

Thermal Stability of Explosive Mixture with Additives at Different Ambient Temperatures

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Abstract: Thermal stability of explosive mixture containing solid-liquid phase of trinitrohexahydrotriazine (RDX), isopropyl nitrate (IPN, 2-propyl nitrate) and aluminum powder (Al) with addition of different rates of 5%, 10%, 15% and 20% of sulfuric acid H₂SO₄ to the (RDX/IPN/Al) mixture was measured based on numerical simulation. Kissinger, equation of state (EOS) method and Maxwell approximation were used to compute the physic-chemical characteristics of the mixture. We add an amount of acid to present a new

explosive component. To obtain the ignition temperature, Cookoff model of cylindrical test is performed. The heating process of mixture at different ambient temperatures was progressed, and the ignition temperature was found that it depends on both acid rate added and different ambient temperatures applied and focused by SADT analysis. Temperature distributions over time, different ambient temperatures effect on ignition delay time, ignition position are carried out.

Keywords: thermal stability • explosive mixture • temperature effect • SADT

1 Introduction

Explosive materials, are substances that contain a great amount of stored energy that can produce an explosion, a sudden expansion of the mixture after initiation, usually accompanied by the production of light, sound, and pressure. The energy stored in this explosives may be: chemical energy, pressurized compressed gas, and nuclear energy [1]. It may be known as substances that exothermically rapidly react when subjected to external stimuli such as mechanical impact or heating [2–3]. Explosion phenomena lead to huge energy after burning process of explosive compositions, the detonation is the first source of this energy [4]. The detonation energy of classical explosives such as 2,4,6-trinitrotoluene (TNT), cyclotetramethylene tetranitramine (HMX) cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX), CL-20 (hex-anitrohexaazaiso-wurtzitane), is considered to be of high destructive ability and enough thermal effects [5]. With a reason to enhance and improve the efficiency of energetic materials, many recent researches have proven that addition of metal particles [6] such as Al and Mg [7] increases the total energy and enhances the blast effects. Aluminum is the main common ingredient used in explosive mixtures to increase energy and reaction temperature of explosions [8], the wide ranging needs of both military and civil uses of aluminized explosives necessitate caution and vigilance in application, transportation and storage. The explosive mixture may combine different components such as a high explosive, oxidizer, fuel, additives and binder [9, 10], in general are often of heterogeneous compositions. Adequate thermal stability and low thermal sensitivity condition are important keys to keep safe and avoid fatal accidents from explosive detonation [11, 12]. The mixtures are susceptible by

temperature, impact, shock, and other factors [13]. Many unfortunate incidents have taken place in the past decades and have led to huge damages and losses during the processing, transportation and storage [14, 15]. The danger arises under certain external stimulus, can lead to violent reactions, many investigations have been predicting a modeling process to prove the thermal stability of explosives. M. A. McClelland et al. in [16] reported on the development of ALE3D models for Cookoff of PBXN-109 in the NAWC system, Sandusky has modeled on the RDX-based explosive PBXN-109 and on the HMX-based explosive. Pre-and post-ignition behavior for PBXN-109 was distinguished on [17]. Philip [18, 19] has used equation of state (EOS) of RDX-TNT, HMX-RDX for the solid-liquid mixture to calculate different measurements of temperature, pressure, density and capacity of component mixtures. Numerical simulations are progressively being employed as a means to study thermal stability of mixtures. The focus of this work was to numerically simulate the explosive mixture (25–35% RDX as a high explosive powder, 20–30% IPN isopropyl nitrate as a fluid fuel, 20–30% Al powder as a metallic fuel, and 5–20% solid sulfuric acid as additives) using ANSYS software. The simulation results has been used to study the thermal behavior of mixture under atmospheric pressure at different ambient temperatures.

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2 Experimental Work

A cylindrical test, modeled and devised, where the mixture situated in the center and confined by steel wall as described in Figure 1. A constant length to diameter ratio of 2:1 is used. For a charge of 0.17 m diameter, 0.34 m length, the respective wall thickness was 0.003 m, under an atmospheric pressure. The heating process raised by raising ambient temperature gradually. The loading temperature is assured by conductivity from the wall edges toward inside of the mixture. The properties of steel material are referred from [20]. Rybakov [21] has used the methods of field theory of many bodies to distinguish the values of a few parameters of component mixtures. He revealed that the results calculated by the proposed model correspond to experimental data. Therefore the coefficients of correlation do not exceed 2% for density and 4% for heat of the explosion. Green's has solved the reaction of concentration (*)

with dependence on time and space $n(\vec{r}, t)$, (*) has the form:

$$\frac{\partial n(\vec{r}, t)}{\partial t} = -\vec{\nabla} \cdot \vec{j}(\vec{r}, t) - s(\vec{r}, t) \cdot n(\vec{r}, t) + S(\vec{r}, t) \quad (*)$$

Where $S(\vec{r}, t)$ is the density of particle sources, $s(\vec{r}, t)$ is the reaction rate, $\vec{j}(\vec{r}, t)$ is a diffusion stream that is proportional to the concentration gradient, $\vec{j}(\vec{r}, t) = -D(\vec{r}) \cdot \vec{\nabla} \cdot n(\vec{r}, t)$

$D(\vec{r})$ is diffusion coefficient. Followed by Fourier transformation and Maxwell-Garnet approximation, it can be reached to extract the following:

$$D'_{eff} = 1 + \frac{3}{\alpha + 2 \cdot \frac{1}{v} - 1} \quad (1)$$

where $D'_{eff} = \frac{D_{eff}}{D_M}$ and $\alpha = \frac{D_{inc}}{D_M}$, D'_{eff} is effective diffusion parameter, D_M is Maxwell diffusion, D_{inc} is an include particle diffusion. α is a physical factor in Green's function $\alpha = \frac{D_{inc}}{D_M}$.

