Thermal decomposition and kinetic evaluation of decanted 2,4,6-trinitrotoluene (TNT) for reutilization as composite material

M. F. Ahmad, A. Hussain and A. Q. Malik
School of Chemical and Materials Engineering, National University of Sciences and Technology Islamabad-44000, Pakistan
E-mail: farooqahmed@scme.nust.edu.pk

Abstract. Use of energetic materials has long been considered for only military purposes. However, it is very recent that their practical applications in wide range of commercial fields such as mining, road building, under water blasting and rocket propulsion system have been considered. About 5mg of 2,4,6-trinitrotoluene (TNT) in serviceable (Svc) as well as unserviceable (Unsvc) form were used for their thermal decomposition and kinetic parameters investigation. Thermogravimetric/ differential thermal analysis (TG/DTA), X-ray diffraction (XRD) and Scanning electron microscope (SEM) were used to characterize two types of TNT. Arrhenius kinetic parameters like activation energy ($E$) and enthalpy ($\Delta H$) of both TNT samples were determined using TG curves with the help of Horowitz and Metzger method. Simultaneously, thermal decomposition range was evaluated from DTA curves. Distinct diffraction peaks showing crystalline nature were obtained from XRD analysis. SEM results indicated that Unsvc TNT contained a variety of defects like cracks and porosity. Similarly, it is observed that thermal as well as kinetic behavior of both TNT samples vary to a great extent. Likewise, a prominent change in the activation energies ($E$) of both samples is observed. This in-depth study provides a way forward in finding solutions for the safe reutilization of decanted TNT.

1. Introduction
2,4,6-trinitrotoluene (TNT), being one of the most widely used military high explosives, has extensively been investigated for its thermal behaviour and decomposition kinetics. Since 1870, it is available in pure form as an explosive substance for use in various ways [1-4]. TNT forms part of aromatic nitro compounds with three nitro groups attached to carbon atoms. Out of all constitutional isomers of TNT, only $\alpha$-TNT also known as Tolite or Trotyl, is used for military grades with 99% of purity and a small fraction of impurity of ~1% mainly due to 2,4-DNT. A huge quantity of unwanted and unserviceable (Unsvc) munitions containing TNT has been discarded through conventional disposal techniques i.e. Open Burn Open Detonation (OB/OD), incineration, demolition, etc. after WW1 [5-6]. Since all of these methods produced adverse climatic and health hazards, any significant move towards the safest disposal of these Unsvc energetic materials is well appreciated all around the globe. In this paper, structural analysis as well as kinetic study of TNT thermo chemical decomposition has been carried out to examine its feasibility for further use. About 5mg of decanted TNT Unsvc has been used for comparative analysis with serviceable (Svc) TNT. Both the samples were investigated for their thermal and kinetic behaviour with the help of available techniques such as
Thermo gravimetric/differential thermal analysis (TG/DTA), X-ray diffraction (XRD) and Scanning electron microscope (SEM). Samples for this study were arranged through defence organizations. TG curves were used for the determination of Arrhenius kinetic parameters, like activation energy ($E$) and enthalpy ($\Delta H$) of both Svc and Unsvc TNT samples using Horowitz and Metzger method. Simultaneously, weight loss/gain and thermal decomposition range were evaluated from TG/DTA curves. For structural investigation of the samples, XRD was used which gave distinct diffraction peaks showing crystalline nature. Similarly, molecular structures of both the samples were examined through SEM. SEM analysis revealed a variety of defects present in Decanted TNT Unsvc sample such as voids, porosity, cracks, etc. Interestingly, it was observed that thermal as well as kinetic behavior of both TNT samples vary to a great extent, keeping in view various aspects such as shelf life, environment conditions, manufacturing, filling and formulation processes. Additionally, the decomposition temperature of Decanted TNT Unsvc sample increased substantially. A prominent change in activation energies ($E$) of both the samples under investigation was also observed.

2. Experimental procedure

2.1 Material and methods

TNT Svc sample was arranged from National Defence Organizations. However, Decanted TNT Unsvc sample was recovered from Unsvc munitions containing TNT through detailed decanting plant available in Pakistan army institute. In this process, hot water spray was injected through shell nozzle resulting into melting of TNT. Decanted TNT Unsvc sample was then collected and dried in open air for subsequent use in chemical laboratory.

2.2 Analytical techniques

Samples were analysed through various instrumental techniques. Multiple tests were conducted for the identification of various parameters such as thermochemical decomposition, structural analysis and kinetic evaluation. Instruments used in the present work include SEM-6490A JEOL made in Japan, TG/DTA-Perkin Elmer Model Pyris Diamond and XRD- made by Theta-Theta Toe, Germany.

2.2.1 SEM characterization

SEM is used for the extraction of structural and chemical information of both the samples under investigation through topographic imaging, e.g. fracture surface, cracks etc. SEM version 6490A JEOL (made in Japan) was used for the microscopic study of samples from various dimensions. Different electron beam energies were applied to obtain maximum output from the SEM images with magnifications ranging from 10000X to 1500X.

