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# INSIDE THIS ISSUE



### FROM THE EDITOR'S DESK

am thankful to Dr. Tanu Rattan for her efforts in bringing out this special issue of ITAS Bulletin on "High Energy Materials". The term 'high energy materials' (HEM s) refers to the class of materials known as explosives, propellants and pyrotechnics. The articles on HEM in this issue covers the potential of recently reported HEMs for various applications in the light of additional requirements in the present scenario, that is, cost - effectiveness, recyclability and eco – friendliness. Thermal Analysis plays important role in the development of such materials. I hope that the articles on HEMs appearing in this bulletin will provide useful information and new directions of research in this area.

As the new Editorial Board is taking over from this issue of ITAS Bulletin, I request the ITAS Members to contribute articles on interesting topics in thermal analysis so that we can bring out the Bulletins at regular intervals and also share the new frontiers in this field with fellow members of ITAS

I also request the members to send me information regarding any event like symposium, workshop etc on thermal analysis and honours and bouquets received by ITAS Members. Let us all be connected through this medium of ITAS Bulletin and share our knowledge in this important area of applied research.

With best wishes from the Editorial Team Shyamala Bharadwaj



Shyamala Bharadwaj

### PRESIDENT'S MESSAGE

# Dear Members

It gives me great pleasure that the ITAS brings a specials bulletin on "High Energy Materials" under the leadership of Prof. Tanu Rattan. I am thankful to Prof. Tanu Rattan for her immense effort to collect the article from the experts working in the field and critically reviewed same before coming to the final stage. ITAS wishes to thank Prof. Charlie Oommen, Indian Institute of Science ,Bangalore, for an article entitled " A glance at future eco-friendly monopropellants for space applications", Prof. Tanu Mimani Rattan ,Sri Staya Sai Institute of Higher Learning, Prasanthinilayam, A.P for her article entitled " Electrical power from nuclear energy : An up to date overview ",Prof. Anuj A. Vargeese, University of Hyderabad, Hyderabad for his article entitled " Thermal decomposition kinetics of 4,10-Dinitro-2,6,8,1-tetraoxa-4,10-diazatetracyclo[5.5.0.0<sup>5</sup>°0<sup>3,19</sup>]dodecane : An energetic nitramine oxidizer " and Prof.Gao Meng and his group for the article entitled " Carbon Bridge Igniter".

I feel strongly that the information given in these articles are useful to the people who are working in the area of high energy materials and related field. I hope that the readers will enjoy while reading these articles and will appreciate the untired effort put by the editorial team to make this special bulletin.

I request the ITAS members to give their suggestions to bring out future bulletins and give their valuable contributions to make the task success.

I wish to thank and congratulate all the editorial committee members for nicely bring out this special bulletin.

S.Kannan



S.Kannan

### **GUEST EDITORIAL**

## Dear Readers

The theme of this issue concerns itself with a class of materials called 'High Energy Materials" or HEMs. Literature provides us with two basic definitions of High-Energy: firstly, 'of or relating to elementary particles having energies of hundreds of thousands of electron volts'; a second definition of High-Energy is: providing a relatively large amount of energy upon undergoing a chemical reaction

For physicists, the first definition wherein matter is studied in terms of particles is more suitable. The second definition encompassing chemical reactions is obviously more pertinent to chemistry. However, the study of materials is an interdisciplinary field, and both physicists and chemists explore it. Keeping in view the above I thought that the field of HEMs often associated with chemistry related studies should also be looked at from both perspectives. Chemists and physicists equally have the knowledge and potential of deriving high energy from materials around us.

A significant research activity in the HEM field is by Chemists whose focus is at discovering new and efficient CHNO based energetic molecules or their composites. While engaged in this pursuit we need to keep in mind that one cannot cross the limit of the potential energy that is likely to be stored in CHNO chemical bonds from energy point of view. Therefore the exercise to discover new energetic molecules thorough molecular engineering is restricted by this and, the new game plan is to shrink the sizes of fuel and oxidizer to nano in order to get speed. This has led to the birth of 'Nanoenergetics' where there is promise of more energy release when compared to CHNO; the task however lies in controlling the kinetics and preparing nano formulations.

Nonetheless, the thrust areas of current progress in HEM's are also to meet the challenges of global demand for evolving green energetic materials. One such thrust has been towards the development of ionic liquids as a replacement for green monopropellants. Dr. Charlie Oommen has vividly described this aspect in his overview on popularly used environmental friendly monopropellants in the article entitled 'A glance at future eco-friendly monopropellants for space applications'. The thrust for green HEM's is further explored by Dr. Anuj A. Vargheese and his associate: through thermal analysis data, kinetic parameters are evaluated in their paper on 'Thermal decomposition kinetics of 4,10-Dinitro-2,6,8,12-tetraoxa-4,10diazatetracyclo [5.5.0.0<sup>59</sup> 0<sup>3,11</sup>] dodecane (TEX): An energetic nitramine oxidizer'. Among known N-nitramines, TEX has the highest energy density and a very high detonation velocity but it is insensitive towards external stimuli. In order to take advantage of its capabilities the authors have made attempt to unravel the decomposition mechanism of TEX so that future research efforts could lend to increase its sensitivity aspects. One of the technological uses of HEM's lies in the fabrication of electronic devices called igniters. These are important units primarily used to ignite other or more difficult to ignite materials. Igniters are like electronic switches whose function is to perform the make- and- break actions. Currently, Semiconductor Bridge igniters are evaluated as possible replacements for conventional hot-wires igniters . However, semiconductor bridge igniters being expensive to produce and less safe, alternate materials are sought for. Prof. Zhu Shunguan and his group have developed an igniter device using cheaply available finely ground carbon wires as electrically igniting materials with better safety as depicted in their paper entitled 'Carbon Bridge Igniter'.

Today's energy crisis is characterized by a shortage or lack of access to electricity supply affecting every length and breadth of development. Over the past decade, a need for more efficient materials for power generation has gained ground, leading to a heightened interest in energy production by various means. Nuclear decay energy from elementary particles of radioactive materials is a rich packet of energy measuring in the order of MeV or keV. As a replacement for alternate conventional power sources, which also contribute to climate change, scientist are focusing in this area to generate electrical power from nuclear energy for commercial usage through thermoelectric phenomena. From Physics vantage point of high energy definition we have an article by Prof. K. Venkataramaniah's group on 'Electrical power from nuclear energy: An up-to-date overview' highlighting newer methods of using nuclear materials together with nanomaterials for generation of electricity.

I hope this focus on high energy materials will provide some current insights to researchers and pave for the way forward in their respective fundamental and applied research fields.

Tanu Rattan Guest Editor



Tanu Rattan

# A GLANCE AT FUTURE ECO-FRIENDLY MONOPROPELLANTS

### FOR SPACE APPLICATIONS

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#### ABSTRACT

Monopropellant thrusters are the most common power plant for reaction control systems in satellites for applications such as orbital insertion, attitude control and correction. While hydrazine is the most commonly used monopropellant, many other chemicals are currently being explored which are environmental friendly unlike hydrazine. Some of these include CH<sub>3</sub>NO<sub>2</sub>, N<sub>2</sub>O, ionic liquids like hydroxylammonium nitrate (HAN) and hydrogen peroxide. Merits and challenges associated with their development into high performing propellants for replacing hydrazine is discussed. Development efforts at Indian Institute of Science, Bangalore on HAN are briefly reviewed.

