

ESTIMATION OF IGNITION TEMPERATURE FOR TWO KINDS OF ENERGETIC MATERIALS BY THERMAL ANALYSIS AND KINETIC EVALUATIONS

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Abstract. Some kind of energetic materials are substantially unstable and decompose slowly during their storage at room temperatures. Decomposition releases heat and gases which cause decomposition processes was accelerated. This process reduces performance and storage lifetime. Also because of released heat, this process could results to an unsafe situation like unexpected thermal explosion. Thermal analysis is an important tool for evaluation thermal hazard of energetic materials. Kinetic calculations are done by thermal analysis and kinetic parameters are obtained by thermal analysis. Determination of thermal explosion temperature is very important. Our study is based on two kinds of methods, first Invariant Kinetic Parameters (IKP) method such as Iso-kinetic Point and second method is based on Kissinger method. In this article for two kinds of propellants ignition temperatures (T_{ign}) were calculated from TGA experiments in some various heating rates. At final part, this temperature was validated by Differential Scanning Calorimetry (DSC) experiments at isothermal mode. Experimental results are shown that IKP method predicted more accurate results than Kissinger method.

Keywords: ignition, thermal analysis, energetic materials, isokinetic, invariant kinetic parameters

Introduction

Some kinds of energetic materials are thermodynamically unstable. Storing them always raises the question about which is the highest permitted temperature to meet (Herder et al., 2003; Janković & Mentus, 2008; Popescu et al., 2003). The propellants are one category of energetic materials which decompose slowly at ambient temperatures. The rate of decomposition increases exponentially with temperature and the products of decomposition are usually dissipated to the surroundings. Above certain temperatures, the dissipation process cannot take over all the produced energy and the explosive begins to self-heating. The lowest temperature at which self-heating was occurs, explosion initiation of the propellant is done. Thermal analysis

is useful tool for investigation of decomposition kinetic and interpretation of kinetic parameters. Evaluation of kinetic parameters from thermal analysis is based on two kinds of methods - model free and model fitting methods. Model free evaluation is independent of reaction model and is done by iso-conversional methods (Khawam & Flanagan, 2006; Lesnikovich et al., 1992). Model fitting methods are based on different kinds of reaction models (Khawam & Flanagan, 2006; Lesnikovich et al., 1992; Wang et al., 2015; Yan et al., 2013). A model is a theoretical-mathematical description of what occurs experimentally (Khawam & Flanagan, 2006). One of the model free methods is Kissinger. Harris (Lesnikovich et al., 1992; Wang et al., 2015; Yan et al., 2013; Vyazovkin et al., 2011) suggested using Kissinger method (Wang et al., 2015; Yan et al., 2013) for calculation of activation energy (E) and pre-exponential factor (A). Kissinger's method is described by:

$$\ln \frac{\beta}{T_p^2} = -\frac{E_a}{RT_p} + \ln \frac{AR}{E_a} \quad (1)$$

where $\beta = dT/dt$ is heating rate (K/min), T_p is peak temperature (K), E_a is the activation energy (J/mol) of thermal process, R is the gas constant (8.314 J/mol.K) and A is the pre-exponential factor (s^{-1}). By plotting $\ln \frac{\beta}{T_p^2}$ vs. $\frac{1}{T_p}$, the slope was giving E_a and the intercept was giving A . At zero heating rate, ratio $E\beta/RT^2$ approximately equal to 0.1 so the peak value for zero heating rate are obtained by (Lesnikovich et al., 1992):

$$T = -\frac{E/R}{\ln A - \ln 0.1} \quad (2)$$

This temperature is stated to be the ignition temperature (T_{ign}) (Lesnikovich et al., 1992).

Another method is based on isokinetic method. Like in all the kinetic studies the empirical relationship of the reaction rate for over-all process after substituting time with temperature (Vyazovkin et al., 2011):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) \exp\left(\frac{-E_a}{RT^2}\right) \quad (3)$$

where α is the conversion degree or reaction progress, and $f(\alpha)$ is the kinetic function. The reaction progress in each time (t_i) or each temperature (T_i) for TGA

experiment is calculated by Eq (4) (Surender et al., 2013; Koga et al., 2013; Rodnit et al., 2015):

$$\alpha = \frac{(m_i - m_0)}{(m_f - m_0)} \quad (4)$$

The total experimental data were obtained from a non-isothermal experiment can be then summed up as:

$$\ln \left[\left[\frac{\frac{d\alpha}{dT}}{f(\alpha)} \right] \beta_j \right] = \ln A - \frac{E_\alpha/R}{(T_i)_j} \quad (5)$$

By plotting $\ln \left[\left[\frac{\frac{d\alpha}{dT}}{f(\alpha)} \right] \beta_j \right] \ln \left[\left[\frac{\frac{d\alpha}{dT}}{f(\alpha)} \right] \beta_j \right]$ versus $\frac{1}{T_i T_i}$ for different kind of mod-

els, the slop and intercept give E and A at this model respectively. Reaction models which were used, listed in Table 1.

