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Test-Based Thermal Decomposition Simulation of AP/HTPB and AP/HTPE Propellants

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The ammonium perchlorate composite propellant is a common choice for solid rocket propulsion. The externally heated rocket via fires, for instance, can cause the energetic substance to ignite, and this may lead to a thermal runaway event or a slow cook-off phenomenon marked by a severe explosion. To develop preventive measures to reduce the possibility of such accidents in propulsion systems, we investigate the ignition and initiation characteristics of ammonium-perchlorate-based propellants and perform the thermal decomposition simulation of a thermally loaded solid rocket motor.

Nomenclature

B_i	=	preexponential factor
C	=	heat capacity, kcal/kg-K
E_i	=	activation energy, kJ/mol
P	=	pressure, Pa
q_i	=	heat of reaction, kJ/kg
R	=	gas constant, J/K-mol
R_1	=	first-step reaction rate
R_2	=	second-step reaction rate
T	=	temperature, K
X	=	mass fraction of ammonium perchlorate
Y	=	mass fraction of binder
Z	=	mass fraction of decomposed ammonium perchlorate
β	=	stoichiometric mass ratio
κ	=	heat conduction coefficient, W/m-K
ρ	=	density, kg/m^3

Subscript

i	=	reaction step

I. Introduction

AMMONIUM perchlorate (AP) has been used as a common oxidizer of rocket propellant because of its known stability with respect to combustion and its burning rate that can be controlled by varying the AP particle-size distribution, which is a major difference from nitramines such as cyclotrimethylenetrinitramine (RDX) or cyclotetramethylenetetranitramine (HMX). Hydroxyl-terminated polybutadiene (HTPB) has been a common polymeric binder/fuel in the AP-based solid rocket propellants [1–4]. More recently, hydroxyl-terminated polyether (HTPE) is used in place of HTPB to meet the motor safety requirement for external stimuli.

The propellant surface is usually assumed to be nonuniform because the surface is a mixture of oxidizer and binder grains, whose microscopic structures and sizes vary. Hermance [5] considered this structural feature of propellant and proposed a statistical combustion model where the propellant surface condition was considered. Beckstead et al. [6] modified and complemented [5] by suggesting a model of a multiflame structure that includes premixed flame, primary flame, and final diffusion flame, named the BDP (Beckstead–Derr–Price) model. Both models considered the condensed-phase decomposition of the propellant before generation of product gases. The BDP model builds a mixed (condensed and gaseous) structure from various sets of chemical reaction mechanisms. The premixed flame is formed by the decomposition process of AP, the primary diffusion flame consists of a mixture of AP and HTPB, and the final diffusion flame consists of the product gases produced from decomposition of AP and HTPB.

When a solid rocket motor is exposed to the thermal loading via fires, the microscopic morphology of the propellant grains changes and as a result an exothermic chemical reaction can usually proceed. Some of the well-known explosion hazards were observed in the munitions warehouse, where such thermal loading has been the major cause of the cook-off. Understanding and predicting the process of cook-off is important for developing a methodology to prevent hazardous accidents induced by the fire. However, the thermal decomposition or slow cook-off of AP composite propellant has not been fully investigated in the past decades [7–9], because of the complexity of the pathway in the state of thermal decomposition. In this paper, we present a simplified deflagration reaction of AP propellant for estimating the thermal runaway. The thermal decomposition process consists of two steps of the BDP model; AP decomposes and the decomposed AP and binder react under endothermic condition. We perform the one-dimensional time to explosion (ODTX) to validate present chemical mechanisms and compare numerical results with experimental cook-off data of AP/HTPB and AP/HTPE propellants.

II. Chemical Kinetics of Thermal Decomposition

The chemical reaction that accounts for a decomposition of AP/HTPB propellant is proposed by [10] as

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$$(R_1)\text{: AP}(X) \rightarrow \text{decomposition product}(Z) \quad (1)$$

$$(R_2)\text{: } \beta Z + \text{binder}(Y) \rightarrow \text{final product} \quad (2)$$

where each reaction rate is given as

$$R_1 = B_1 \exp(-E_1/RT)\rho_X P^{1.744}$$

$$R_2 = B_2 \exp(-E_2/RT)\rho_Y \rho_Z P^{1.75}$$

where B_i and E_i, are the preexponential factor and the activation energy for each reaction step, and pressure $P = \rho RT$. The step R_1 is associated with the AP decomposition flame, and R_2 is associated with the final diffusion flame. Parameters used in the model for AP/HTPB propellants employed in independent experiment of [11,12] are summarized in Tables 1 and 2, respectively.