#### **1. INTRODUCTION**

The power plant for most of the satellites use monopropellants in their reaction control systems (RCS) for applications like orbital insertion and attitude maneuverings. They can be either nonreactive gases (cold gas propellants) or reactive chemicals that decompose exothermically when passed over a heated catalytic or non-catalytic bed. Cold gas thrusters employ gases like nitrogen, argon, dry air, krypton, hydrogen, helium and Freon 14 depending on the thrust requirement and weight or volume limitation of the spacecraft. They employ simple pressure feed systems and are generally used for pulsing operations that need small level of thrusts. Unlike cold gas thrusters which are the simplest, thrusters that employ reactive chemicals need catalytic bed for the spontaneous decomposition of the chemical. They too are relatively simple, reliable and offer wide range of thrust levels. In a typical monopropellant thruster the propellant is injected over a catalytic exothermic bed.The decomposition of the propellant produces hot gases which are expanded through a nozzle toproduce required thrust levels.

A schematic of a cold gas and а monopropellant thruster are shown in Fig. 1. Obviously there are no multiple tanks, complex system valves and constraints of specific mixture ratios as in the case of bipropellants. On the shortcoming side the performance of these thrusters will be limited and propellant should be stable over a longer period of time due to the longer operational time of spacecraft. While the thermal catalytic bed need adequate power for pre-heating, spontaneous catalytic bed needs only warming to prevent issues related to cold starts which degrade the catalyst bed gradually over long period of operational time. In addition to this, catalyst poisoning also induces loss in reactivity and brings in inconsistency and irreproducibility during operation.



Fig.1 Schematic of a cold gas and monopropellant thruster power plant [1]

It can be seen from the literature and also from the propulsion units of various operational satellites that hydrazine is the most commonly used monopropellant due to its reliability, performance and stability [2-4]. N<sub>2</sub>H<sub>4</sub> initially decomposes into ammonia and nitrogen in an exothermic process. The ammonia produced further decomposes to nitrogen and hydrogen gas in a subsequent endothermic process. While the second stage is not favored as it absorbs energy, the average molecular weight of the products comes down which is beneficial for an increased characteristic velocity. An optimized performance is obtained by controlling the degree of dissociation of ammonia via catalyst bed geometry which mainly decides the dwell time of products species. Development of catalysts like Shell 405, precise manufacturing techniques to prepare high purity hydrazine, and extreme stability on storage have ensured hydrazine an enviable position among monopropellants as evident from its consistent use in space thrusters. However, hydrazine is an extremely toxic chemical and is currently branded as a carcinogen. Besides it has high crystallization point and high vapor pressure at room temperature. The hazards and cost associated with handling of such chemicals is a matter of concern of late. Greater environmental awareness in recent times has initiated an extensive search for more environmental friendly chemicals which are equally good as

environmental friendly chemicals which are equally good as hydrazine in performance and reliability. There have been many green space propulsion initiatives in recent time that ensures usage of environmental friendly propellants. Since it is not possible to alter the nature of combustion products much, the initiatives mainly focus on identifying and developing chemicals that are easier and safer to handle during ground operation and transportation. A list of green propellant candidates identified by Green Advanced Space Propulsion Project (GASP) funded by the European Union is available in literature [4].

#### **2. MONOPROPELLANTS**

Some of the monopropellants that have gained prominence in recent times are hydrogen peroxide, nitrous oxide. nitromethane and fuel blends based on ionic liquids (IL) like hydroxylammonium nitrate (HAN), ammonium dinitramide (ADN), and hydraziniumnitroformate (HNF). The volumetric specific impulse of some of these propellants along with hydrazine and cold gas thruster given in Fig. 2 shows the superiority of these chemicals over hydrazine. Ionic liquid based propellants seem to have the best performance due to higher density. The solubility of ILs becomes extreme aconvenient design tool for tailoring the exhaust temperature in many of these



Fig. 2 The volumetric specific impulse of various monopropellants

propellant blends. Besides it helps in tailoring the viscosity and modifying thermal stability of the propellant. The main challenge however remains with the storage stability of many of these compositions. The following sections are a glance at the worldwide development scenario of these propellants.

#### **2.1 HYDROGEN PEROXIDE**

Hydrogen peroxide (HP) is a well-studied energetic compound and has been in use as an oxidizer for decades in bipropellant systems. Monopropellant systems employing  $H_2O_2$  have been developed for emergency power units of aircrafts, power plant for micro air vehicle and various RCS thrusters [5-6]. Temperature of over 1000K could be generated with the use of 90% HP. Environmental friendly products like steam and oxygen, low IR signatures, and even the scope of generating the compound in field by electrolytic techniques are some of the attractive features of HP. Though its storage stability is not as good as hydrazine, usage of suitable material for container and conditions of storage could ensure fairly long storage life. Silver screen, manganese dioxide, noble metals like Pt, Ru, Ir over ceramic oxide supports are some of the reported catalyst that can decompose HP instantly. With the level of expertise in handling extremely high concentration of HP increasing and possibility of a higher density specific impulse (6%) more than hydrazine), HP is likely to emerge as a promising monopropellant in the future.

#### **2.2 NITROUS OXIDE**

Nitrous oxide is another non-toxic chemical that could be developed into a high performing monopropellant [7-8]. It is a stable compound at normal conditions and its decomposition can raise temperature to around 1900K releasing nontoxic products like nitrogen and oxygen. It is used as a liquefied gas and its high vapor pressure can be effectively used for selfpressurization and delivery through feeder pipes. It is also compatible with many structural materials like SS, aluminum, copper etc. Though the decomposition is exothermic and the activation energy barrier is high, use of a heated catalytic bed can ensure efficient decomposition. Similar to the one used for hydrazine decomposition, catalysts could be chosen from alumina supported noble metals. Since oxygen molecule release is considered as the rate limiting step in the multistep catalytic decomposition mechanism proposed, catalysts with weak metaloxygen bond are presumed to be more reactive. Unlike hydrazine, N<sub>2</sub>O decomposition may need much higher catalytic bed temperature. Also high temperatures produced during decomposition calls for high temperature tolerant catalysts. The extent and efficiency of decomposition could however be adjusted by proper configuration of the catalytic bed.

#### **2.3 NITROMETHANE**

Nitromethaneis a colorless liquid at room temperature and is currently employed in various combustion applications. Though its inherent advantages were overshadowed by the high performing hydrazine, the current search for greener propellants has revived interest in nitromethane of late [9]. High energy density, good thermal stability and low toxicity are some of the features that aid nitromethane in its revival as a promising monopropellant in micro and meso-scale propulsion systems. Nitromethane is cheaper, more widely produced, less toxic anddenser when compared to hydrazine. From the comparison of the critical parameters that is given in Table-1, it can be assumed that nitromethane holds promise as a high performing monopropellant than hydrazine.