Bruggeman approximation of a self-congruent has also solved (*) and found that:

$$D'_{eff} = \frac{1}{4} \left\{ (2 - \alpha) - 3(1 - \alpha)v \pm \sqrt{[(2 - \alpha) - 3(1 - \alpha)v]^2 + 8\alpha^2} \right\} \quad (2)$$

v is a volume fraction of components.

Using the equation (1) and (2) to calculate density ρ and heat Q of explosive mixture.

By adapting the procedures described in [18], the author has applied the Peng-Robinson equation of state to prove a

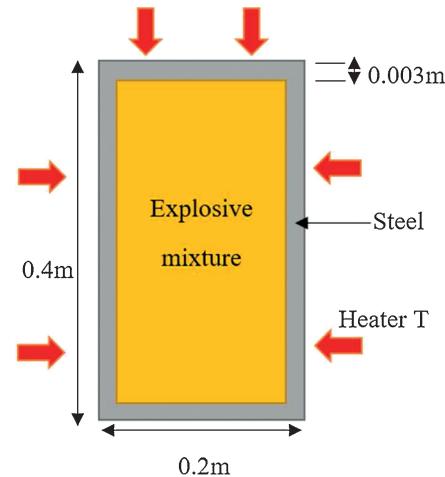


Figure 1. Schematic of thermal analysis (Cookoff test).

good representation of experimental volumetric, thermal and phase behavior data, either pure components or multicomponent mixtures. Following Ref. [22], the molar heat capacity c_p predictions given by $c_p = (\frac{\partial h}{\partial T})_P$ of a pure component as:

$$c_p = c_p^{ig} - 2RT \left(\frac{\partial \ln \phi(T, P)}{\partial T} \right)_P - RT^2 \left(\frac{\partial^2 \ln \phi(T, P)}{\partial T^2} \right)_P \quad (3)$$

Where h is the molar enthalpy, c_p^{ig} is the ideal gas molar heat capacity, ϕ is the fugacity coefficient, R is the ideal gas constant, T and P are temperature and pressure respectively. In the multicomponent mixtures state and all p phases of multiphase, the quality of chemical potentials at given P and T requires that the fugacity of component i in phase j satisfy:

$$f_i^1(T, P, z^1) = f_i^2(T, P, z^2) = \dots = f_i^l(T, P, z^l) = \dots = f_i^p(T, P, z^p) \quad \forall i \quad (4)$$

The reaction (4) is the fundamental condition for thermodynamic equilibrium solved in [18]. As cited the molar volume ϑ of multiphase p and multicomponent c at given (T, P) point:

$$\vartheta = RT \sum_{j=1}^p \chi_j^i \sum_{i=1}^c Z_j^i \left[\frac{1}{P} + \left(\frac{\partial \ln \phi_i^j}{\partial P} \right)_{T, z^j} \right] \quad (5)$$

Where Z_j^i and ϕ_i^j are the mole fraction and fugacity coefficient of component i in phase j , respectively. And the following equation presents the molar heat capacity c_p :

Table 1. Physic-chemical parameters obtained from Eq. (1) to (10) for explosive mixture.

Parameter	Thermal conductivity λ , [W/mK]	Specific heat c_p , [J/kg K]	Density ρ , [kg/cm ³]	Heat Q , [kJ/kg]	Activation energy E , [kJ/mole]	Pre-exp. factor A , [s ⁻¹]
Explosive mixture	1.967	1076.16	1360	1029.3	194	3.177×10^{-8}
Steel	49.56	474.98	7870	–	–	–

$$c_p = \sum_{j=1}^p \chi^j \sum_{i=1}^c Z_i^j \left[-2RT \left(\frac{\partial \ln \phi_i^j}{\partial T} \right)_{P,z^j} - RT^2 \left(\frac{\partial^2 \ln \phi_i^j}{\partial T^2} \right)_{P,z^j} + c_{p,i}^g \right] \quad (6)$$

Where $c_{p,i}^g$ is the ideal gas molar heat capacity of component i , χ^j is the mole fraction of the phase j .

Thermal conduction is one of five physical models who can describe a linear relationship between flux and driving force (negative gradient of a potential filed). Kapitza [23] was the first research observed the discontinuous temperature fields at metal-liquid helium interfaces. It is expected that the solid-liquid interfaces are more desirable than the solid-solid interfaces [24].

According to Kapitza resistance R_K , the continuity of fluxes and jumping of temperature at interfaces between species are extracted as:

$$\begin{aligned} -k_A \nabla T_A \cdot n &= -k_B \nabla T_B \cdot n = -k_C \nabla T_C \cdot n = \dots \\ &= -k_i \nabla T_i \cdot n = \frac{1}{R_K} (T_A - T_B - T_C - \dots T_i) \end{aligned} \quad (7)$$

Assume $\beta = \frac{\alpha}{k_m k_p}$ where α is the radius of the particles inclusion, k_m is the conductivity of the "matrix" or continuous phase, also k_p is the conductivity of the "inclusions" or particulate phase. The effective thermal conductivity is given by:

$$\frac{k_{eff}}{k_m} = \frac{2(1-\nu) + \beta[(1+2\nu) + 2k_m/k_p(1-\nu)]}{2+\nu+\beta[(1-\nu)+k_m/k_p(2+\nu)]} \quad (8)$$

ν : is being the volume fraction of the inclusion particles.

The model described in [24] revealed the relation of the transport properties on extremity film thickness.

The Kissinger method in [25] was used to predict and estimate the activation energies E , the latter is defined as the lowest energy that the reacting species must possess in order to undergo a specified reaction. The reaction rate of chemical transformation is expressed by an Arrhenius equation: $K = A \exp(-E_a/RT)$

Where A is the pre-exponential factor, E_a is the activation energy (energy per mole), and $R = 8.315 \text{ J K}^{-1} \text{ mol}^{-1}$ is the universal gas constant.