To allow reaction progress variables to evolve in time, we employ the thermal transport through Eq. (3) and the species mass fraction Eqs. (4–6) as shown below:

$$\rho C \frac{\partial T}{\partial t} = k\nabla^2 T - \sum R_i q_i \quad (3)$$

$$\rho \frac{\mathrm{D}X}{\mathrm{D}t} = -R_1 \quad (4)$$

$$\rho \frac{\mathrm{D}Y}{\mathrm{D}t} = -R_2 \quad (5)$$

$$\rho \frac{\mathrm{D}Z}{\mathrm{D}t} = R_1 - \beta R_2 \quad (6)$$

where the stoichiometric mass ratio β is 7.51, C is the heat capacity 0.3 kcal/kg-K, and k is heat conduction coefficient 0.389 W/m-K for AP/HTPB.

Unlike the historically common AP/HTPB composite, there has been an increase in use of insensitive rocket propellants that meet the stringent safety requirement of rocket propulsion. The AP/HTPE propellant, on the other hand, is less well known and its physical and thermal properties are being studied for understanding its cook-off behavior. Since the HTPE is chemically similar to HTPB with addition of low-temperature response characteristics due to AN and energetic additive (BuNENA), we assume the same thermal decomposition path of AP/HTPB; therefore, the same properties of heat capacity, heat conduction, and heat of reaction, are assumed in place of AP/HTPE with the ignition occurring earlier than AP/HTPB at about 110°C; at this temperature, BuNENA is known to undergo its thermal decomposition process. The lower ignition temperature reduces the level of runaway violence because AP becomes more brittle and easily cracked as temperature increases, resulting in the rapid rise of reaction rate throughout the enlarged burning surface area. Therefore, the additive oxidizer (AN) in AP/HTPE assists the propellant to burn mildly in the low-temperature regime. Therefore,

Table 1 Parameters of AP/HTPB propellant tested in [11]

Reaction step i	B_i	E_i, kJ/mol	Heat of reaction q_i, kJ/kg
1	800	137.18	−297
2	1100	178.75	9643.2

Table 2 Parameters of AP/HTPB propellant tested in [12]

Reaction step i	B_i	E_i, kJ/mol	Heat of reaction q_i, kJ/kg
1	800	124.72	−297
2	1100	161.30	9643.2

Table 3 Parameters of AP/HTPE propellant

Reaction step i	B_i	E_i, kJ/mol	Heat of reaction q_i, kJ/kg
1	900	103.93	−297
2	1300	120.55	9643.2

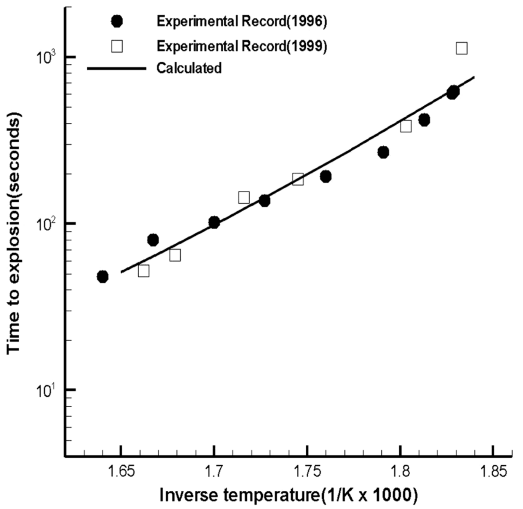


Fig. 1 One-dimensional time to explosion validation of AP/HTPB propellant from test [13].

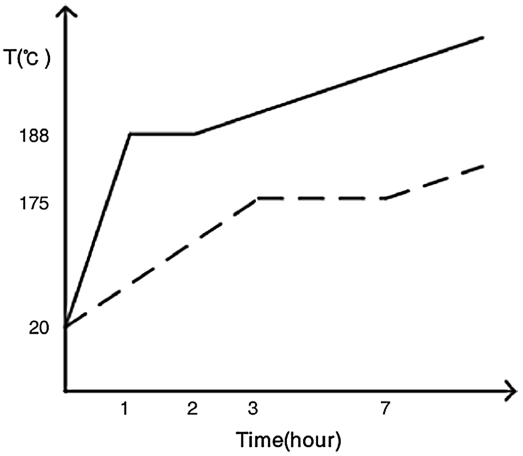


Fig. 2 Control temperature (heater) profiles of test [11] (solid line) and test [12] (dotted line).