#### Table-1 Selected performance values for CH<sub>3</sub>NO<sub>2</sub>

and N<sub>2</sub>H<sub>4</sub>

Property	Nitromethane	Hydrazine
Molecular Weight	61.04 g mol <sup>-1</sup>	32.05 g mol <sup>-1</sup>
Density	1.1278 g cc <sup>-1</sup>	$1.013 \text{ g cc}^{-1}$
Specific impulse	276 s	234 s
Density impulse	311 g s cc <sup>-1</sup>	237 g s $cc^{-1}$
Flame temperature	2188 (°C)	1121(°C)
Toxicity LD <sub>50</sub> (rat)	940 mg kg <sup>-1</sup>	60 mg kg <sup>-1</sup>

Though high combustion temperature is a favorable feature, availability of high temperature tolerant materials for thruster manufacture becomes a constraint. However nitromethane does not require a catalytic bed for ignition unlike hydrazine or other ionic liquids like HAN. Nitromethane decomposes to products which are generally non toxic in nature. Despite these advantages, nitromethane also suffers from sensitivity to shocks and needs to be handled carefully.

#### 2.4 IONIC LIQUIDS (HAN, ADN, HNF)

By definition, an ionic liquid is a salt with a melting point below 100°C and used as concentrated aqueous solution. The most common of the ionic liquids monopropellants explored as are based on hydroxylammonium nitrate (HAN) [NH<sub>3</sub>OH]<sup>+</sup>[NO<sub>3</sub>]<sup>-</sup> , ammonium dinitramide (ADN)  $[NH_4]^+[N(NO_2)_2]^$ and hydraziniumnitroformate (HNF)  $[N_2H_5]^+[C(NO_2)_3]^-$ . Some of their properties are mentioned in Table-2.

#### **Table-2 Selected properties of ionic liquids**

Salt	Formula	MW (g/mol)	Solubility in water at 20 <sup>0</sup> C (%)	Melting Point ( <sup>o</sup> C)	Oxygen balance (%)
HAN	$[NH_3OH]^+[NO_3]^-$	96	95	44	33.3
ADN	$[NH_4]^+[N(NO_2)_2]^-$	124.1	78	92	25.8
HNF	$[N_2H_5]^+[C(NO_2)_3]^-$	183.1	53	118	13.1

Availability of excess oxygen, as indicated by the positive oxygen balance, provides ample scope for inclusion of compatible fuel components which can make the final IL-fuel-water blends high performing. Many of these ionic liquids were developed earlier for other applications in propulsion. Their superior solubility in water, and the ensuing advantage in tailoring final combustion temperatures, and ability to decompose exothermically in the presence of catalysts make them attractive as promising monopropellants. ADN was first developed in Russia four decades ago as a replacement for ammonium perchlorate in composite solid propellants. Some of the monopropellants based on ADN developed in the recent past include LMP-103S by Swedish Space Corporation and AFM 315E by US Air Force [10-FLP-106 is 12]. another ADN based monopropellant developed using a high boiling fuel component by Swedish Defense Research Agency FOI. This propellant is reported to have higher density, low vapor pressure, less sensitivity to shock and higher performance. Though ADN has issues related to thermal stability, the monopropellant systems appear promising. HNF is another compound developed as a substitute for ammonium perchlorate but found promising also as a monopropellant. However it is not explored to the extent of either HAN or ADN.

#### *Hydroxylammonium nitrate (HAN)*

Of all the ionic liquids explored, hydroxyl ammonium nitrate (HAN) based systems are the most studied and missions have been planned employing HAN based monopropellants. US, French and Japanese groups have done substantial work on the development of this compound [13-14]. HAN formulations are reported to have lower points, crystallization higher density and volumetric impulse. It is also used as an insensitive liquid oxidizer in gun propellants. Nuclear industry uses HAN at low concentration in the presence of nitric acid for the reduction of Plutonium (IV). Some of the HAN based compositions that have been

developed in the past are LP1846 (HAN with tri-ethanol-ammonium nitrate), HANGLY26 (HAN with glycine), HAN284-MEO17 (HAN with methanol) and AFM-315E (HAN with unspecified fuel). Critical parameters of some of these monopropellants are given in Table-3. The data show the superiority of IL based propellants. Obviously the development of HAN based propellants deserve top priority in the space program of the country. Currently, owing to its strategic use in areas related to propulsion space and nuclear industry information related to HAN preparation is not freely available in the open literature. Besides, the compound is not available for commercial purchase within India. Apart from the aspects related to HAN preparation there are many more avenues that need to be explored and mastered in this field. Since the emergence of HAN as a promising environmental friendly monopropellant has evolved only recently, many of the studies carried out earlier on HAN properties with lower concentrations are either irrelevant or demands a re-examination in the context of catalytic decomposition in a thruster wherein higher concentration are used. Furthermore, thermal stability, long term storage stability, compatibility with other compounds are some of the other issues that need systematic investigation for a successful development of a reliable and high performing monopropellant to replace hydrazine.

	Current	Green propellant						
	Propellant Hydrazine		HAN Based <sup>*1</sup>			ADN- based <sup>*2</sup>	HNF- based <sup>*3</sup>	Hydrogen peroxide
		LP1846 <sup>*4</sup>	SHP <sup>*5</sup>	LTHG <sup>*6</sup>	HAN/HN- BASED <sup>*7</sup>	LMP- 103S		
Freezing point (°C)	2	-100	≤-30	-35	-35	-7	?	-6
Density g (cm <sup>3</sup> ) <sup>-1</sup>	1	1.4	1.4	1.3	1.4	1.3	1.4	1.4
Theoretical specific impulse <sup>*8</sup> (s)	239	262	276	191	210	255	260	182
Density specific impulse g (cm <sup>3</sup> s) <sup>-1</sup>	241	376	396	254	294	332	354	256
Adiabatic flame temperature (K)	1183	2171	2401	1251	1455	2054	2218	1154

#### **Table-3** Critical parameters for various monopropellants

\*1: NH<sub>3</sub>OHNO<sub>3</sub> :hydroxylammonium nitrate \*2: N<sub>2</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> ammonium dinitramide \*3: N<sub>2</sub>H<sub>5</sub>C(NO<sub>2</sub>)<sub>3</sub>: hydraziniumnitroformate \*4: Composed of HAN, TEAN and water chamber pressure \*5: Composed of HAN, AN, water and methanol

\*6: Composed of low-temperature HAN/glycine and water

\*7: Composed of HAN, HN, TEAN and water

\*8: Calculated based on the frozen flow assumption, with a combustion of 0.7 MPa and a nozzle open area ratio of 50

Our group at Indian Institute of Science also has been working in the area of HAN development in the last few years with funding from ISRO [15]. Our focus has been primarily on two critical aspects of HAN thruster development. The first one is on the synthesis of HAN as the compound is not available for commercial purchase in India. The second thrust of our research program was on developing high temperature tolerant catalyst for HAN decomposition. Traditionally all the catalyststhat were tried and tested for HAN decomposition were initially developed for hydrazine decomposition. These are primarily noble metal catalysts like iridium, platinum, palladium etc., supported on alumina pellets. However the temperature levels experienced in HAN based thrusters are much higher and

conventional hydrazine catalysts do not sustain continuous high temperature operation as the support may crumble or precious metal may get deactivated by the NOx emission from HAN. Our group is also working on high temperature tolerant catalysts that can decompose HAN effectively without getting deactivated. Some of the important properties of HAN are given in Table-4.