Activation energy in chemical processes is estimated by Kissinger from data obtained at several conditions [26]. Under the conditions cited in [25] Kissinger has demonstrated that:

$$\frac{\phi E_a}{RT_p^2} = -qA \exp\left(-\frac{E_a}{RT_p}\right) \text{ or} \quad (9)$$

$$\frac{d \ln\left(\frac{\phi}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)} = -\frac{E_a}{R} \quad (10)$$

The results gathered in the Table 1 are obtained since the resolution of previous reactions (1) to (10) for explosive mixture (RDX/IPN/Al/H₂SO₄).

As mentioned before, explosive mixture subjected to thermal effects (such as fire) or in higher environment temperature leading to destabilize the thermal stability of the system by rising temperature and releasing more heat, reaching the ignition temperature causes self-ignition and explosion of mixture. The relationship of heat generation rate and temperature is assured by Arrhenius equation $\ln k = -\frac{E_{mix}}{RT} + \ln A_{mix}$

The heat exchange with surrounding is expressed by the Frank-Kamenetskii relation: $\lambda \nabla^2 T$ where the exothermic intensity q''' (J/m³) of mixture can be expressed by:

$$q''' = \rho_{mix} Q_{mix} A_{mix} f(\alpha) \exp(-E_{mix}/RT) \quad (11)$$

$$\rho c \frac{\partial T}{\partial t} = \lambda \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{1}{r^2} \frac{\partial^2 T}{\partial \varphi^2} + \frac{\partial^2 T}{\partial z^2} \right) + q''' \quad (12)$$

The above formula can also be written as: $\rho c \frac{\partial T}{\partial t} = \lambda \nabla^2 T + q'''$

In the steady state of the system $\partial T / \partial t = 0$ indicating that the heat accumulation will continue rising to cause thermal explosion.

Using Frank-Kamenetskii model and assuming that $f(\alpha) = 1$ and the reaction order is zero, the reaction (11) can simplified as:

$$q''' = \rho_{mix} Q_{mix} A_{mix} \exp(-E_{mix}/RT) \quad (13)$$

3 Results and Discussion

According to the definition of SADT, this method is used in the determination of the lowest temperature at which a sample undergoes auto-accelerative decomposition, and determination of safety parameters associated with the packaging and transportation of materials. In the simulation process of explosive mixture, the initial temperature is

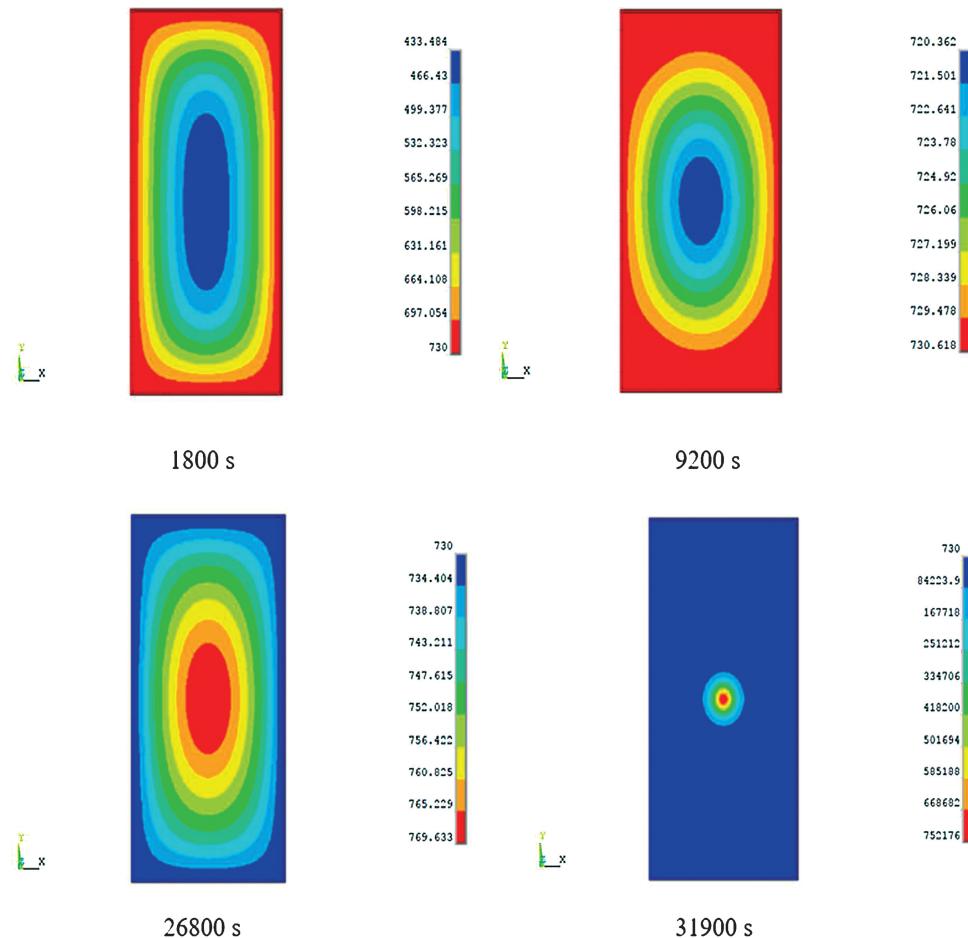


Figure 2. Temperature distribution over time of explosive mixture with 5 % of H₂SO₄ at ambient temperature 730 K.

293 K, this temperature is lower than heating process temperatures. By raising the ambient temperatures until getting the point of ignition (T, t)_{ig} making chemical and physical changes of sample. Figure 2 shows the temperature distribution of the mixture with 5 % of sulfuric acid over time at ambient temperature of 730 K in x-y direction.