Table 1. Reaction models used for calculations

f (α)	Reaction model	Description
2α ^{1/2}	P2	Power law
3α ^{2/3}	P3	
4α ^{3/4}	P4	
2 (1 - α) [-ln (1 - α)] ^{1/2}	A2	Avrami–Erofeev (1D, 2D, 3D)
3 (1 - α) [-ln (1 - α)] ^{2/3}	A3	
4 (1 - α) [-ln (1 - α)] ^{3/4}	A4	
α (1 - α)	B1	Prout–Tompkins
1 / 2α	D1	Diffusion (1D, 2D, 3D, 4D)
[-ln (1 - α)] - 1	D2	
[3 (1 - α) ^{2/3}] / [2 (1 - (1 - α) ^{1/3})]	D3	
3 / (2 [(1 - α) ^{-1/3} - 1])	D4	
1	F0	First order, F1

By using the experimental data (da/dT), and various kinetic functions f (α) for each heating rate β_j, one may plot a straight line. The group of all these straight

lines forms, (Wang et al., 2015; Yan et al., 2013; Vyazovkin et al., 2011), a pencil of lines in the plane (X,Y) (Wang et al., 2015; Yan et al., 2013; Vyazovkin et al., 2011). The crossing point (or better saying crossing region) has coordinates that are invariant for all the straight lines which was plotted in that plane. These are called the invariant values of the kinetic parameters E and A, as they are not depending on the choice of the kinetic function any longer. By extrapolating to zero heating rate T_{ign} is determined (Renet et al., 2015; Vyazovkin et al., 2001).

Experimental

Two kinds of energetic material (Sample A and Sample B) were used for this study. In table 2, chemical composition of sample A and B are shown.

Table 2. Chemical composition of energetic materials

	NC	NG	DBP	2NDPA
mass%				
Sample A	95	-	3.5	1.5
Sample B	58.6	24.5	15.3	1.6

Nitrocellulose (NC) and Nitroglycerine (NG) are main components in gun propellants. Stabilizers such as 2-Nitro diphenylamine (2NDPA) are also added to improve stability of propellant and avoid autocatalytic decomposition of propellants. Di-butyl phthalate (DBP) is also added as plasticizer.

Thermal Gravimetry Analysis (TGA) is done by METTLER TOLLEDO TGA/SDTA 851 e1600 LF/MT5. Temperature range was (25°C-300°C). For Sample A, heating rates are 10, 15, 20, 25 and 30 K/min. For Sample B heating rates are 5, 10, 15 K/min. Differential Scanning Calorimetry (DSC) analysis was done by Mettler TOLLEDO DSC 1 instrument. Both DSC and TGA experiments were done under 50 ml/min flow rate of nitrogen as purge gas to remove evolved gasses from samples during experiment period.

Results

In Figs. 1 and 2 TGA curves for samples A and B are shown respectively. As shown in Fig. 1, thermal decomposition started from temperature $T=180^{\circ}\text{C}$ and rapid mass loss is occurred between (185 -210°C). For sample B mass loss was occurred in two stages. First stage was up to 150°C and for NG evaporation. Second stage is started from 150°C and for thermal decomposition of NC and NG cf. Fig.2.