2.2.2 TG/DTA characterization

Wide utility of TG/DTA makes it one of the most versatile tools for the verification and thermal cum kinetic studies of material sample using a controlled temperature environment. In order to obtain thermal data about the samples, Perkin Elmer Model Pyris Diamond TG/DTA instrument was used. Nitrogen ($N_2$) gas was used as purge gas for maintaining inert environment for the samples. A heating rate of 10°C/min was kept constant throughout the analysis along with temperatures ranging between room temperature to 340°C.

2.2.3 XRD analysis

XRD analysis, being a widely used method for the crystallographic identification of material sample, was selected to identify crystal structure of both the samples. XRD analysis gave useful information about the samples which includes their crystalline phases, atomic arrangement, orientation of a single crystal, lattice parameters, density etc.
2.3 Kinetic Method

Literature finds various methods for the measurement of activation energy \( (E) \) and enthalpy \( (\Delta H) \) of explosive material. Few of the most commonly known methods are; Doyle method, Coats and Redfern method, Horowitz and Metzger method, Free man and Carroll method, Newkirt method. Although all of these methods are quite accurate and reliable in use, however, present study for the calculation of activation energy \( (E) \) and enthalpy \( (\Delta H) \) of TNT explosive samples was carried out with help of Horowitz and Metzger Method using a Curve Fitting Program.

3. Results and discussions

3.1 SEM analysis

3.1.1 Decanted TNT unsvc

For an in-depth analysis of Decanted TNT Unsvec, about 5mg of sample was examined at 5kV electron beam energy and with various magnifications through SEM. All three images at different magnifications show an irregular dough shaped morphology with no definite orientation of TNT sample Figure 1. A predictable number of pores in the size range of 247-608 nm are visible on the surface, giving an indication of less possibility for potential use as military grade high explosive. Similarly, a wide range of cracks on the sample surface renders it unsuitable for use in pure form. One of the primary reasons for these pores and cracks may be linked to treatment with hot water spray during decanting process along with storage conditions and handling processes.
3.1.2 TNT Svc

About 5mg of TNT Svc in powder form was utilized for SEM analysis. This particular sample was selected for comparison of structural changes occurring in Decanted TNT Unsvc vis-a-vis TNT Svc. Once exposed for investigation, it was revealed that TNT Svc sample has a smooth surface, with irregular pebble like shape and no distinct orientation Figure 2. The number and size of pores (between 240.00 nm to 905.54 nm) visible on sample surface are fewer than those on Decanted TNT Unsvc sample surface. Similarly, less number of cracks can be found on the microstructure. It can be deduced from both the samples under investigation that TNT Svc sample covers the basic requirement of pure explosive use for military grade because of its clear, compact, smooth and homogeneous microstructure; in contrast with the Decanted TNT Unsvc sample. Variation in storage conditions, handling procedure and environmental conditions greatly affect the explosive’s physical as well as chemical properties and its shelf life.

3.2 TG/DTA analysis

3.2.1 TG analysis

For thermal analysis, Decanted TNT Unsvc and TNT Svc were examined through Perkin Elmer TG/DTA instrument. Figure 3 gives TG curves for both the samples. Study of TG curves shows that weight loss occurred in both samples in one step with both the samples diminishing nearly 98% around 285°C which is in agreement with literature data [7-8]. Interestingly, onset of weight loss of both the samples seems to occur around 152-155°C. A rapid change in mass loss is generally observed between 175-266°C, which can be related to thermal decomposition of both TNT samples. Consequently, total weight loss for Decanted TNT Unsvc sample under inquiry over prescribed temperature range of 155- 266°C is observed to be nearly 98%, whereas for Svc TNT sample, the decline in weight loss seems to progress further and comes closer to 95% exhaustion around 285°C. Thisimplies that Decanted TNT Unsvc sample decomposes earlier than TNT Svc sample, which could be due to impurities, prolonged exposure to high temperature environment, a long shelf life or even treatment with hot water spray during decanting process.
3.2. DTA

DTA curves for Decanted TNT Unsve and TNT Svc are observed in Figure 4. DTA thermogram indicates that both the samples nearly exhibit similar curves until 1st sharp endothermic peak for melting point of TNT between 81-83°C is visible [9-12]. On closer observation, it is revealed that melting of TNT Svc samples takes place earlier than Decanted TNT Unsve sample. Similarly, second endothermic event with slightly broad peaks between 245-255°C corresponds to endothermic decomposition of both TNT samples [13-15]. A slightly earlier decomposition of Decanted TNT Unsve in contrast to TNT Svc was also observed, which may be linked primarily to the existence of the impurities in Decanted TNT Unsve sample. However, presence of moisture content in this particular sample may also contribute as impurity. However, results shows that Decanted TNT Unsve can be effectively used with number of other energetic materials as composite materials for energy blast applications as well as for use as commercial blasting agents (commercial mining, metal brazing, cutting etc) [16].