As can be seen from Figure 2, when the high temperature is located in the surrounding edges of the sample at 1800 s, the heat is concentrated in this position then gradually progresses toward the lower temperature inside by conduction. 9200 s, the heating process continues to rise and the internal temperature of sample exposes to more heat. 26800 s, the high temperature region formed a ring temperature distribution according to heating graduation. The heating process continues to raise the temperature until the self-heating exothermic reaction occurs and eventually ignites in 31900 s.

Figure 3 shows the different ambient temperature effects on the mixture, it can be seen that the higher the ambient temperature the shorter ignition time figured out. In conclusion, the results obtained for ignition temperature of the mixture converges.

When the ambient temperature is below than 725 K, the mixture cannot reach the ignition temperature in 7 days (168 h), while the ambient temperature rises to 730 K the ignition of the mixture is carried out. The following self-acceleration decomposition temperatures are taken to determine the average of the maximum temperature of the unexposed and the minimum ignition temperature. Provoking the exothermic reaction of the mixture by raising ambient temperatures, the heat generated after the exothermic reaction is estimated to be fast.

The Figures 4–9 present the temperature distribution over time of explosive mixture with 10%, 15% and 20% H₂SO₄ respectively.

The results of SADT show the self-acceleration decomposition temperature is lower as ambient temperatures lower. The higher the ambient temperatures, the more amount of heat transferred to interior of the mixture and the shorter the ignition time. Evidently the acid rate in the explosive mixture greatly influences the determination of the ignition point (time and temperature) as can see in Figure 10.

This figure shows that the ignition temperature of mixture is inversely proportional with additional acid rate.

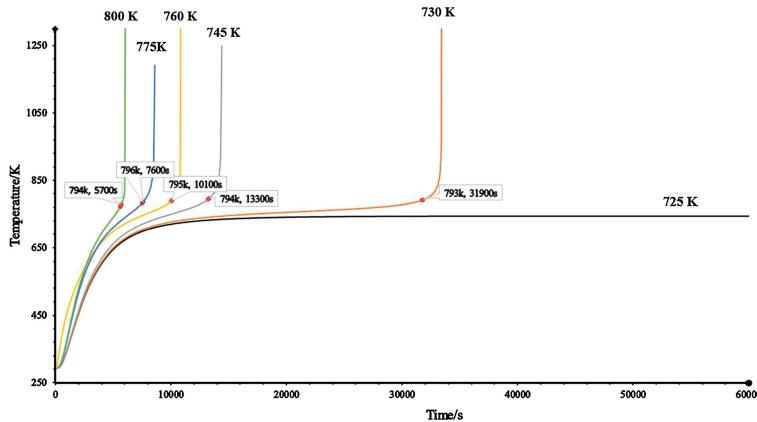


Figure 3. Different ambient temperatures effect on the mixture (with 5% H_2SO_4).

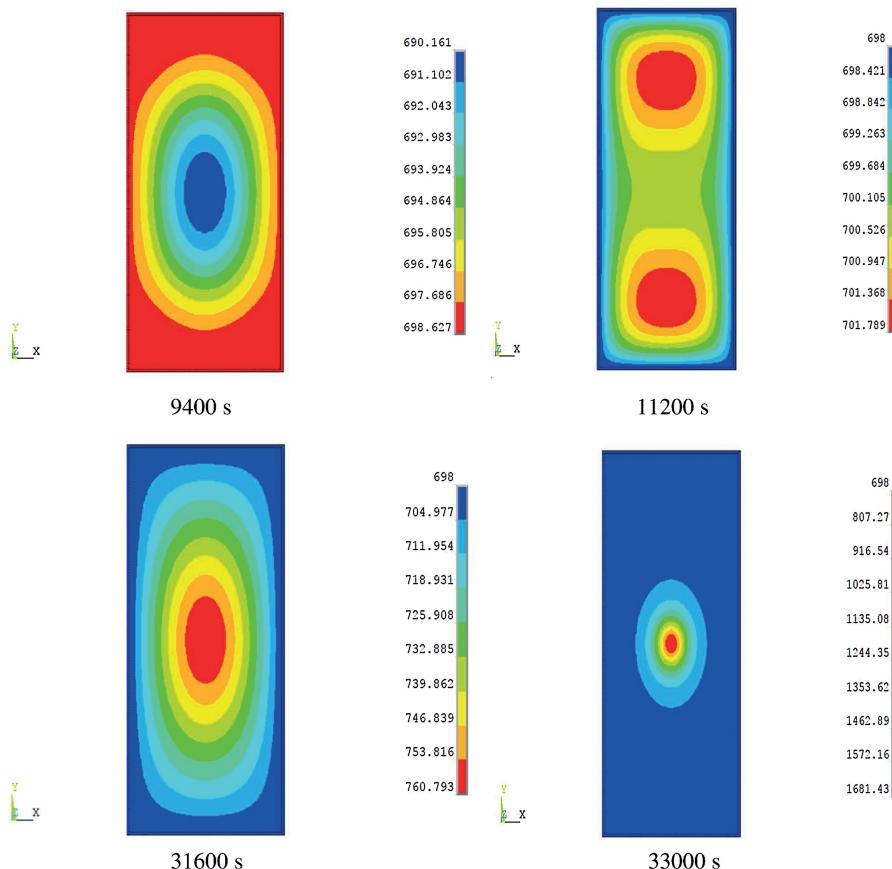


Figure 4. Temperature distribution over time of explosive mixture with 10% H_2SO_4 at ambient temperature 698 K.

For the purpose of studying ignition time and ignition position over time in x-y direction of the sample, we intentionally apply the different ambient temperatures on the upper walls surrounding the sample. Figure 11–14 respectively, for ambient temperatures of 745 K, 765 K, 770 K and 780 K in case of explosive mixture with 5% H_2SO_4 , show temperature distributions over time, ignition time and

ignition position in x-y direction. The figures display that the ignition position is close to border of confined vessel whenever the ambient temperature applied is high.

