$	2.261	41.7 / 58.3	1.79	1.87	4.06
5-ATZ / KNO_3	2.109	37.5 / 62.5	1.78	1.83	2.77
5-ATZ / $Sr(NO_3)_2$	2.986	36.5 / 63.5	2.15	2.19	2.02
5-ATZ / CuO	6.32	23.4 / 76.6	2.48	3.61	31.3

2. Experimental

2.1 Sample

As a fuel component of the gas generating agent, 5-ATZ was used. This compound has drawn attention as a substitute for harmful sodium azide, and it has been used as gas generating agents for part of the airbags. As oxidizers, LP, KP, KN, SN, SrN, and CuO were tested.

5-ATZ and oxidizers were crushed in separate ball mills and the particle diameter for each sample was controlled within 75 ~149μm by using standard sieves. The samples were dried through a vacuum dryer at chamber temperature of 320K for 4 hours, and they were mixed at stoichiometric ratios so that the oxygen balance were zero. Sample of approx. 4 g was pressed into a strand, whose dimension was approx. 5×5×70 mm, by using a hydraulic press in which approx. 1 GPa was exerted for 5 min. The surface of the strand was restricted with epoxy resin, so that the comparison of the rate of gas generation would not be affected by the change in burning surface area. Apparent density was derived by measurement of the mass and dimension of the strand.

Table 1 gives the mixing ratio and porosity of each sample mixed at a stoichiometric ratio. Density of 5-ATZ is 1.50 g cm^{-3}, and density of each oxidizer is shown in the table. Apart from a mixture containing CuO, porosities of the samples were within a few percent.

2.2 Measurement of linear burning rate

Details of testing procedures of the linear burning rate (r) are described elsewhere[4].

2.3 Measurement of pressure and temperature within the vessel

The closed vessel used in this study is originally a 4 liter chimney-type strand burner, which is generally used for the measurement of r, and no modification has been undertaken other than closing the exit of gas flow. Initial operational pressure was designated as 2 MPa, because some samples were not ignited at a lower pressure than 2MPa. After placing the strand in the vessel, the atmosphere inside the vessel was replaced with nitrogen gas and the strand was ignited by a hot nichrome wire. Pressure within the vessel (P) was recorded on a pen recorder through a direct current amplifier. Temperature within the vessel was measured by using K-type (alumel-chromel) thermocouple, which was installed at the upper part of the burner, and the measured result was recorded on a pen recorder.

2.4 Adiabatic flame temperature

Chemical equilibrium calculatios[9] were conducted in order to estimate the adiabatic flame temperature (T_f) , assuming heats of formations of 5-ATZ, LP, KP, SN, KN, SrN, and CuO to be 207.78, -381.0, -432.79, -467.85, -494.63, -978.22, and -155.85kJmol^{-1} [9], respectively.

3. Results and discussion

3.1 Linear burning rate

Generally, it is better for the gas generating agents to demonstrate higher r, since the higher the r, the larger the amount of gas will be released within a short period of time.

The relationship between r and P, which is known as Vielle's law, can be expressed as the next equation (1).