**Table-4 Properties of HAN** 

Property	Value
Specific gravity	1.68 (95% HAN)1.8 g(cm <sup>3</sup> ) <sup>-1</sup> (pure)
Freezing point ( °C)	-15 (95% HAN)
Boiling point ( °C)	170 (95% HAN)
Vapor pressure (atm)	1.36x10 <sup>-4</sup> (95% HAN)
Heat of formation Cal g <sup>-1</sup>	-940 (95% HAN)
Molecular formula	$H_4N_2O_4 (96.04 \text{ g mol}^{-1})$
Explosive classification	Class 1.3
Oxygen balance	33.33%

Preparation of HAN without any contaminants at high concentration levels is a challenging task as most of the reported methods are either not efficient or safe or leave metal ions or nitric acid in the final product. Many of the compounds that are retained during the preparation can induce thermal instability problems in HAN during long term storage. In one of our works we compared the merits and demerits of various preparatory routes that can be adopted in the laboratory for the preparation of HAN [16]. The preparatory routes adopted for HAN were (1) the double decomposition reaction between barium nitrate and hydroxyl ammonium sulfate (HAS), (2) calcium nitrate and HAS and (3) reaction between hydroxylamine and nitric acid. HAN prepared by these routes were analyzed using various spectral (IR, Raman) and analytical techniques (for water content, hydroxylamine content, ICP, density etc.). The final thermal decomposition characteristics were studied using standard thermal analysis techniques and an inhouse built constant volume batch reactor. HAN decomposition is not as easy as hydrazine needs decomposition and much higher temperature initiate the exothermic to decomposition. However, a catalyst can facilitate the decomposition at a much lower temperature. These crucial parameters could be monitored effectively using thermal analysis techniques like DTA and TG. The advantages of catalytic decomposition over thermal decomposition in

in terms of lower decomposition temperature and higher reaction rate are evident from the TG-thermogram shown in Fig. 3. We used these techniques efficiently for screening our newly developed catalysts and HAN samples prepared by various synthetic routes. Since details of HAN preparation is classified due to its strategic use we carried out a systematic study on the merits of different preparatory routes mentioned above. We methodically examined the effect of metal ions that remain within the product even after purification on the thermal decomposition behavior of HAN. It was observed that double decomposition methods using calcium and barium nitrate deliver HAN with metal ion traces which adversely affect the thermal decomposition of HAN. Neutralization method involving HA and nitric acid on the other hand has the probability of introducing nitric acid, another undesirable compound that may introduce uncertainties in the thermal decomposition behavior of HAN. The effect of excess nitric acid and critical pH required for synthesis of pure HAN were examined in our studies. The detrimental compounds like metal ions, nitric acid etc., that leach into the final product may introduce unreliability and reproducibility issues during operation and shelf-life of HAN based thrusters. The effects of these undesirable compounds on the final thermal stability of HAN and corrective

measures that need to be adopted during the preparatory routes have been reported [16]. During our sustained efforts to prepare HAN without any impurity and hazards we could evolve a preparatory route that is extremely safe and deliver HAN without any trace of impurity. This method deliver 99.99% pure HAN in solid form and does not involve any high temperature distillation which has been reported to be hazardous. This process is highly cost effective and the bi-products generated during HAN synthesis can efficiently be reused. This unique process developed at IISc has unmatched advantages and is being patented [17].



Fig. 3 Thermogravimetric curves for HAN decomposition

(a) Thermal (b) Catalytic

A schematic of the constant volume batch reactor which was used to characterize the thermal and catalytic decomposition of HAN is shown in Fig. 4. In a typical experiment 200µL of HAN solution was injected through a syringe infusion pump onto a heated catalytic bed or directly into a chamber preheated to a fixed temperature. The pressure and the temperature rise inside the chamber are recorded against time. Batch reactor analysis gives information on rate of decomposition by following the rate of pressure rise when HAN is decomposed thermally either or catalytically. This isothermal decomposition simulates a realistic condition and isolates the thermal history of the sample unlike in a conventional thermal analysis technique. Moreover the sustainability of the catalyst in decomposing the propellant and catalyst poisoning can also and be monitored. A typical pressure temperature rise inside the reactor for nearly 25 injections on a catalyst developed in-house is shown in Fig. 5. Some of the catalysts developed in our group were found to be more effective than conventional alumina supported precious metal catalysts.



Fig. 4. Schematic of batch reactor



Fig. 5. Pressure and temperature rises inside the batch reactor during decomposition of HAN

#### CONCLUSION

The paper gives an overview of the recent developments in the area of environmental friendly monopropellants. Monopropellants such as hydrogen peroxide, nitromethane, nitrous oxide and ionic liquids are discussed and their present technological standing and developmental challenges are mentioned. A brief outline of the research programs at Indian Institute of Science, Bangalore on the development of hydroxyl ammonium nitrate based monopropellant is given. It is evident from recent literature and technology updates that the current propellants may soon give way to greener propellants

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### **CHERMAL DECOMPOSITION KINETICS OF 4,10-DINITRO-2,6,8,12-**TETRAOXA-4,10-DIAZATETRACYCLO[5.5.0.0<sup>5,9</sup>0<sup>3,11</sup>]DODECANE (TEX): AN ENERGETIC NITRAMINE OXIDIZER

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#### ABSTRACT

Since the early 2000 millennium there is an increased quest for the development of more energetic and environmental friendly high energy density molecules. This has resulted in the synthesis of thousands of new energetic molecules. Caged or strained molecules and polynitrogencompounds constitute a major part of these interesting energetic molecules. However, except a few, all these molecules irrespective of their performance suffer from the drawback of sensitivity towards various stimuli. The molecule 4,10-Dinitro-2,6,8,12-tetraoxa-4,10diazatetracyclo[5.5.0.0<sup>5,9</sup>0<sup>3,11</sup>] dodecane (TEX) exhibits highest density among known N-nitramines, and a very high detonation velocity, while it is insensitive towards shock, impact and friction. TEX being an insensitive high density material, understanding the thermal decomposition kinetics of TEX is of practical interest. Isoconversional kinetic analysis, a method of studying thermally stimulated processes, involves evaluating the dependence of the effective activation energy on the extent of conversion. This information is further used for exploring the mechanisms of the processes has been emerged as a handy tool for kinetic analyses. The present study employs a non-linear integral isoconversional method to understand the decomposition kinetics of TEX. The data obtained from TGA, DTA and DSC are compared with the computed activation energy values and possible decomposition pathway is proposed and the results are discussed.