Figure 15 demonstrates different ambient temperature effects on the mixture in case of additional 5% H_2SO_4 .

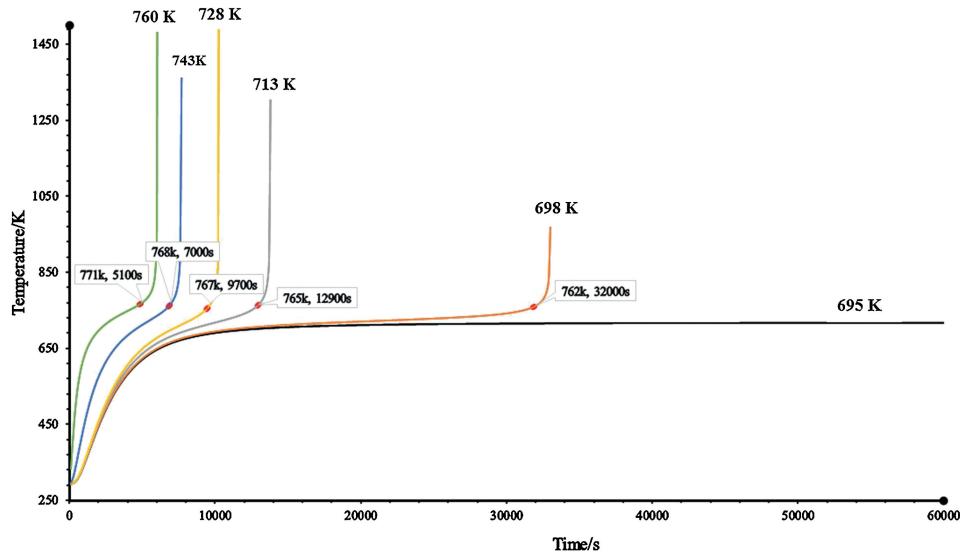


Figure 5. Different ambient temperatures effect on the mixture (with 10% H₂SO₄).

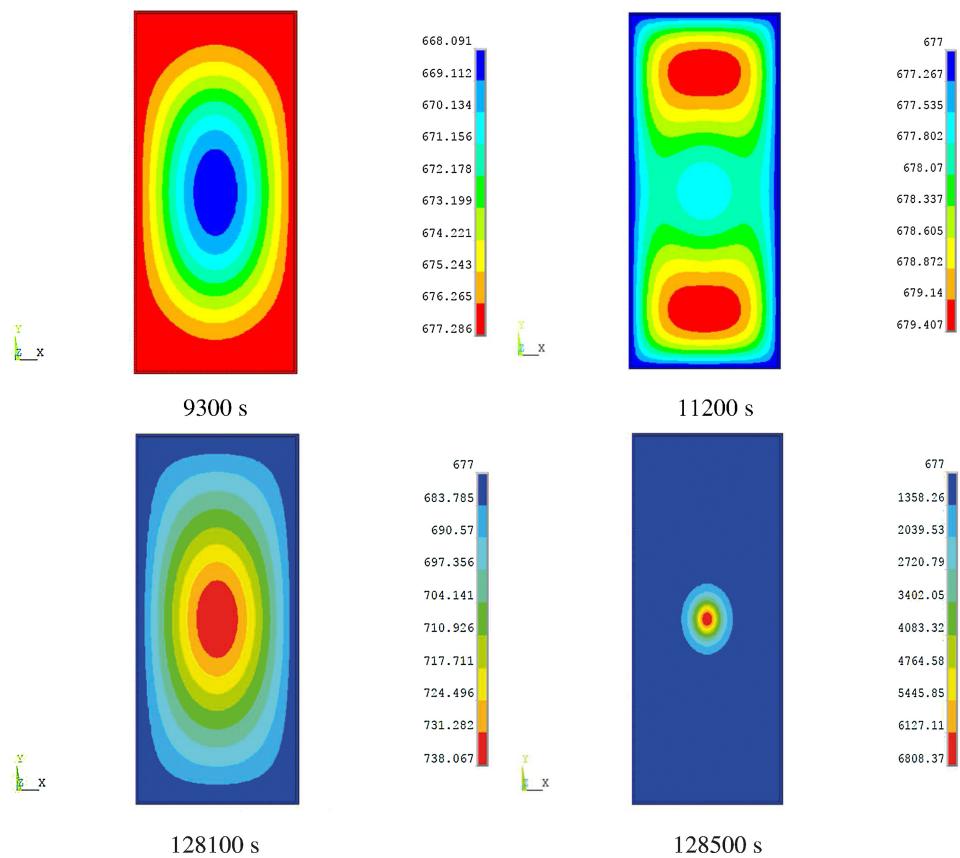


Figure 6. Temperature distribution over time of explosive mixture with 15% H₂SO₄ at ambient temperature 677 K.

The ignition time, ignition delay time, ignition temperature and ignition location of the explosive mixture at different ambient temperatures are listed in Table 2.

The ignition point of the mixture is situated in the center at low ambient temperature, it then moves up gradually with increasing ambient temperatures, and the ignition time is greatly reduced. The higher the ambient temper-