$$r = a P^n \tag{1}$$

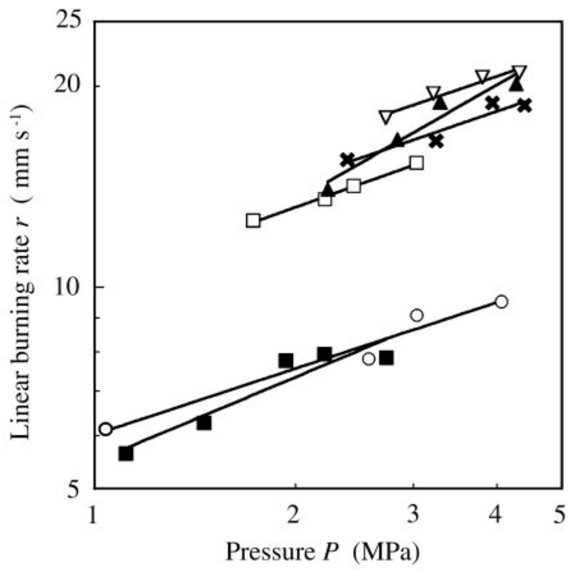

Fig. 1 Linear burning rates of 5-ATZ/oxidizer mixtures.
□ : 5-ATZ / $LiClO_4$, × : 5-ATZ / $KClO_4$,
▽ : 5-ATZ / $NaNO_3$, ▲ : 5-ATZ / KNO_3,
■ : 5-ATZ / $Sr(NO_3)_2$, and ○ : 5-ATZ / CuO.

Table 2 Theoretical amount of generated gas of various 5-ATZ/oxidizer mixtures.

Sample	Amount of generated gas per unit mass ($\times 10^{-2}$ mol g^{-1})	Amount of generated gas per unit volume ($\times 10^{-2}$ mol cm^{-3})
5-ATZ / $LiClO_4$	1.96	3.68
5-ATZ / $KClO_4$	1.70	3.35
5-ATZ / $NaNO_3$	2.06	3.85
5-ATZ / KNO_3	1.85	3.39
5-ATZ / $Sr(NO_3)_2$	1.80	3.94
5-ATZ / CuO	0.963	3.48

Here, a and n can be derived as constants for each energetic material sample. Figure 1 gives the relationship between r and P. Within the pressure range tested in this study, r were found to be larger, when SN, KN, KP, and LP were used as oxidizers, as compared to 5-ATZ/SrN mixture, which is already put into practice.

3.2 Amount of generated gas

As an important requirement for automobile airbags, the inflator should be small, i.e. large amount of gas should be released with small mass of gas generating agent.

Since the samples were prepared to give stoichiometric fuel-oxgen ratio so that the sample burns completely, all carbon and hydrogen atoms contained in the fuel, in theory, should oxidize completely to become carbon dioxide and water. Reaction equations are given in (2) ~ (7).

In the case of 5-ATZ/LP mixtures:

$$CH_3N_5 + 0.875LiClO_4 \rightarrow CO_2 + 1.5\,H_2O + 2.5\,N_2 + 0.875\ LiCl \quad (2)$$

In the case of 5-ATZ/KP mixtures:

$$CH_3N_5 + 0.875\,KClO_4 \rightarrow CO_2 + 1.5\,H_2O + 2.5\,N_2 + 0.875\,KCl \quad (3)$$

In the case of 5-ATZ/SN mixtures:

$$CH_3N_5 + 1.4\,NaNO_3 \rightarrow CO_2 + 1.5\,H_2O + 3.2\,N_2 + 0.7\,Na_2O \quad (4)$$

In the case of 5-ATZ/KN mixtures:

$$CH_3N_5 + 1.4\,KNO_3 \rightarrow CO_2 + 1.5\,H_2O + 3.2\,N_2 + 0.7\,K_2O \quad (5)$$

In the case of 5-ATZ/SrN mixtures:

$$CH_3N_5 + 0.7Sr(NO_3)_2 \rightarrow CO_2 + 1.5\,H_2O + 3.2\,N_2 + 0.7\,SrO \quad (6)$$

In the case of 5-ATZ/CuO mixtures:

$$CH_3N_5 + 3.5CuO \rightarrow CO_2 + 1.5\,H_2O + 2.5N_2 + 3.5Cu \quad (7)$$

From the equations above, the amount of generated gas per unit mass of sample and the amount of generated gas per unit volume of sample were calculated. Results are given in Table 2.

Although the maximum temperature reached above boiling point of water in some experiments, water was assumed to be in liquid state for theoretical calculations. Sample which can generate large volume of gas enable to downsize the inflator. From Table 2, it is clearly seen that 5-ATZ/SrN mixture requires the least volume to generate the same volume of gas among the samples tested in this experiment. However, when it comes to reducing the weight of the inflator, SN and LP seem to be better oxidizers as compared to SrN. Although CuO is comparable to other oxidizers in terms of the amount of generated gas per unit volume, the amount of generated gas per unit mass is considerably smaller, due to its large density .