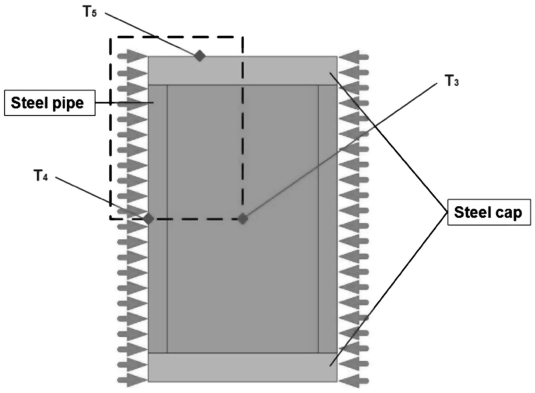
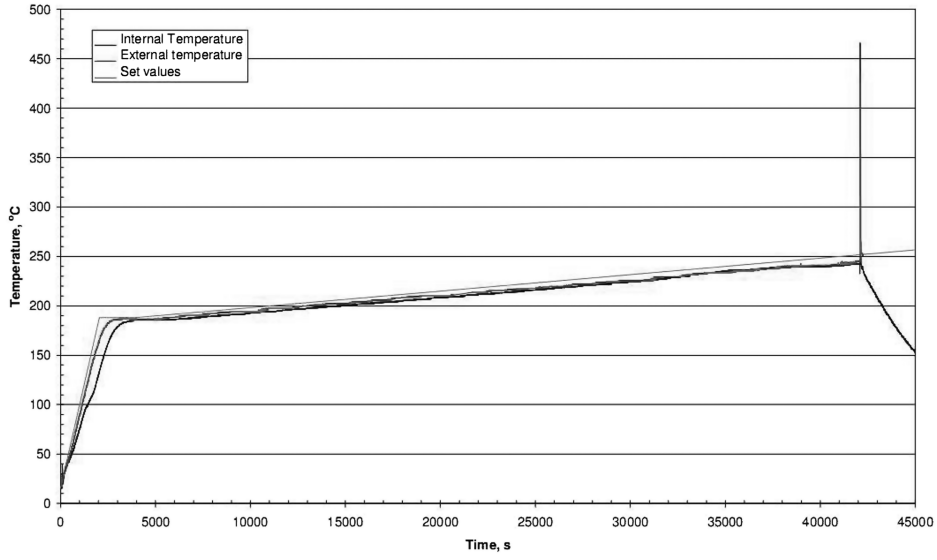
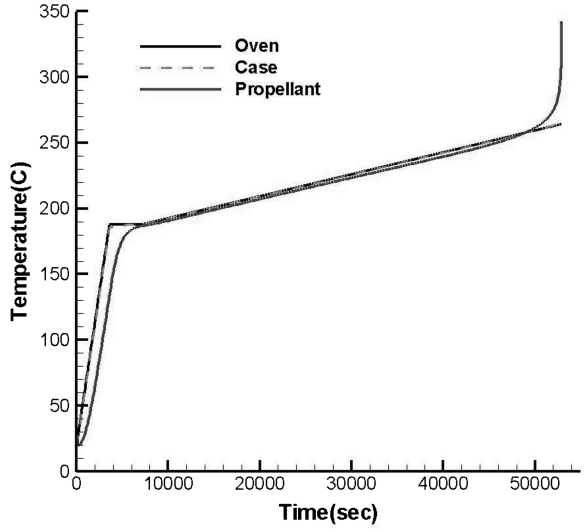


Fig. 3 Schematic of the numerical test setup.



a)



b)

Fig. 4 Comparison of experimental and numerical thermal runaway results for AP/HTPB from [11]: experiments (solid line), simulations (dashed line).