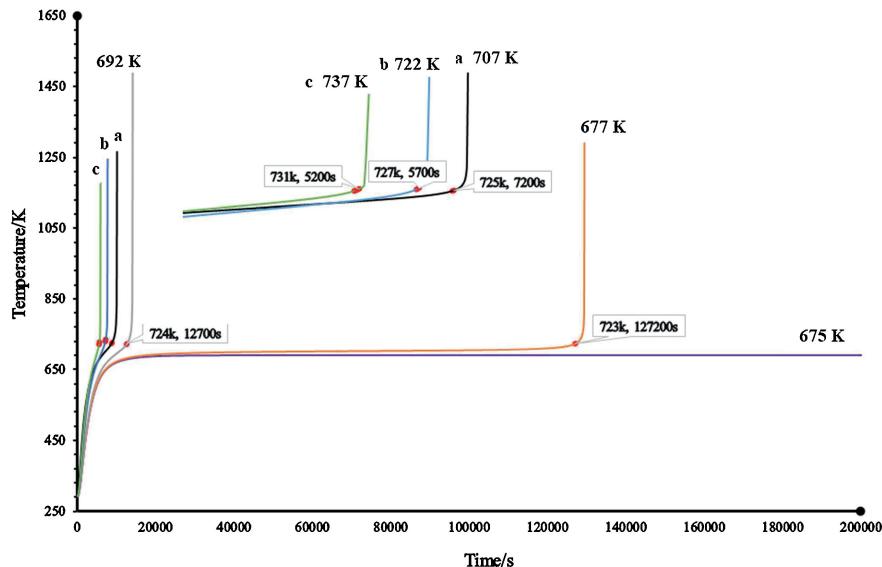


Figure 7. Different ambient temperatures effect on the mixture (with 15 % H_2SO_4).

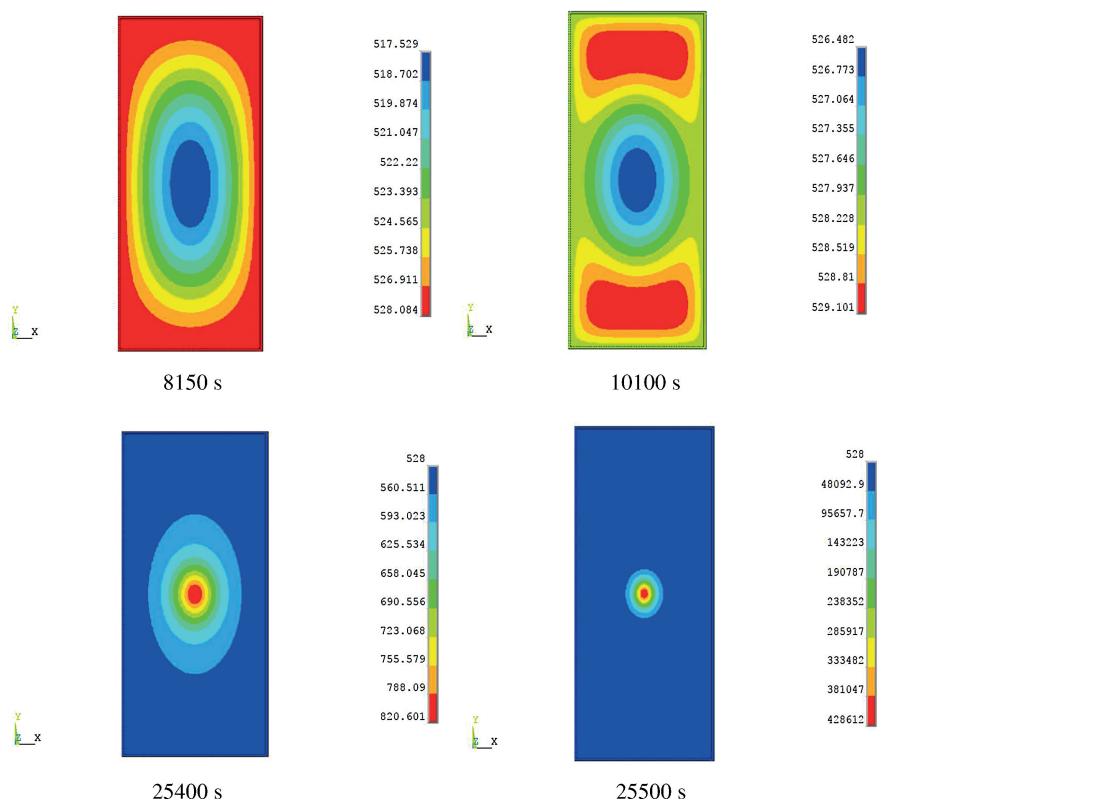


Figure 8. Temperature distribution over time of explosive mixture with 20 % H_2SO_4 at ambient temperature 528 K.

ature, the more amount of heat transferred to interior of the mixture and the shorter the ignition time.

4 Conclusions

The numerical simulation of explosive mixture containing solid-liquid phase has been studied by ANSYS software, as was figured out the physic-chemical characteristics of the

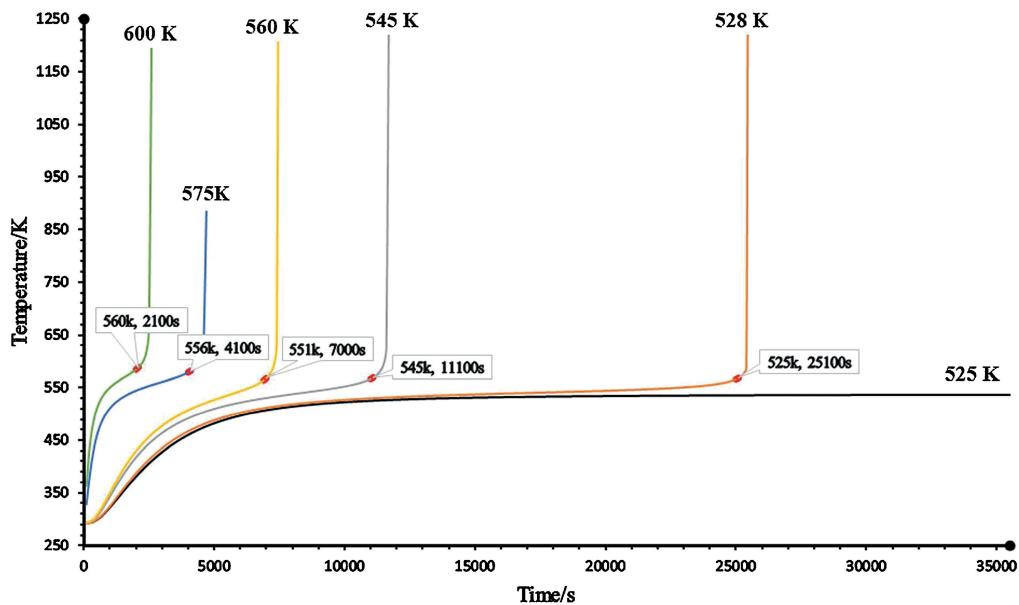


Figure 9. Different ambient temperatures effect on the mixture (with 20% H_2SO_4).