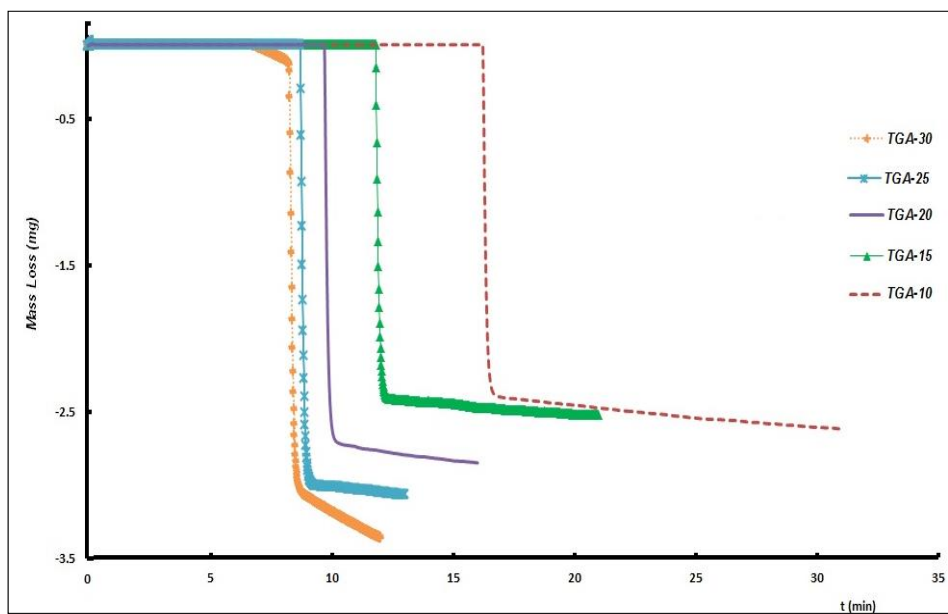


Fig. 1. TGA curves for sample A

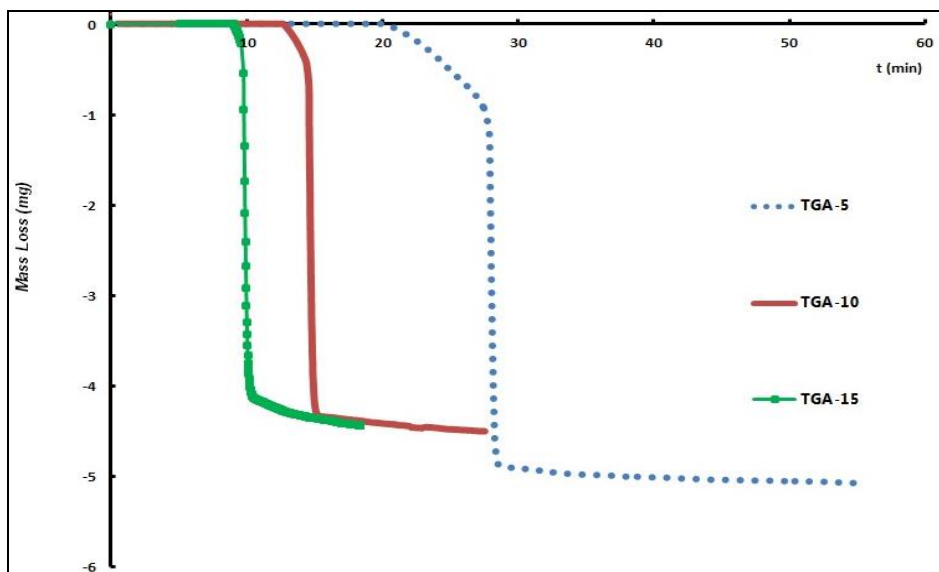


Fig. 2. TGA curves for sample B

In Figs. 3 and 4 the reaction progress curves which were resulted from TGA experiments for samples A and B with different heating rates are shown respectively. The vertical axis is reaction progress and the horizontal axis is time (min).

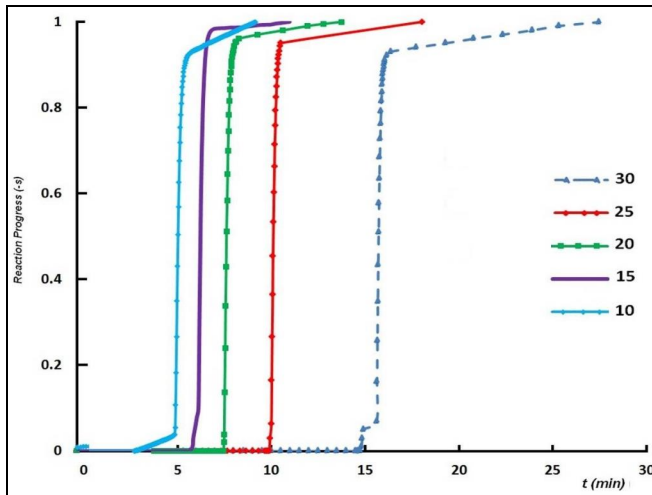


Fig. 3. Reaction progress curves for the Sample A

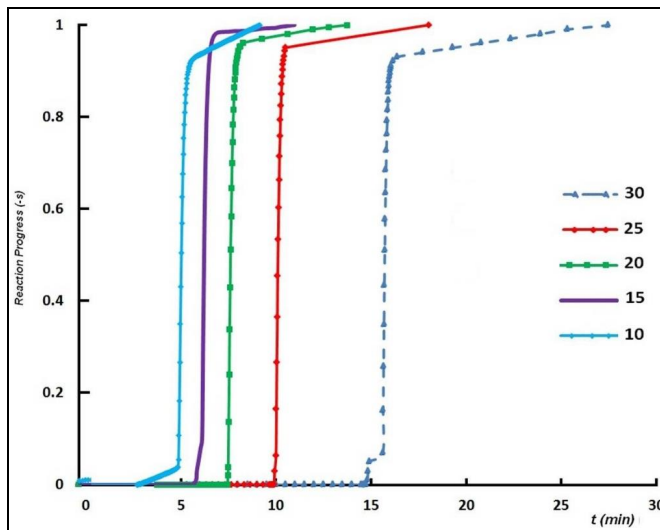


Fig.4. Reaction progress curves for the Sample B

In Figs. 5 and 6 the reaction rate curves for sample A and B are shown. By increasing β , peak temperature shifted to higher temperature.