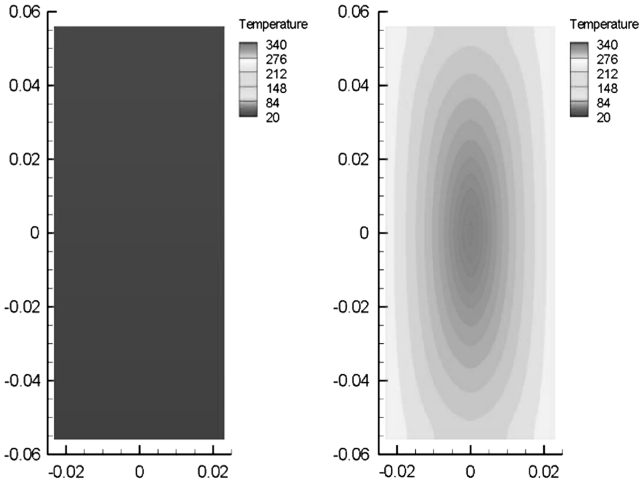
decreasing the ignition temperature effectively reduces the chemical reaction rate of the propellant. Also, the preexponential factor and activation energy are calibrated to meet the sensitivity of chemical kinetics measured. Parameters for modeling AP/HTPE propellant are given by Table 3.

III. One-Dimensional Validation

ODTX apparatus is ordinarily used to validate the thermal kinetics of energetic materials subject to a sudden increase in temperature to a specific value. The thermal decomposition kinetics requires a mechanism for modeling solid-solid phase transition (endothermic) while producing intermediate solids and gases before the final exothermic chemical reaction that may lead to a thermal runaway. Figure 1 compares the test results against the calculation of time to explosion [13]. Quantitative performance of ODTX modeling provides confidence to the actual motor cook-off simulation that is based on the fitted deflagration kinetics described here.

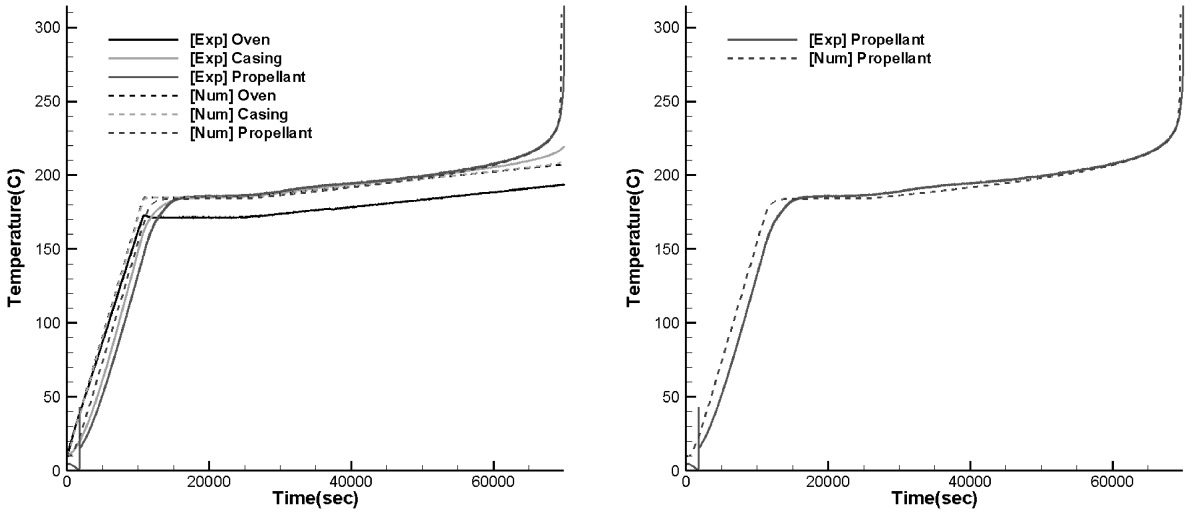
IV. Thermal Decomposition Simulation of AP/HTPB in Cylindrical Charge

We apply the modified BDP model [13] discussed earlier to explain the thermal decomposition under the thermal loading. In



a) b)

Fig. 5 Temperature (unit: Celsius) shown with elapsed time at a) 0 h and b) 14.7 h for AP/HTPB of [11].