3.3 Mass burning rate

In order to compare the amount of generated gas per unit mass, the amount of generated gas was derived through calculation of mass burning rate (r_m) from r. Figure 2 gives

Table 3 Amount of generated gas per unit time of various 5-ATZ/oxidizer mixtures.

Sample	Amount of generated gas per unit mass* ($\times 10^{-2}$ mol g^{-1})	Mass burning rate r_m at 2MPa (g s^{-1})	Amount of generated gas per unit time** ($\times 10^{-2}$ mol s^{-1})
5-ATZ / $LiClO_4$	1.96	0.728	1.43
5-ATZ / $KClO_4$	1.70	0.801	1.36
5-ATZ / $NaNO_3$	2.06	0.902	1.86
5-ATZ / KNO_3	1.85	0.743	1.38
5-ATZ / $Sr(NO_3)_2$	1.80	0.408	0.733
5-ATZ / CuO	0.963	0.397	0.383

Note: * theoretical value; ** based on mass burning rate.

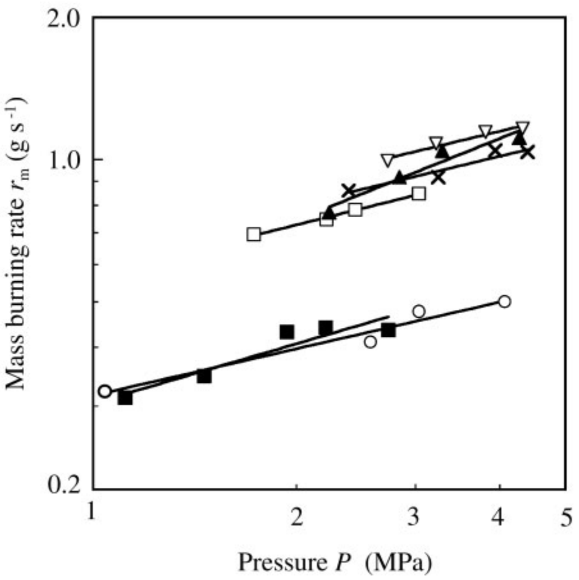

Fig. 2 Mass burning rates of 5-ATZ/oxidizer mixtures.
□ : 5-ATZ / $LiClO_4$, × : 5-ATZ / $KClO_4$,
▽ : 5-ATZ / $NaNO_3$, ▲ : 5-ATZ / KNO_3,
■ : 5-ATZ / $Sr(NO_3)_2$, and ○ : 5-ATZ / CuO.

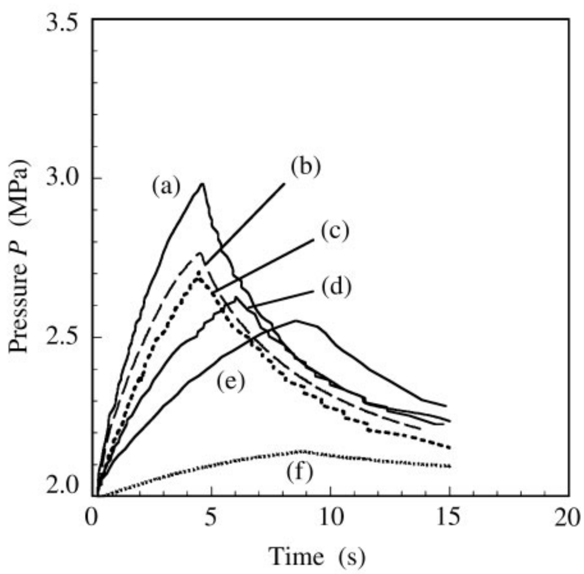

Fig. 3 Pressure-time history of 5-ATZ/oxidizer mixtures from the closed vessel experiments.
(a) 5-ATZ / $LiClO_4$, (b) 5-ATZ / $KClO_4$,
(c) 5-ATZ / $NaNO_3$, (d) 5-ATZ / KNO_3,
(e) 5-ATZ / $Sr(NO_3)_2$, and (f) 5-ATZ / CuO.

the relationship between r_m and P. As r became larger, r_m also decame larger with the increase in P, the order of r_m were the same as those of r except SrN and CuO. However, as for 5-ATZ/CuO mixture, which had high porosity, r_m displayed the smallest value at higher P.