#### 1. Introduction

Chemical kinetics deals with the study of reaction rate and its relation to the extent of conversion ( $\alpha$ ) and to temperature (T) by different and independent functions. The basic kinetic relation is given as follows [1].

$$\frac{d\alpha}{dt} \propto f(T)f'(\alpha) \tag{1}$$

Nevertheless, it must be noted that there exists a dependence on the pressure (not considered in the present study) [2,3]. In the nonisothermal kinetic analysis the temperature is varied in a systematic and controlled manner so as to determine the complete kinetic behaviour or the computation of kinetic triplets A, E and  $f(\alpha)$ . The temperature T, at time t during a linear scan is  $T = T_0 + T_0$  $\beta t$ , where  $T_0$  is the initial temperature and  $\beta$  is the temperature scan rate in °C min<sup>-1</sup> or K min<sup>-1</sup>.The dependence of temperature on rate is described by the Arrhenius as in equation 2 and the relation in Equation 1 can be expressed as a single step kinetic equation 3[1,4,5].

$$f(T) = A \exp\left(-\frac{E}{RT}\right)$$
(2)

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f'(\alpha) \tag{3}$$

Where A is the Pre-exponential factor (Arrhenius factor), E is the activation energy and R is the gas constant. As documented in the literature, Arrhenius parameters can be

determined by the form of the reaction model  $f(\alpha)$  assumed and it may take various forms [6]. On the other hand, the isoconversional method or model free method can be employed to computationally derive the A and E. As the name states, the method is developed on the principle that the reaction rate at constant extent of conversion is only a function of temperature. In other words, the reaction model is not dependent on temperature or heating rate and hence assumption of any particular form of  $f(\alpha)$ , the reaction model is not required. However, isoconversional the methods employ multiple heating rates to obtain data on varying rates at a constant extent of conversion. The extent of conversion ( $\alpha$ ) can be computed from the mass loss data obtained from TGA runs or heat release data obtained from DSC runs. The basic concept of the isoconversional kinetic analysis is well explained in the International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Project [7] and ICTAC recommendations [5] and is further illustrated inFig. 1 [8].



Fig. 1: An isoconversional method applies the Arrhenius equation to a narrow temperature region,  $\Delta T$ , related to a given extent of conversion. The temperature region changes with the extent of conversion that allows one to follow a variation in the value of E throughout the whole experimental temperature region. The use of different heating rates,  $\beta_1$  and  $\beta_2$ , allows for determining different rates  $\left(\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\beta\right)$  related to the same conversion,  $\alpha_3$ .

The major advantage of the isoconversional method over the single curve method is the applicability to determine the kinetics of multistep processes. As the method considers the kinetics of the process by using multiple single-step kinetic equations, it permits to explore the kinetics of the multistep thermal decomposition reactions (or any thermally stimulated process) and helps in drawing mechanistic conclusions about the process under investigation. Using the Equations 1, 2 and  $T = T_0 + \beta t$ , alternative kinetic equations can be obtained. There are a number of methods which makes use of the principle but, a few have been very popular in the literature, namely,, Flynn-Wall-Ozawa's

Ozawa's liner integral method [9,10], Friedman's differential method [11] and Vyazovkin's non-linear integral method [12]. Being a differential method the Friedman method has an upper hand over the other methods, however, the method uses the instantaneous rate values which are quite susceptible to experimental noise, leading to larger variations in  $E_{\alpha}$  values.

In this paper, we explore the kinetics of thermal decomposition of 4,10-Dinitro-2,6,8,12-tetraoxa-4,10diazatetracyclo[5.5.0.0<sup>5,9</sup>0<sup>3,11</sup>]dodecane or hexahydro-4,7-dinitro-5,2,6-(Epoxymethenoxy)-1,3-dioxolo[4,5-b] pyrazineor4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane or commonly known as TEX. It is a nitramine oxidizer first synthesised in the early 1990's [13].



According to literature, TEX ( $C_6H_6N_4O_8$ ), exhibits the highest density of 2.008 g cm<sup>-3</sup> among known *N*-nitramines, due to its closepacked crystal structure [14]. It displays the highest density recorded for a nitramine and therefore a very high detonation velocity (7470 m s<sup>-1</sup>), while its sensitivity towards shock,impact or friction is extremely low. These features make TEX not only an interesting explosivebut also an interesting model compound for the development of new energetic materials [15] In the present study, the Vyazovkin's non-linear integral isoconversional method is used for the kinetic computations

#### 2. Experimental

TEX was synthesised through a two-step process in our laboratory, in which the first step was preparation of *1,4-diformyl-2,3,5,6tetrahydroxypiperazine,* and then its subsequent reaction with glyoxal to yield TEX.

2.1 Preparation of 1,4-Diformyl-2,3,5,6tetrahydroxypiperazine (THDFP)



According to the procedure reported earlier, 10 mL of aqueous NaOH solution (20% w/w) was slowly added to 100 g of aqueous glyoxal solution (40% w/w). After cooling the solution to 10 °C, 31 g of formamide was added drop wise over a period of 10 minutes [16,17]. Once the formamide addition was completed, the temperature of the reaction mixture was allowed to rise to room temperature and maintained at ambient temperature till the solid product precipitated from the mixture. After an hour, the solid was filtered and washed twice withwater and then with acetone, and then dried overnight. A white solid weighing 60 g of dry1,4-diformyl-2,3,5,6-tetrahydroxypiperazine (THDFP) was obtained (yield 83%). The product had a melting (and decomposition) point of 201 °C (reported 205 °C).



#### 2.2 Preparation of TEX

To a solution of sulphuric acid maintained at 0 °C, 40% glyoxal was added and stirred for 10 minutes. It was followed by the slow addition of (THDFP). The reaction mixture was stirred for 5 h and then the temperature of the mixture was reduced to -5 °C. To this fuming nitric acid was added slowly. After fuming nitric acid addition, the reaction mixture was stirred at room temperature for 48 hour, and then it was poured on crushed ice. The solid product separated was filtered, washed with aqueous ethanol and dried to obtain pure product (Yield: 22%). The product was further recrystallized from 1:1 mixture of acetone and methanol solvents to get highly crystalline and pure TEX.

#### 2.3 Characterization of TEX

The synthesised TEX was characterized by <sup>1</sup>H-NMR spectroscopy as well as melting point determinations. The <sup>1</sup>H-NMR was measured on a Bruker 400 MHz instrument at room temperature, in deuterated DMSO/acetone mixture. Melting points were measured on a noncalibrated melting point apparatus using capillary method.

#### 2.4 Thermogravimetric analysis

Thermogravimetric (TG) analysis of TEX was carried out under a flowing nitrogen atmosphere in a TA instruments SDT Q600 TG/DSC instrument. In all experiments, 1-1.3 mg of sample was loaded in an open 90  $\mu$ L alumina pan and heated. Nitrogen at a flow rate of 100 mL min<sup>-1</sup> was used as the purge gas. The non-isothermal TG runs were conducted at heating rates ( $\beta$ ) 5, 7.5, 10 and 12.5 °C min<sup>-1</sup> and the collected data was used for further analysis.

#### 2.5 DSC analysis

The DSC analysis was carried out on a PerkinElmer DSC8000 instrument. During the DSC experiment, 0.78 mg sample was loaded into a sealed aluminium pan and scan was performed at 10 °Cmin<sup>-1</sup> heating rate. The purge gas (nitrogen) flow was maintained at 40 mL min<sup>-1</sup>.