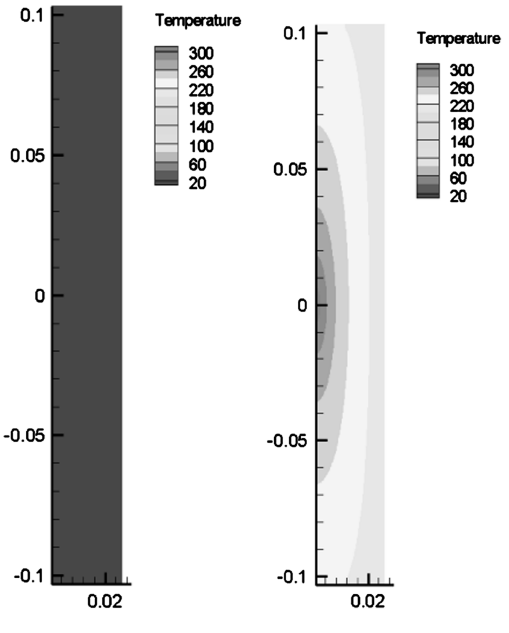
a) b)

Fig. 6 Comparison of experimental and numerical cook-off tests of AP/HTPB [12]: a) temperatures at various locations and b) temperature of propellant.

[11,12], the slow cook-off experiment of an AP/HTPB rocket propellant is performed and the ignition time to thermal runaway is measured. The control temperature of the heater of [11,12] is depicted in Fig. 2. The compositions of AP/HTPB and heating ramp considered by [11,12] are different. AP/HTPB is heated to 188°C in 1 h, soaked for 1 h and increased at 6°C/h in [11]. In the test of [12], AP/HTPB is heated to 171°C in 3 h, soaked for 4 h, and then increased at 1.8°C/h. The scaled-down rocket motor [12] (or a mockup) consists of a hollow pipe, whose length, radius, and thickness are 200, 22.5, and 4 mm, respectively. The charged pipe is sealed at both ends with two 3 mm end caps.

The heating conditions are modeled as zero energy flow through the end caps, thus the heat exchange occurs only through the sides. The axisymmetric calculation domain is shown in Fig. 3. The top and bottom of the boundary condition are adiabatic, and thermal load is only applied to sides of the pipe. The experimental and numerical results of AP/HTPB [11] are shown in Fig. 4. The runaway times between the numerical and experimental tests are about 52,000 and 54,420 s, respectively, and follow qualitatively a similar pattern. Figure 5 provides the sequential temperature field of the propellant during the cook-off process. The temperature of propellant slowly increases during the slow heating of early on time; when ignition occurs in the center (a corner of a quadrant), however, the temperature rise is very rapid until the entire domain thermally explodes. This phenomenon is characteristic of the slow cook-off process where thermal transport (or cooling) of the inside of AP/HTPB is slower than that of the outside. The hot spot or the ignition point is generated in the center of AP/HTPB.

Various types of AP/HTPB propellants are synthesized by various countries and organizations. AP/HTPB tested by [12] uses a special blend of additives for performance enhancement. Figure 6 shows the unique performance of this propellant where the temperature of the oven and the propellant increases to 171 and 189°C, respectively. Undisclosed additives result in exothermic reactions leading to this unusual thermal response, which occurs only in the region blow 200°C. For this reason, we assume that temperature of the oven at 3 h is modified from 171 to 189°C. This adjustment explains correctly the process of the exothermic reaction as shown in Fig. 7. Similar characteristics of slow cook-off phenomena are also observed as the hot spot generation inside and the uniform temperature profile till the ignition. The ignition and the runaway time between the numerical and experimental tests are approximately 698,000 s. Numerical data are in good agreement with experimental data.



a) b)

Fig. 7 Temperature (unit: Celsius) shown with elapsed time at a) 0 h and b) 18 h for AP/HTPB of [12].

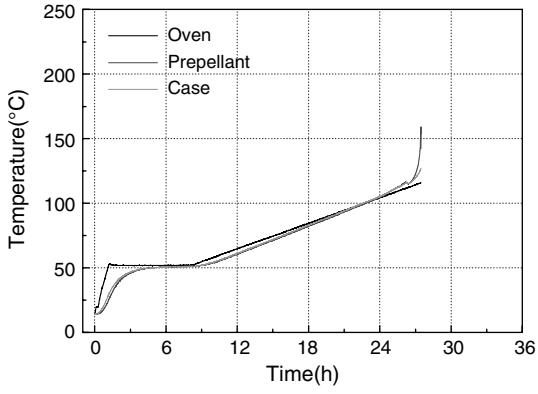


Fig. 8 Experimental thermal runaway result of AP/HTPE.