![Figure 3. TG Curves of Decanted TNT Unsve and TNT Svc samples](image)

![Figure 4. DTA Curves of Decanted TNT Unsve and TNT Svc samples](image)

3.3 Horowitz and metzger method

Kinetic parameters like activation energy ($E$) and enthalpy($\Delta H$) for Decanted TNT Unsve vis-à-vis TNT Svc explosive samples were determined with the help of Horowitz and Metzger method using TG curves. Graphs used for the calculation of kinetic parameters are shown in Figure 5(a) and 5(b) for Decanted TNT Unsve and TNT Svc samples respectively.
It is revealed in Figure 5 that activation energy ($E$) of Decanted TNT Unsvc sample under controlled temperature program is lower i.e. 203.40kJmol$^{-1}$ (48.613 kcalmol$^{-1}$) than literature values for the pure TNT i.e. 222 kJmol$^{-1}$ (53.06 kcalmol$^{-1}$). However, activation energy of TNT Svc measured with the help of Horowitz and Metzger method is 217.78 kJmol$^{-1}$ (52.05 kcalmol$^{-1}$), which is in close agreement to the literature value for pure TNT [15,17]. On the other hand, enthalpy ($\Delta H$) of Decanted TNT Unsvc sample is determined to be 203.20kJmol$^{-1}$ (48.56 kcalmol$^{-1}$), whereas, the same is 215.91 kJmol$^{-1}$ (52.08 kcalmol$^{-1}$) for TNT Svc sample. It is deduced from comparative analysis that TNT Svc sample will result into better performance in terms of its thermal stability and sensitivity. Its rate of thermal decomposition and activation energy ($E$) are well defined. On the contrary, Decanted TNT Unsvc shows slight variation in its chemical properties which may be due to multiple reasons such as ingress of moisture contents, impurity, voids etc. All or some of these properties may have affected serviceability of TNT and resulted into change of its chemical or physical properties for instance, decrease in activation energy ($E$) and enthalpy ($\Delta H$). This decrease in activation energy ($E$) of the Decanted TNT Unsvc has negative impact on its thermal stability and shock sensitivity because thermally stable compounds are more difficult to detonate. The summary of TNT samples results is presented in Table 1.
Table 1. Summary of TNT samples result

| S.No | Type of Sample  | Melting point(°C) | Activation energy Ea (kJmol⁻¹) | Eₐ Literature Value of Ea for pure TNT(kJmol⁻¹) | Enthalpy ∆H (kJmol⁻¹) | Decomposition Range(°C) |
|------|-----------------|-------------------|--------------------------------|-----------------------------------------------|-----------------------|-------------------------|
| 1.   | Decanted TNT Unsvc | 81.30             | 203.40                         | 222                                           | 203.20                | 155–266                 |
| 2.   | Svc TNT         | 80.81             | 217.78                         | 222                                           | 215.91                | 155–285                 |

ₐAhmed S R and Cartwright M 2014 Laser Ignition of Energetic Materials John Wiley & Sons 1161-62

3.4 XRD analysis

XRD results of Decanted TNT Unsvc and TNT Svc shown in Figure 6 reveals several different distinctive diffraction peaks with varying intensity. XRD spectra exhibited these peaks in the range of 20 to 40 (2 theta degree). The diffraction pattern of TNT Svc can be easily distinguished from Decanted TNT Unsvc. XRD Spectra reveals that both the TNT samples exist in monoclinic structure possessing more stability than meta-stable state [18]. Miller indices are identified on XRD spectra with number of h, k, l values of (004), (021), (-315), (1021) for both the TNT samples. Similarly, TNT peak with h, k, l value of (004) seems to be the most crystalline peak of XRD spectra. From XRD spectra, it is revealed that experimental results for Decanted TNT Unsvc sample are in agreement with literature values reported for pure TNT sample and thus prove its existence in its real state even after aging and treatment with hot water spray.

Figure 6. XRD spectra of Decanted TNT Unsvc and TNT Svc samples

4. Conclusion

Present research work was aimed at finding out various characteristics of two types of TNT samples which includes thermal decomposition, microstructure analysis, surface morphology etc. From experimental results, it is revealed that Decanted TNT Unsvc has gained impurity during manufacturing, storage, handling and transportation. Presence of impurities adversely affected its thermal properties, where its activation energy (Eₐ) became lower than the intended value thus making it more sensitive to accidental initiation by friction or shock. Surface morphology of Decanted TNT Unsvc sample also reveals that the surface is rougher with visible cracks and porosity thus giving rise to the creation of hotspot. Similarly earlier decomposition of Decanted TNT Unsvc sample reveals that the sample contains impurities thus making it decompose prematurely. Although, numerous changes were observed for the Decanted TNT Unsvc sample during analytical study, but interestingly it has maintained its crystalline nature even though after a long shelf life, aging and exposure to variant environmental condition. This in-depth study has opened up a new dimension for reutilization of Decanted TNT Unsvc as composite material with metals for high energy blast applications. It can also be used as composite material for formulation of composite explosive materials. Similarly its conversion into commercial explosive for later use in mining, quarrying or even rock blasting cannot be ruled out.
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