#### 2.6 Kinetic computations

A model free (isoconversional) non-linear integral method was employed for the computation of kinetic parameters and further kinetic analysis [12]. The mass loss data obtained from the nonisothermal TG runs were converted to  $\alpha$  using the standard equation $\alpha = (m_0 - m_t)/(m_0 - m_f)$ . Where  $m_0$  is the initial mass  $m_f$  is the final mass and  $m_t$  is the mass at a given temperature. A 0.01 increment in  $\alpha$  was used to compute the  $E_{\alpha}$  values using the nonlinear integral isoconversional method. 2.6.1 Vyazovkin's non-linear integral Method Vyazovkin's method is a non-linear integral isoconversional method which can be used for nonisothermal experiments. Vyazovkin's method provides more precise apparent energy performing activation values by numerical integration[12,18]. For a set of 'n' experiments carried out at different heating rates, the apparent activation energy can be determined at any particular value of  $\alpha$  by finding the value of  $E_{\alpha}$  for which the given function, equation 4, is a minimum. The minimization procedure is repeated for each value of  $\alpha$  to find the dependence of the apparent activation energy on the extent of conversion.

$$\sum_{i}^{n} \sum_{j \neq i}^{n} \left[ I(E_{\alpha}, T_{\alpha, i}) \beta_{j} \right] / \left[ I(E_{\alpha}, T_{\alpha, j}) \beta_{i} \right] = min \quad (4)$$
  
Where,  $I(E, T) = \int_{0}^{T} \exp\left(-\frac{E}{RT}\right) dT \quad (5)$ 

 $\beta$  in equation 4 represents the heating rates, and the indexes *i* and *j* denote the set of experiments performed under different heating rates, and *n* is the total number of experiments performed.The third degree approximation, equation6, proposed by Senum and Yang[19] was used in the present study to evaluate the integral equation 5.

$$f(x) = \frac{\exp(-x)}{x} \times \frac{x^2 + 10x + 18}{x^3 + 12x^2 + 36x + 24}$$
(6)

Where, 
$$x = \frac{E}{RT}$$
 and  $I(E,T) = \frac{E}{R}f(x)$  (7)

Mat Lab 7.0.1 was used to perform the kinetic computations.

#### 3. Results

#### 3.2 Synthesis and characterization of TEX

The reaction between 1,4-Diformyl-2,3,5,6tetrahydroxypiperazine and glyoxal resulted in the formation of TEX as confirmed by <sup>1</sup>H NMR (Fig. 2). In <sup>1</sup>H NMR two major signals at 7.5 ppm and 6.4 ppm are observed confirming the formation of TEX. Apart from this, two small peaks corresponding to dmso-d6 solvent and moisture are observed at 2.5 and 3.6 ppm and respectively а peak at 2.9 ppm corresponding to methanol (since the compound is recrystallized from acetone and methanol mixture) is also observed in the <sup>1</sup>H NMR spectrum. The melting point determined to be 285 °C is accompanied by decomposition.



Fig. 2: <sup>1</sup>H NMR spectrum of TEX.

#### 3.3 Thermogravimetric analysis

The results of thermogravimetric analysis carried out at different heating rates are shown in Fig. 3. The TEX molecule is stable till 200°C and starts slow decomposition above this temperature. The decomposition is completed at around 280 °C.. The TGA curve indicated a complete decomposition and nearly 100% weight loss.. The DTA curve also exhibits a

single endothermic decomposition at 275 °C. The TGA curve being integral data, the first order derivative is computed and this DTG analysis revealed that TEX decomposition involves two different stages of mass loss. The TG-DTA-DTG curve of TEX obtained at 10 °C min<sup>-1</sup> heating rate is shown in Fig. 4.



Fig. 3: TGA curves of TEX obtained at different heating rates



Fig. 4: The TG-DTA-DTG curves of TEX.

#### 3.1 DSC analysis

As revealed in the DTG analysis that TEX decomposition involves two different stages, the DSC analysis confirmed the same with an endothermic peak centred at 302 °C followed by

an exothermic peak at 304 °C. DSC analysis curve obtained at 10 °C min<sup>-1</sup> heating rate is shown in Fig.5.



Fig. 5: DSC analysis curve of TEX obtained at  $10 \,^{\circ}$ C min<sup>-1</sup> heating rate.

#### 3.4 Kinetic analysis

According to the isoconversional principle, the reaction rate at a constant conversion depends only on the temperature and based on this assumption calculations are performed to compute the  $E_{\alpha}$ . The  $\alpha$  values and their corresponding temperatures are calculated from the TG data obtained at four different heating rates and used to compute the  $E_{\alpha}$  values for the decomposition reaction of TEX. To get more insights into the decomposition phenomena the kinetic curves,  $\alpha$  against T, are plotted and shown in Fig. 6.



Fig. 6: α-T kinetic curves of TEX.

The plots of  $E_{\alpha}$  against  $\alpha$  for TEX is shown in Fig. 7.It can be seen that, the apparent activation energy of the decomposition process varies with  $\alpha$ . It is found that in the 0.03–0.15 region of  $\alpha$  a slight decrease in the  $E_{\alpha}$ -dependence (151-138 kJ mol<sup>-1</sup>) and a significant decrease from 138-101 kJ mol<sup>-1</sup>in the 0.16–0.4 region of  $\alpha$  is observed. The E<sub> $\alpha$ </sub> remains practically constant at ~102 kJ mol<sup>-1</sup> in the 0.41-0.99 region of a.The first two stages accounts for the ~40% decomposition of the molecule. The first region of decomposition is described by an average activation energy of 145 kJ mol<sup>-1</sup>, second region is characterized 111 kJ mol<sup>-1</sup> and while that of third region of decomposition is described by 102 kJ mol<sup>-1</sup>. The apparent activation energy values obtained for  $\alpha$ corresponding to 0.01 and 0.02 are 113 kJ mole<sup>-1</sup> and 143 kJ mol<sup>-1</sup> respectively.



Fig. 7: Variation of Ea with respect to reaction progress for TEX

#### 4. Discussions

The TEX molecule being symmetrical in nature and the <sup>1</sup>H NMR spectrum indicated two signals occurring at 7.5 ppm and 6.4 ppm, and each signal must correspond to two chemically equivalent hydrogen nuclei. The integration of the signals confirmed this fact and gave 4 and 2 H atoms (2:1 ratio) in each environment. <sup>1</sup>HNMR (DMSO- $d_{6r}$   $\delta$ ): 7.5 (4H, S), 6.4 (2H, S).