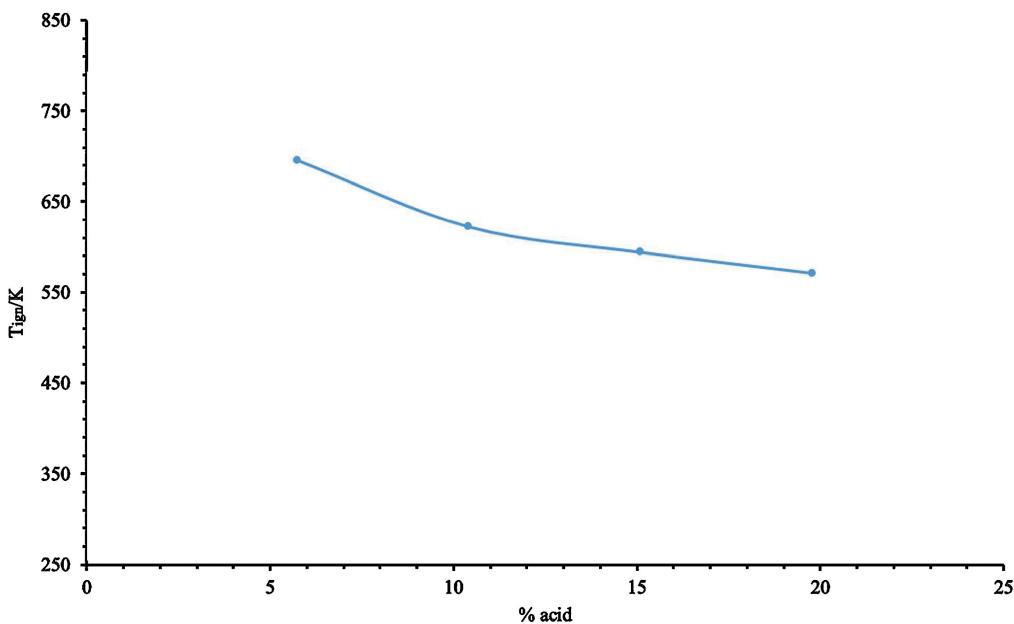


Figure 10. Effect of different rate of additional acid on the ignition temperature of the mixture.

Table 2. Ignition time and ignition position at different ambient temperatures.

Ambient temperature/K	Ignition time/s	Ignition delay time/s	Ignition temperature/K	Ignition position
745	53300	13300	794	center
765	42200	10000	795	0.1 m above the center
770	40100	7900	796	0.14 m above the center
780	36400	7700	797	0.16 m above the center

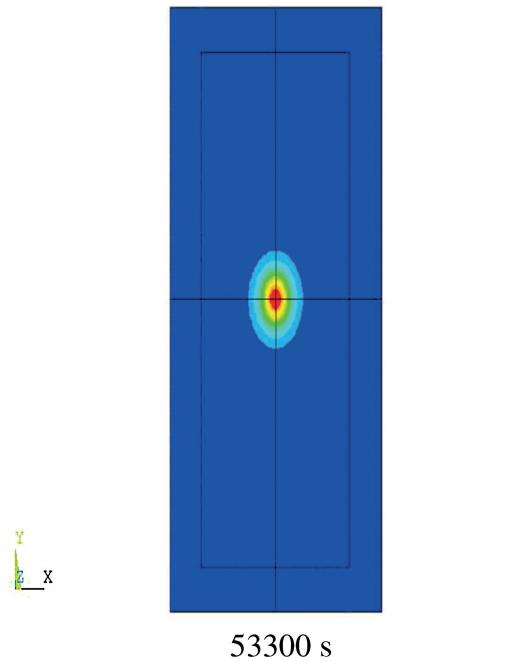


Figure 11. Ignition position and ignition time of the mixture with 5 % H_2SO_4 at 745 K

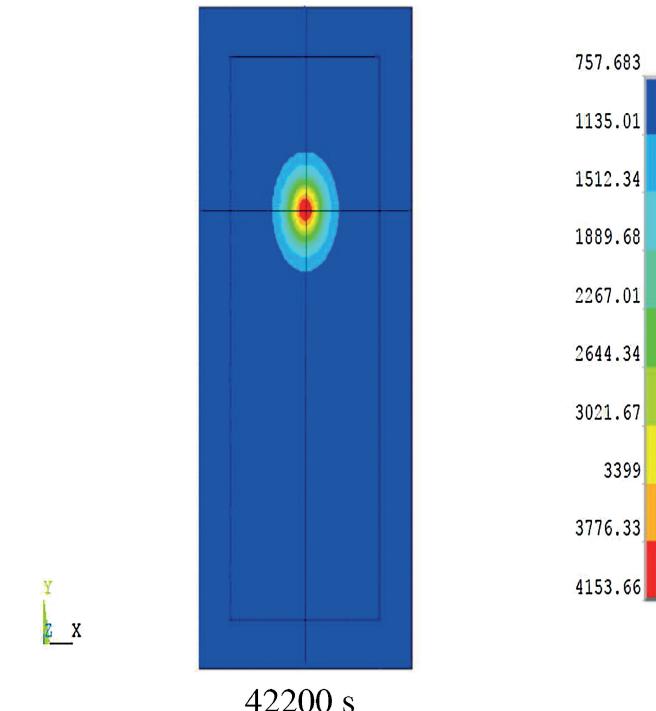


Figure 13. Ignition position and ignition time of the mixture with 5 % H_2SO_4 at 770 K.