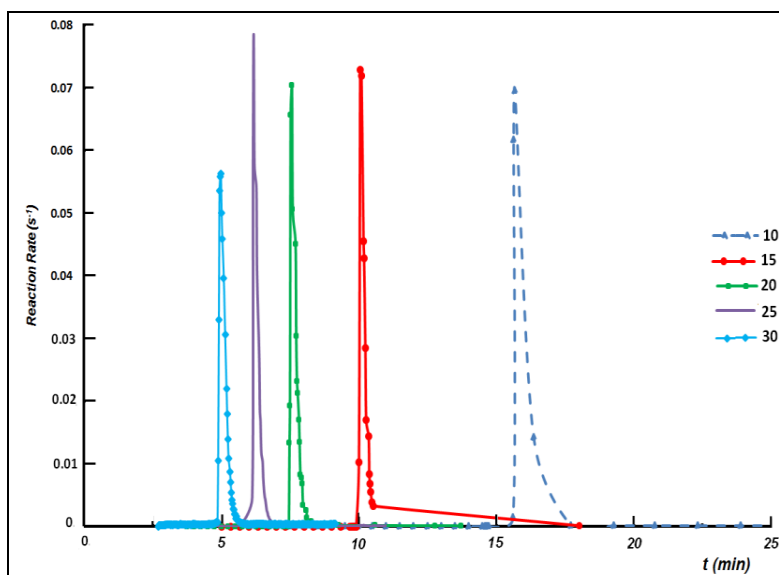


Fig. 5. Reaction rate curves for sample A

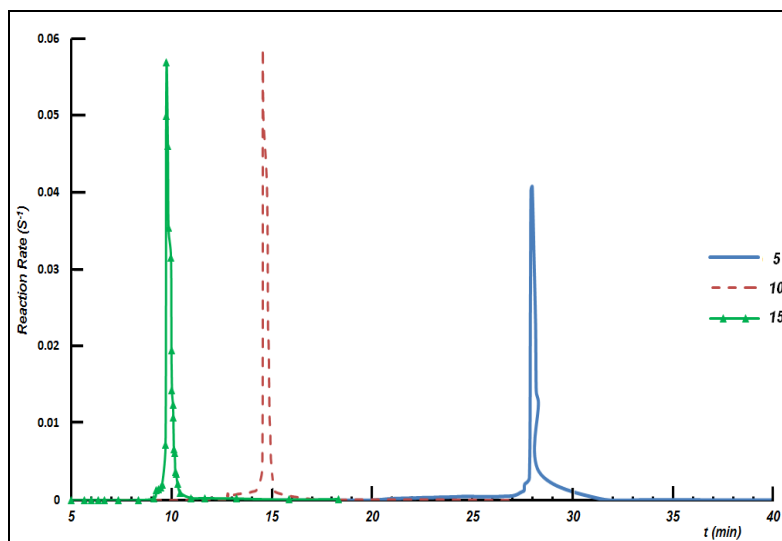


Fig. 6. Reaction rate curves for sample B

As shown in Figs. 3 and 4, and described above, for sample A, reaction progress is rapidly increased between (185 – 210°C). In this temperature range thermal decomposition occurred spontaneously. Shape of reaction progress curves, are shown that reaction pass through autocatalytic model. An autocatalytic reaction is a chemical reaction where a product also acts as catalyst (Herder et al., 2003). In such a reaction the observed rate of the reaction is often found to increase with conversion.

In the case of an autocatalytic decomposition an acceleration of the reaction with increasing conversion is observed (Fig. 5).

The corresponding reaction rate passes through a maximum and then decreases again. Furthermore, the acceleration period is often preceded by an induction period where no thermal signal and therefore no noticeable thermal conversion can be observed.

In Table 3, peak temperatures for DTG curves of sample A and B are shown.

Table 3. Peak temperatures for DTG curves of sample A and B

Sample B		Sample A	
Peak Temperatures (°C)	Heating rate (K/min)	Peak Temperatures (°C)	Heating rate (K/min)
164.925	5	175.58	10
171.275	10	176.23	15
173.23	15	177.28	20
		179.37	25
		181.18	30

The peak temperatures for sample B is lower than sample A and these phenomena are related to different composition between these two samples.

In Figs. 7 and 8 plot of $\ln \frac{\beta}{T_p^2}$ versus $\frac{1}{T_p}$ for sample A and B respectively are shown. In each curve a linear trendline is fitted.

The regression coefficient (R^2) for linear fitted trendline is about 0.8695 and 0.9759 for plots of sample A and B respectively. Kinetic parameters (E_a) and T_{ign} can calculate by using Eqs. (1) – (2).

Calculated activation energy (E_a) and pre exponential factor (A) and T_{ign} for both samples A and B by Kissinger method is shown in Table 4.