The amount of generated gas per unit mass derived from r_m at 2 MPa is shown in Table 3. The amount of generated gas per unit time were in the order of SN > LP > KN > KP > SrN > CuO.

However, estimation of gas generation capability based on r_m did not take into consideration the gas temperature, so the evaluation of the ability of the actual bag inflation performance was imperfect.

3.4 Pressure within the vessel

Gas generating agents for automobile airbags are required to generate enough gases to fill the bag within a short period of time. Measurement of r does not take into consideration the amount of generated gas per unit mass of sample and the gas temperature, so the actual process of bag inflation cannot be simulated without complicated calculations.

Pressure-time curve is given in Fig. 3. Pressure gradients were in the order of LP > KP > SN > KN > SrN > CuO. It was also clarified that the maximum pressure reached by a LP mixture was greater than mixtures which used other oxidizers. Furthermore, it was also clarified that there was no correlation between the order of calculated values of the amount of generated gas and the order of pressure gradients. If the temperature of the generated gas was assumed to be equal for all samples, the amount of generated gas per unit time would be the greatest for SN, as shown in Table 3. However, the order of the amount of generated gas per unit time is not the same as that of pressure gradients. The factors which cause this difference will be discussed later.

Table 4 Linear burnig rate and burning rate at 2MPa of various 5-ATZ/oxidizer mixtures.

Sample	Linear burning rate r (mm s^{-1})	Burng rate* r_v (mm s^{-1})
5-ATZ / $LiClO_4$	13.2	15.1
5-ATZ / $KClO_4$	14.5	15.6
5-ATZ / $NaNO_3$	16.3	15.7
5-ATZ / KNO_3	13.5	11.6
5-ATZ / $Sr(NO_3)_2$	7.4	8.2
5-ATZ / CuO	7.6	10.0

Note: * based on Fig. 3.

In this experiment, the strands of same length were undergoing end-burning, hence strands with shorter time required for maximum pressure reached were thought to have higher burning rates. The strand length divided the time required to reach the peak pressure gives the burning rate (r_v) , as shown in Table 4. Therefore, r_v at 2MPa was the highest when SN was used as an oxidizer, followed by LP, KP, KN, CuO and SrN. The linear burning rate r were in the order of SN > KP > KN > LP > CuO > SrN at 2MPa, as shown in Table 4. The order of r_v was the same as that of r except LP and KN.

3.5 Temperature within the vessel

Temperature of the generated gas should be as low as possible, because the gas temperature within the bag should not be higher than necessary. For this purpose, temperature-time curve of gases within the vessel was measured, as given in Fig. 4.

Temperature-time curve have shown a tendency similar to pressure-time curve as shown in Fig. 3. The maximum temperature of generated gas (T_{max}) and T_f are shown in Table 5. The order of T_{max} were LP > KP > SrN > SN > KN > CuO.

Despite T_f of SN was lower compared to that of KN, T_{max} was higher probably because generated gas was heated rapidly before heat was lost to the surroundings, because of the higher r of SN. The LP mixture whose theoretical amount of generated gas was slightly less but T_f was greater by approx. 1000K as compared to SN may have leaded to the largest pressure gradient, as shown in Fig. 3.

Temperature gradients were equally high for mixtures containing LP, KP, or SN. The values for SrN and KN came next, and that of CuO was the smallest. Tendency for the magnitude of temperature gradient agreed with tendency for the magnitude of pressure gradient. This is probably because the faster the generation of the hot gas, the higher the temperature within the vessel. As for T_{max}, mixtures containing LP and KP displayed higher values than that of SrN, but those of SN, KN and CuO were lower.