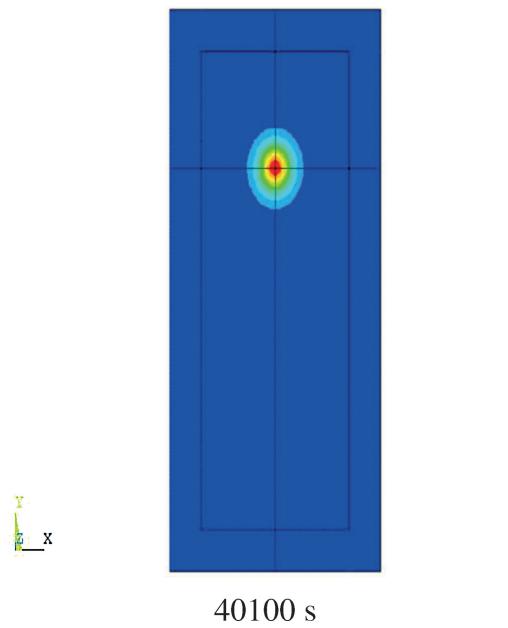


Figure 12. Ignition position and ignition time of the mixture with 5 % H_2SO_4 at 765 K.

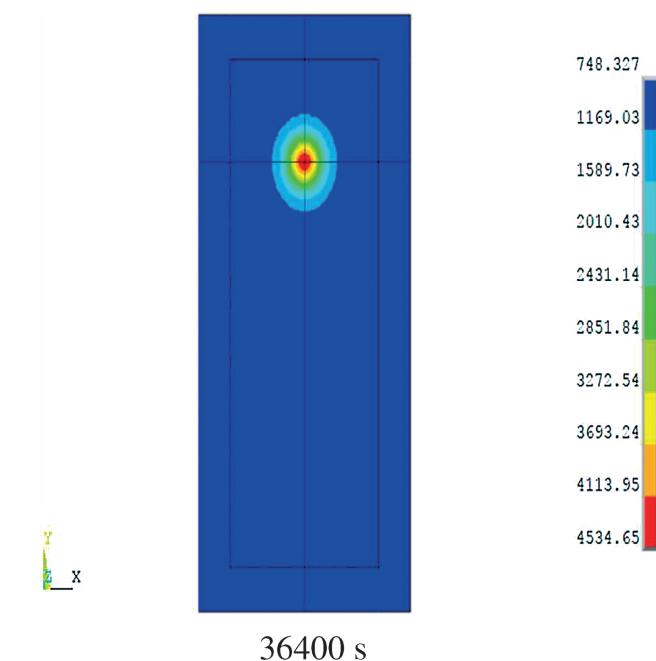


Figure 14. Ignition position and ignition time of the mixture with 5 % H_2SO_4 at 780 K.

mixture by equations of state (EOS) and Maxwell approximation to study the thermal stability of mixture (RDX/IPN/Al) with different additional rate of H_2SO_4 at different ambient temperatures. The heating process of mixture at different temperatures was progressed and the ignition temperatures were found that depend on different ambient

temperatures applied, and different rate of acid H_2SO_4 likewise the ignition delay time was determined at different conditions. The experimental results show the effect of dif-

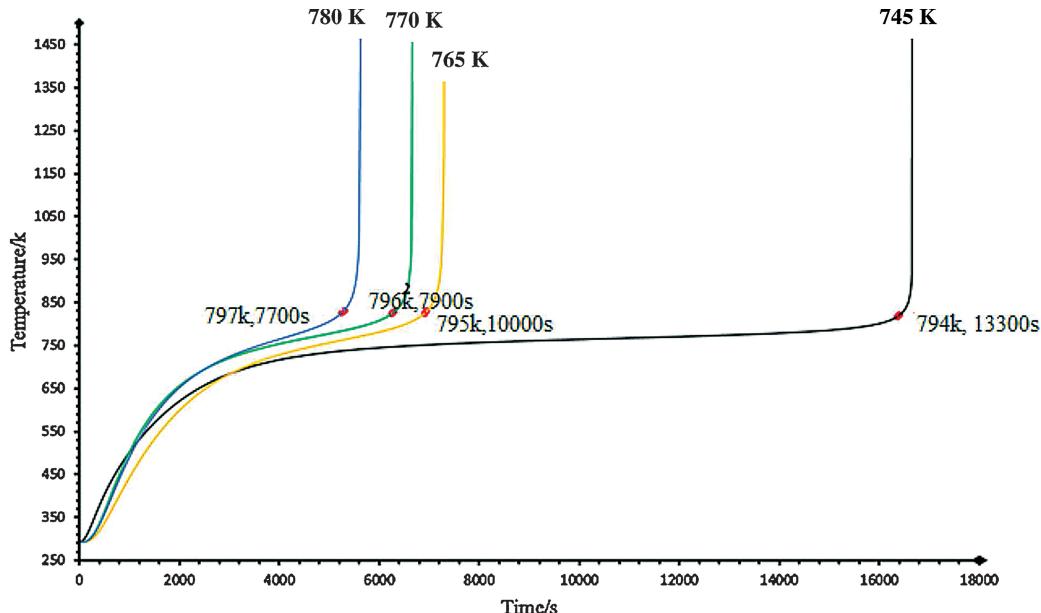


Figure 15. Different ambient temperatures effect on explosive mixture in case of 5 % H₂SO₄.

ferent ambient temperatures on ignition point position and self-acceleration decomposition temperature, with the increase of ambient temperature, the ignition delay time is shortened and the ignition position is changed. There is no significant effect of ambient conditions on ignition temperatures of mixture, otherwise there is a significant effect on ignition delay time and ignition position.

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