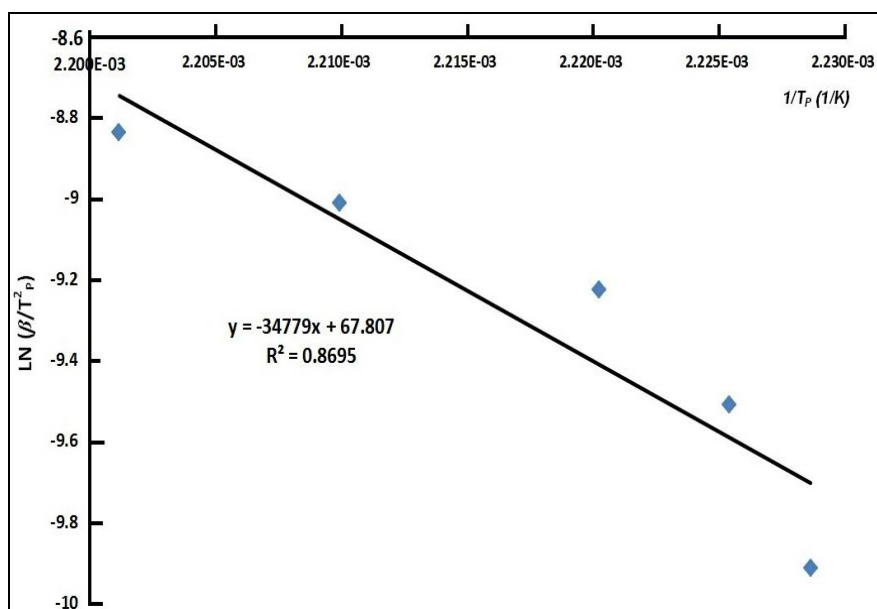


Fig. 7. Plot of $\text{Ln } (\beta/T_p^2)$ versus $1/T_p$ for sample A

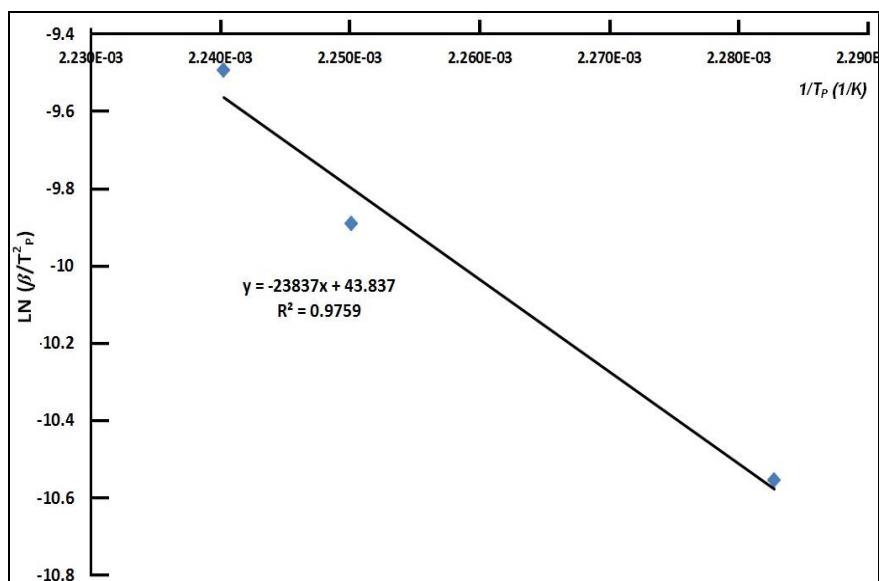


Fig. 8. Plot of $\text{Ln } (\beta/T_p^2)$ versus $1/T_p$ for sample B

Table 4. Calculated Kinetic parameters and T_{ign} for both samples A and B by Kissinger method

Kissinger Method	Sample A	Sample B
E_a (kJ/mol)	289.15	198.18
A (s^{-1})	1.01 E+34	2.6 E+23
T_{ign} ($^{\circ}C$)	158.37	150.86

For sample A and B calculated isokinetic temperatures at various heating rates are shown in Table 5.

Table 5. Calculated Kinetic parameters and T_{ign} ($^{\circ}C$) for both samples A and B by isokinetic method

Sample A	$\beta(^{\circ}C/min)$	T_{iso} ($^{\circ}C$)
	10	180.01
	15	182.51
	20	184.62
	25	187.21
	30	190.10
	.	.
	.	.
Sample B	0	174.93
	$\beta(^{\circ}C/min)$	T_{iso} ($^{\circ}C$)
	5	165.81
	10	170.3
	15	173.11
	.	.
	ш.	.
	0	162.43

According to Table 3 results, calculated T_{ign} for sample A is about 7.5 ($^{\circ}C$) higher than sample B.

Now T_{ign} for samples A and B is calculated by Isokinetic Method.