From the results stated above, it was clarified that pressure gradient was affected not only by the amount of generated gas per unit mass of the sample but also by the temperature of the generated gas. Pressure gradient of mixtures containing SN and KN were greater than SrN, whilst the temperature of generated gas were relatively low, which demonstrated superior combustion performance as gas generating agents for airbags.

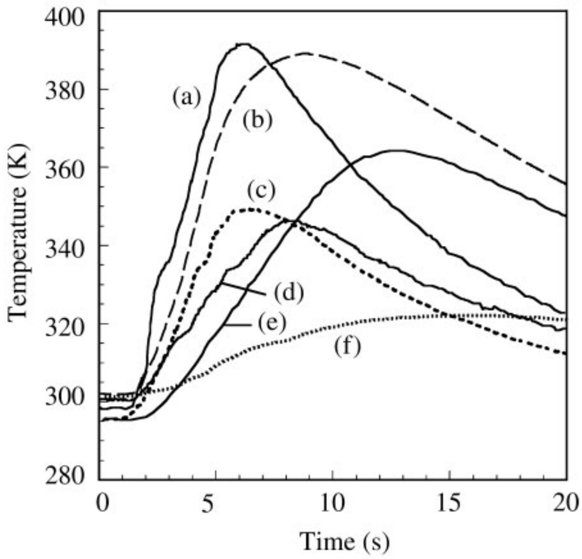

Fig. 4 Temperature-time history of 5-ATZ/oxidizer mixtures from the closed vessel experiments. (a) 5-ATZ / $LiClO_4$, (b) 5-ATZ / $KClO_4$, (c) 5-ATZ / $NaNO_3$, (d) 5-ATZ / KNO_3, (e) 5-ATZ / $Sr(NO_3)_2$, and (f) 5-ATZ / CuO.

4. Conclusions

Evaluation of characteristics of gas generating agents for automobile airbag was conducted for 5-ATZ/oxidizer (LP, KP, KN, SN, SrN, or CuO) mixtures, by using a closed vessel. As a result, the following conclusions were obtained.

(1) The value of pressure gradient became higher for a mixture which used LP, KP, SN, or KN , as compared to the mixture already put into practice, which used SrN.

(2) The reasons for larger value of pressure gradient for mixtures considered in this study, as compared to a mixture which used SrN, were probably due to larger amount of generated gas per unit mass, higher linear burning rate and higher flame temperature.

Table 5 Maximum temperature of generated gas within the vessel and adiabatic flame temperature of various 5-ATZ/oxidizer mixtures.

Sample	Maximum temperature of generated gas within the vessel T_{max} (K)	Adiabatic flame temperature T_f (K)
5-ATZ / $LiClO_4$	391	3101
5-ATZ / $KClO_4$	389	3032
5-ATZ / $NaNO_3$	349	2105
5-ATZ / KNO_3	346	2166
5-ATZ / $Sr(NO_3)_2$	364	2788
5-ATZ / CuO	322	1782

(3) Temperature of generated gas for a mixture which used SN or KN was lower than that of a mixture which used SrN.

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密閉容器試験による5-アミノ-1H-テトラゾールと各種酸化剤のガス発生能力の比較

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5-アミノ-1H-テトラゾールを燃料として，各種酸化剤（過塩素酸リチウム，過塩素酸カリウム，硝酸ナトリウム，硝酸カリウム，硝酸ストロンチウム，酸化銅（II））の混合物のガス発生挙動を4lの密閉容器を用いて調べた。ガス発生速度及び温度上昇速度は上述の酸化剤の順に小さくなった。また，硝酸ナトリウムと硝酸カリウムは硝酸ストロンチウムと比較して，ガス発生速度は速く，発生ガスの温度は低いことがわかった。

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