During the determination of melting point, it was observed that TEX, a white crystalline solid, turns into a black solid before it starts melting. In fact this change is observed at temperatures around 270 °C and subsequently the compound undergoes melting at 285 °C. The simultaneous TGA-DTA-DTG curve gives more insights into the phenomena. The thermal stability of the compound is further established by TGA which shows a similar behaviour wherein the molecule is stable up to 200 °C and starts a slow decomposition above this temperature. The DTA curve exhibits an endothermic peak at 275 °C and convincingly the melting and decomposition is submerged into the endothermic peak. The DTG curve confirms that the compound undergoesa two-stage decomposition with peaks at 255°C and 270 °C. The initial weight loss corresponding to the first stage decomposition is about 35%. The nitro groups accounts for a mass of 92 and the molecular mass of TEX being 262, this agrees with the 35% first stage weight loss. Interestingly this suggests that the N-NO<sub>2</sub> bonds are cleaved first releasing both the nitro groups. The

remaining fragment completely decomposes before 280 °C as seen in the TG-DTG curves.On the other hand the DSC revealed a slightly different behaviour, the sample showed an endothermic peak at 302 °C and this was immediately followed by an exothermic peak at 304 °C, however the onset of melting/decomposition is observed at 290 °C. Even though the DSC curve differed from the DTA curve, the underlying phenomenon seems to be the same. The difference in the thermal analysis curves would have brought in due to the different sample enclosure in which the experiments are carried out. This is rather a common observation which is predominantly reported ammonium perchlorate in the [20] decomposition where the exo-/endothermicity of the second stage decomposition is largely governed by the type of sample enclosure, open pan, closed pan, closed pan with pinhole, etc., employed for the thermal investigation and flow rate/pressure [3] of the purge gas as well as the addition of decomposition catalysts. In the present study, the TG-DTA is carried out in an open pan and DSC is carried out in a closed pan. When the experiment are carried out in open pan the decomposing fragments would be carried away by the carrier gases (here nitrogen) and there is a minimal chance

the DSC analysis a closed aluminium pan was used and this permits the occurrence of secondary reactions, leading to an exothermic second stage decomposition.

Probably the N-NO<sub>2</sub> bond cleavage destabilizes the remaining cage structure and leads to the complete decomposition of the molecule. The -NO<sub>2</sub>being a highly reactive free radical, could easily react with the remaining cage leading to complete decomposition. the the Though possibility of this secondary gas phase reactions during the TG analysis is limited, the possibility of further reactions of -NO<sub>2</sub>at higher temperature and higher decomposition rates cannot be ruled out. Apparently, the influence of  $-NO_2$  in further decomposition of TEX during the DSC analysis can be anticipated from the DSC curve. The cleavage of N-NO<sub>2</sub> is an endothermic event [21] and so is the case of melting, hence both the phenomena together would have appeared as endothermic peak in the DSC curve at 302 °C. Subsequently, with increased possibility of secondary reactions in the sealed crucible, the -NO<sub>2</sub> would attack the molecule leading to an exothermic decomposition.

Since the isoconversional methods can describe the kinetics of the process by using multiple single-step kinetic equations, each of which being associated with a certain process. This feature allows the identification of complex multi-step processes. This can be easily identified as a dependence or variation of  $E_{\alpha}$  with  $\alpha$ . On the other hand, the independence of activation energy on the extent of conversion indicates the possibility of single reaction mechanism or the unification of multiple-reaction mechanisms.

The activation energy values computed using the isoconversional method indicated higher values initially (or dependence or variation of  $E_{\alpha}$  with  $\alpha$ ) indicating the thermal stability of the molecule. As described above, dependence of  $E_{\alpha}$  with  $\alpha$ indicates the occurrence of multiple singlestep kinetics in the decomposition of TEX. This in fact was coinciding with the initial 40% weight loss ( $\alpha$  corresponding to 0.01 to 0.4) pointing towards the N-NO<sub>2</sub> bond cleavage and the  $-NO_2$  release. This assumption seems to be valid from the fact that the activation energy calculations (calculation of  $\alpha$ ) are carried out from basic mass loss data. Thus, the first step is crucial to determine what unimolecular steps lead to substantial energy release at a molecular level. Furthermore, the detailed dynamics of that energy release determines whether the energy is available to drive subsequent chemistry or instead it is dissipated from the site to the surrounding lattice. The apparent activation energy values obtained for  $\alpha$ 

The apparent activation energy values obtained for  $\alpha$  corresponding to 0.01 and 0.02 are lower probably because of self-heating of the sample or looks like an artefact. In TEX, the N-NO<sub>2</sub> bond cleavage being endothermic and it does not release energy that can drive subsequent reactions and may be because of this, the  $E_{\alpha}$  remained high in the range of  $\alpha$ =0.03-0.15. More and more number of N-NO<sub>2</sub>bonds is cleaved and the  $-NO_2$ concentration increase with respect to number of -NO<sub>2</sub> fragments diffusing away through carrier gas, the secondary reactions start occurring and this might have brought down the activation energy to 102 kJ mol<sup>-1</sup>. After the C-C bridge bond is cleaved the molecule becomes unstable and will easily break down to smaller species such as CO, CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O etc. Even though, the  $E_{\alpha}$  dependence remains practically constant in this region, it may not necessarily indicate a single reaction mechanism but there exists an ample possibility of unification of multiple-reaction mechanisms.

#### **5.** Conclusions

The thermal decomposition of TEX was investigated with TGA, DTA and DSC and its decomposition kinetics has been investigated using a non-linear integral isoconversional kinetic method. From the observations and thermal analysis data the molecule starts decomposing before melting and turns into a into a black mass. The thermogravimetric analysis indicated a two stage decomposition matching with the cleavage of N-NO<sub>2</sub> bond. Further, the DSC analysis also indicated a similar behaviour with N-NO<sub>2</sub> bond cleavage coupled withmelting appeared as endothermic signal and further decomposition with secondary reactions appeared as exothermic event. Evidently the isoconversional kinetic analysis also supports this assumption in which there involves three different stages of the decomposition process. N-NO<sub>2</sub> being a weak bond it is cleaved and -NO2 being a reactive species, further decomposition is accelerated and characterized by lower activation energy values. The multi-step kinetic was apparent from the dependence of  $E_{\alpha}$  values on the  $\alpha$ . The  $\alpha$ =0.4-0.99 region was characterised by practically constant  $E_{\alpha}$ possibly indicating unification of multiplereaction mechanisms. Though the mechanism seems apparent, a thermal analysis coupled spectroscopy studies may shedmore light on the decomposition mechanism of TEX.

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#### Abstract

Carbon Bridge Igniter has been prepared by using carbon as the igniting component. The impact of the mass of carbon and electrode distance on the ignition bridge performance is studied, and the ignition sensitivity of five kinds of explosives compared. An end-to-end electrostatic discharge (ESD) experiment was carried out to obtain voltage-time curves, current-time curves and light-time curves. The data is analyzed using D-optimization method. Results show that the carbon ignition bridge attains a lowest minimum total ignition voltage of 17.3V when the quantity of carbon is 1.2mg and the electrode distance is 2.4mm. It is observed that within a certain range, with the increase of carbon filling quantity, the minimum total ignition voltage drops before it rises; and larger theelectrode distancethe higher is the minimum total ignition voltage. The order of electro-spark sensitivity of the energetic material used in ignition of the bridge is lead styphnate>lead azide>nickelhydrazine nitrate>B+KNO<sub>3</sub>>lead picrate. The carbon bridge igniter has good end-to-end antistatic electricity discharge performance of 50KV.

Key words:Bridge Igniter;Carbon layer; simple and safe

#### 1. Introduction

There are two modes of action of the electroexplosive device: one is heat-conduction, like bridge wire and bridge film; theother is microconvection, such as semiconductor bridge (SCB). Both these have an effect on the exothermic material used for ignition by way of heat transfer or plasma saturation by the electric current generated[1]. It induces chemical changes in the exothermic material leading to burning or explosion. Although this kind of energy-change device has been widely used for a long time [2],recently researchers are aiming to substitute simple and cheaper techniques for the fabrication of SCB [3-4].