In Figs. 9 and 10 plot of Isokinetic Temperature (T_{iso}) versus heating rate for sample A and B respectively are shown. In each curve a linear trendline is fitted.

By extrapolating linear fitted trendline for Zero heating rate, T_{ign} is calculated and shown in table 4. For sample A and B extrapolated values of T_{ign} are 174.93 $^{\circ}C$ and 162.43 $^{\circ}C$ respectively.

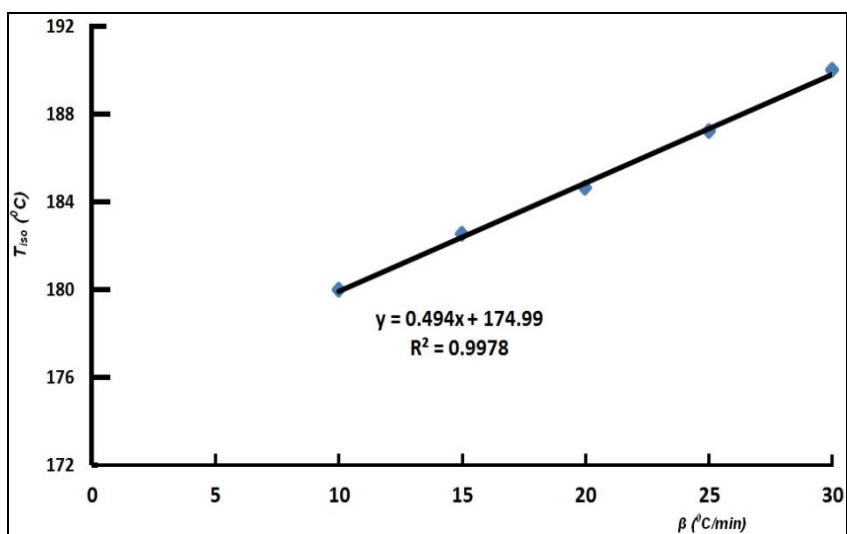


Fig. 9. Plot of Isokinetic Temperature (T_{iso}) versus heating rate for sample A

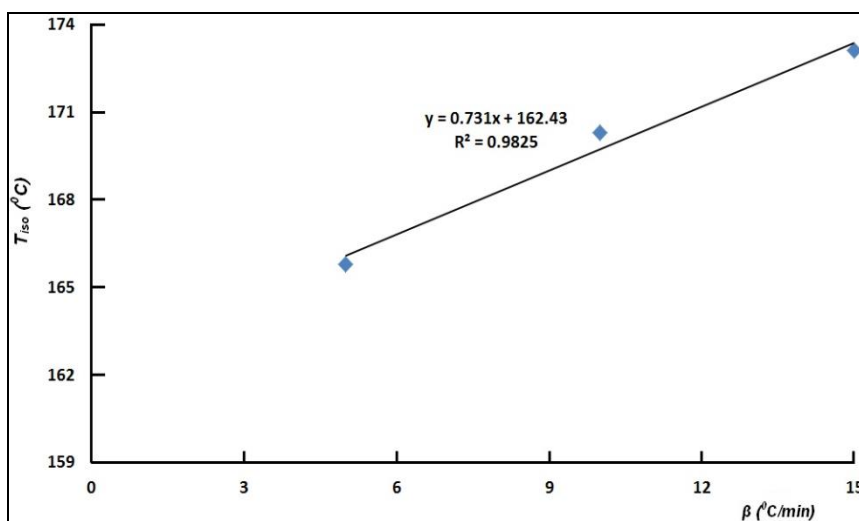
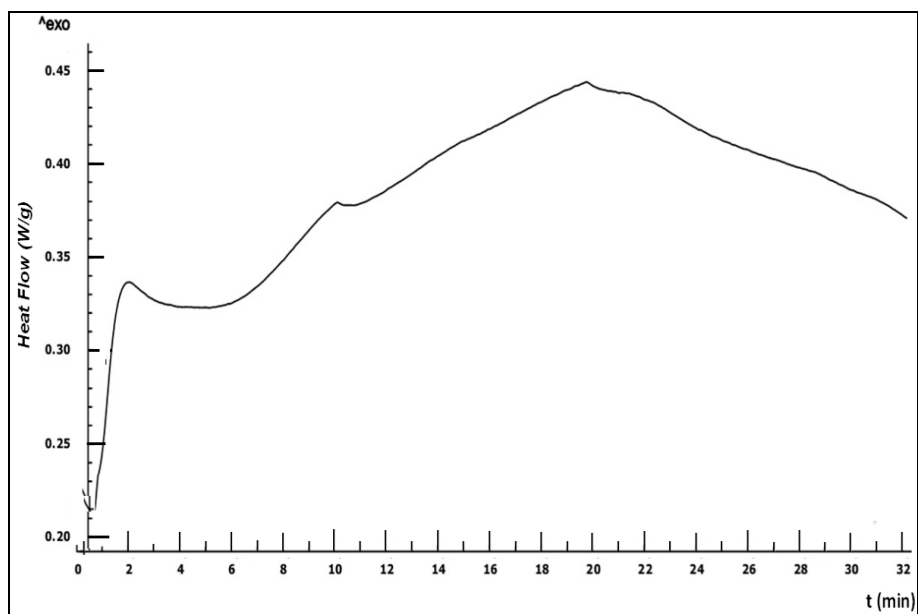
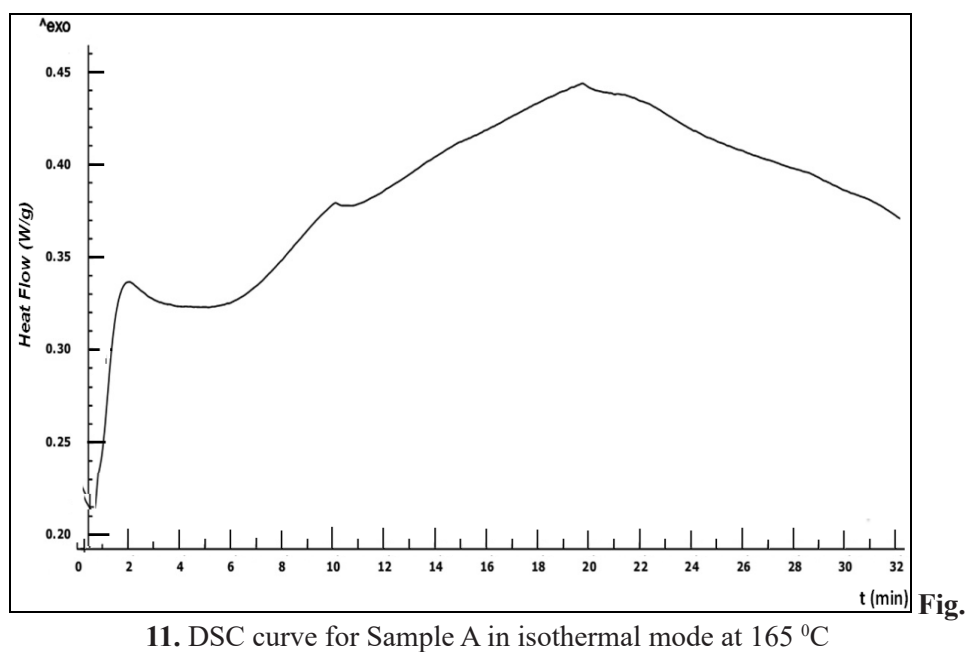