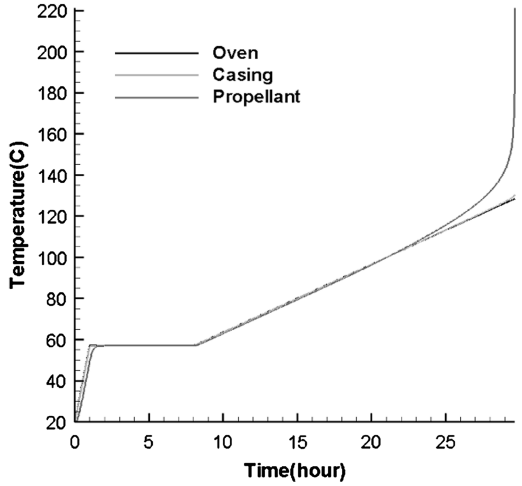


Fig. 9 Numerical thermal runaway result of AP/HTPE.

V. Thermal Decomposition Simulation of AP/HTPE in Cylindrical Charge

In many ways, the thermal response of AP/HTPE is known to be less sensitive when compared with how the AP/HTPB responds to a thermally harsh environment. Additives such as AN and BuNENA help to ignite and burn propellant in relatively lower temperature regime and functionally delay violent response of AP until reaching high temperature stage for the most of exothermic reaction during the cook-off. However, the mechanical and chemical characteristics of AP/HTPE are known to be similar to those of AP/HTPB. Thus we adopt the modified BDP model of AP/HTPB propellant and develop a cook-off model for the AP/HTPE propellant by following the similar steps outlined earlier. The cook-off experimental data of AP/HTPE propellant are provided from [12], as shown in Fig. 8. The additives including AN and BuNENA are responsible for bringing down the runaway point; that is, explosion occurs at lower temperature than AP/HTPB resulting in lesser violence. The numerical result shown in Fig. 9 does not exactly coincide with the experiment; however a bit of modification to the kinetics based on the chemical pathway may significantly enhance the performance. The experiment shows that there exists temperature gap in the initial heating and hold stages because of the heat conduction. We found that propellant temperature is higher than the control thermocouple reading at about 24 h. This means that chemical reaction accelerates and violent explosion occurs shortly after. In the experiment, the runaway happens at 27 h, and the numerical prediction is given at 28.5 h. Figure 10 shows the sequential temperature field of the propellant during the cook-off process. The sequential images of AP/HTPE are similar to those of AP/HTPB.

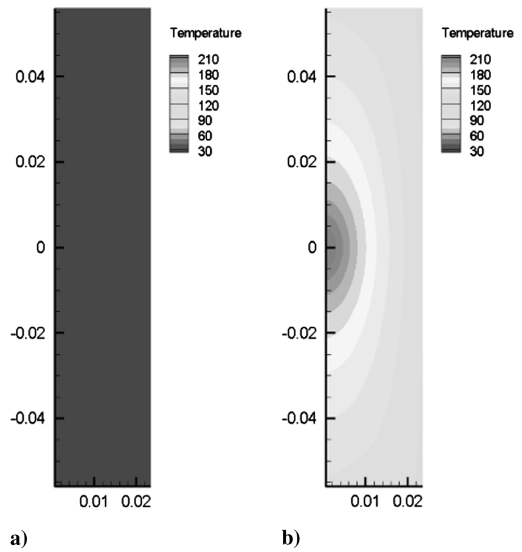


Fig. 10 Temperature shown with elapsed time at a) 0 h and b) 28.5 h for AP/HTPE.

The qualitative responses of modeled AP/HTPB and AP/HTPE to the experiments show good comparison because slow cook-off phenomena are mainly governed by latently slow heat transfer. Propellants are heated and slowly decomposed, irreversibly. That means the thermal runaway has no point of return; thus, predicting the cook-off response is cardinal to the preventive measures.

VI. Conclusions

The AP/HTPB and AP/HTPE propellants exposed to the unexpected thermal environment (fires or abnormal combustion) are investigated. When such a thermal stimulus is applied to a rocket motor, the temperature of the propellant increases slowly which results in a uniform temperature distribution. The onset of ignition occurs abruptly and burning of rocket motor may result in the thermal runaway or a blow up. To predict such hazards, we build a BDP-based cook-off model of three AP-based rocket propellants to explain the chemical and thermal responses. The model is tested against the one-dimensional and two-dimensional cook-off experiments and showed quantitative agreement. The model may be used towards the safety assessment of general AP-based solid rocket motors of greater kinds.

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