Fig. 10. Plot of Isokinetic Temperature (T_{iso}) versus heating rate for sample B

Data validation

For sample A and B sets of Differential Scanning Calorimetry DSC analysis is done. For Sample A, isothermal DSC measurements are done in three temperatures 165 $^{\circ}\text{C}$, 170 $^{\circ}\text{C}$ and 175 $^{\circ}\text{C}$. In Figs.11 to 13 DSC curves for sample A are shown.



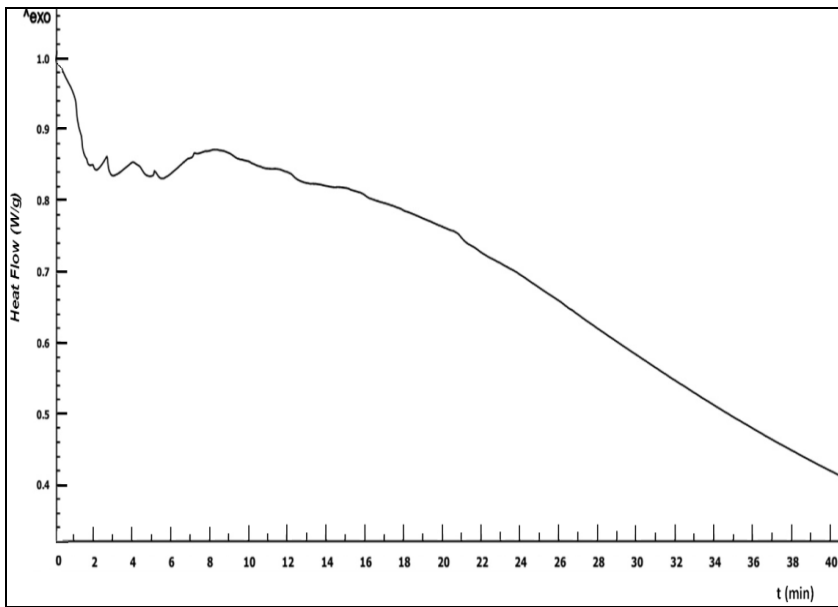


Fig. 13. DSC curve for Sample A in isothermal mode at 175 °C

For sample B isothermal DSC measurements are done in two temperatures 157°C and 162 °C. In Figs. 14 to 15 DSC curves for sample B are shown.

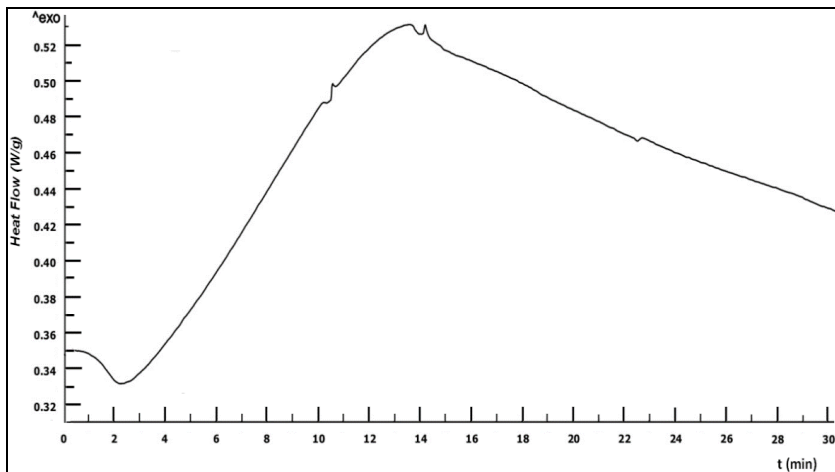


Fig. 14. DSC curve for Sample B in isothermal mode at 157°C

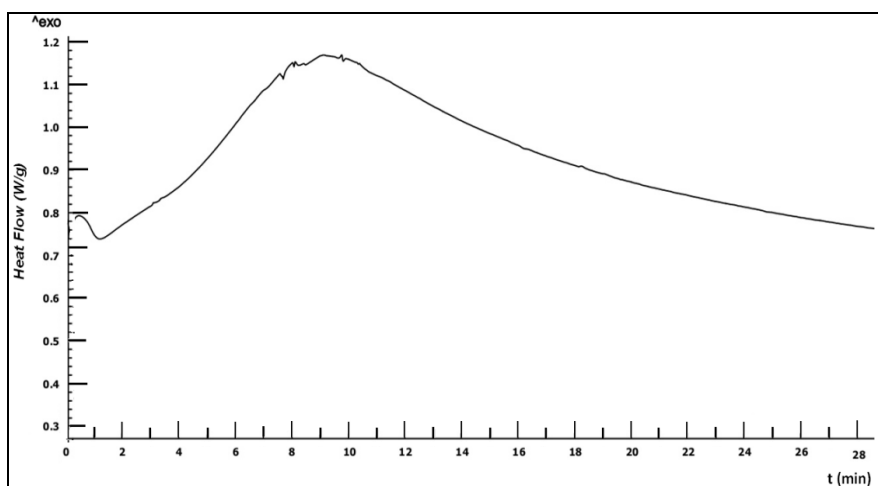


Fig. 15. DSC curve for Sample B in isothermal mode at 162°C

The time which is spent and the reaction after that is started is called reaction induction period. As shown in Figs. 11 to 13, reaction induction period is decreased from 6 minute to zero minute by increasing isothermal temperature from 165°C to 175°C. So T_{ign} is between 165°C to 175°C.

As shown in Figs. 14 and 15 at 162°C, after about one minutes the decomposition reaction is started. Reaction induction period at 162°C is about 1 minute and at 157°C is about 2.5 minute. So it can to conclude that calculated autoignition temperature from isokinetic model method does not have significant difference. In Table 6 experimental T_{ign} temperatures are shown.

Table 6. Experimental values for T_{ign}

Sample	ignition temperatures (T_{ign}) (°C)
Sample A	$170 < T_{ign} < 175$
Sample B	$T_{ign} \geq 162$

In Table 7 experimental and calculated T_{ign} temperatures are shown.

Table 7. Experimental and calculated T_{ign}

	Sample A	Sample B
Method	T_{ign} (°C)	T_{ign} (°C)
Kissinger method (°C)	158.37	150.86
Isokinetic point (°C)	174.93	162.43
Experimental (°C)	$170 < T_{ign} < 175$	$T_{ign} \geq 162$

Conclusion

T_{ign} is an important parameter for evaluation of thermal hazard of energetic materials. It depends on decomposition kinetic of energetic material. TGA experiments were done in various heating rate for two kinds of propellants. T_{ign} was calculated by two different kinetic methods. First method is based on Kissinger method. By this method T_{ign} temperature is calculated. Second method is based on Invariant Kinetic Parameters (IKP) method such as isokinetic point. In this method, 12 reaction models are used for calculation of isokinetic point. By using this point in various heating rate, T_{ign} are calculated by this method. At last DSC experiments were done for these two kinds of propellants. Results are shown that experimental T_{ign} are very close to results which were calculated by IKP method. for sample A, percent of difference was about 0.04% and for sample B is about 0.26%

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