In the 1970s, carbon film was used as an electrically induced exothermic material for energy-change device in Chinain floor heating [5].Graphite was added as a binder to make the sizing agent, and then the sizing agent was smeared on the substrate attached to electrodes. The carbon film formed after solidification had a high resistance (about 700~14000 $\Omega$ ), due to which a large input voltage of >100V was needed to generate enough heat ignite to the charge compositions. In contrast, the ignition energy being only few dozens of micro joules, the carbon based ignition bridge is very sensitive.

In the early antitank guided missile of the US army, carbon films were used in detonators that used a high level of manufacturing technology [6].

Today semiconductor bridge igniters have more various become popular for advantages that they render. The chip of SCB is made up of polycrystalline silicon semiconductor film[7], the production process of which is complicated and expensive, many researchers have improved its performance by modification [8-9].At present, there are onlyfew reports on the making of Ignition Bridge which use simple methodology and cheaper. In this paper, a micro carbon fiber layer is utilized as an ignition component of the Ignition Bridge. This newly developed production technique for fabrication is simple, safe and reliable. Some of the popularly used energetic materials coupled with the carbon layer in the bridge igniter are investigated and their electric blasting performance properties studied.

#### 2. Experimental section

#### 2.1 Fabrication of carbon bridge igniter

The carbon fiber (Poly Long) purchased

From Shanghai Electronic Technology Co., Ltd. was put in a mortar and ground further into powder. The ground powder was soaked into 10% sodium hydroxide solution for 1 hour to remove impurities. The solution is filtered and the filter cake is washed with ethanol and then dried. This cake along with a curing agent is mixed into a solvent like acetone and then whisked to get a smooth mixture. After evaporation of the solvent and before the solidification of the carbon cake, it is put into amould and pressed under pressure to form the carbon layer or the primary layer of the ignition bridge. The measured resistance of the carbon layer ranges from several ohms to more than ten ohms, and it changes with the carbon filling quantity and the distance between the lead wires. The picture of the carbon packing in the bridge is presented in Fig. 1.



Fig. 1 Carbon based bridge: 1. Carbon based layer2. Electrode plug3. Lead wires

Several kinds of primary explosives and ignition compositions such as (B + KNO<sub>3</sub>)were chosen as a test for energetic material appropriately required for making the bridge igniter according to earlier reports [10]. The mass of the charge was 15 mg, and it was pressed under a pressure of 90 MPa on to the carbon layer. The structure diagram of carbon bridge igniterpacked with energetic material is shown in Fig. 2.



Fig. 2 Structure diagram of charge packed carbon based bridge: 1. Paper gasket 2. Primary explosive 3. Carbon layer 4. Shell 5. Electrode plug and 6. Lead wires

#### 2.2 Ignition performance of carbon bridge igniter

Ignition performance of carbon bridge igniter was studied at different conditions including carbon filling quantity, electrode distance, and different kinds of explosive energetic material. The ignition voltage, ignition energy, ignition time was obtained to understand the ignition performance characteristics of carbon bridge igniter.

The experimental setup for evaluating the ignition performancecharacteristics consists of

energy-storage initiator (ALG-CN1, developed by Nanjing University of Science & Technology)optical probe (developed by Nanjing University of Science & Technology), digital oscilloscope (Tektronix MDO3034), andother accessories as presented in Fig 3. The tantalum capacitor with 47 µF was chosen as the energystorage capacitor. It has a small internal resistance and leak current but a high speed of discharge. When the circuit is connected it charges the capacitor to reach the experimental voltage, which then ignites the charge in the carbon based Ignition Bridge. The voltage signal, current signal and optical signal of the ignition bridge are recorded simultaneously by digital oscilloscope.



Fig. 3 Experimental set-up for pulse discharges:1.Discharge facility 2. Ignition Bridge 3.Optical probe4.Optical channels 5.Digital oscilloscope 6.Currentchannels 7.Voltage channels 8.Holder

# 2.3 Safety performance and ambient adaptability of carbon bridge igniter

The most fundamental requirement for initiating any explosive device is its safety and reliability. These are bound to depend on the safe handling and functional exertion the weapon system goes through. Research on

the safety performance of carbon bridge igniter is focused on two aspects: Anti-static electricity capacity and safety current. As for the ambient adaptability of carbon bridge igniter the ignition performance at high-low temperature and high-low humidity conditions were examined.

According to the GJB736.11-90 (the standard number of China military standard) electrostatic spark sensitivity tester (JGY-50Ⅲ) was used to measure the 50%-firing voltage by reducing the series resistance. The experimental study made on the carbon bridge igniter by thelifting-method was performed with a constant current source (ALG-HL-20A, developed by Nanjing University of Science & Technology) to get the minimum no-firing current. Based on the current, further experiment was carried out to get the safe current for 5 min. The samples are placed in a thermostat at a temperature of 70 °C and -50 °C for 2 hours, and in a humidistat (RH=95%, 30 °C) for 48 hours, respectively. Then, the samples are tested for the pulse discharges experiment.

#### 3. Results and Discussion

3.1 The Current-Voltage and light-time curves of the carbon bridge igniter

In order to have a preliminary understanding of the ignition performance of carbon bridge igniter, current-voltage and light-time curves were obtained as shown in Fig 4.



(a) Carbon based



(b) Bridge wire



( c ) Semiconductor Fig. 4 Current-Voltage curve of three common igniting bridge Form the three curves of Fig. 4, one can see that the carbon based electric ignition bridge is similar to the bridge wire ignition bridge in its voltage but curve shows а larger resistance characteristics in its current curve. The currentvoltage curve of carbon bridge igniter is different when compared with semiconductor bridge. From the light-time curves, bridge wire igniter has the shortest firing time (124µs), Carbon based igniter has the longest (256 µs), SCB was intermediate (190 µs). For safety reasons an igniter system need some optimum firing time and so from that point of view the carbon igniter is better.

# 3.2 Effect of carbon filling quantity on the ignition performance

In order to investigate the effect of quantity of carbon filling on the performance of Ignition Bridge, different mass of carbon was added to fabricate the ignition bridge.Minimum all-firing voltage, firing energy etc., were tested the results of which are shown in Fig 5 and Fig 6.





(b)

(a)





Fig.5 Ignition process of different mass of carbon filling quantity on the bridge:

(a) 0.6 mg (b) 1.2 mg (c) 2.4 mg (d) 3.6 mg and (e) 4.8 mg





From Fig. 5 and Fig. 6, it is observed that the highest electrical discharge is at the filling quantity of 1.2 mg carbon with a minimumallfiring voltage of 20.6V. With the increase in the quantity of carbon, theminimum all-firing voltage decreases first, and then rises gradually. The electrical discharge in the carbon component generatesan electric sparkfrom the end face which ignites the charge material. The smallest ignition voltage is obtained when the carbon layer and the end face of the primary explosive layer are equal in length. If the carbon layer is not equal then either the electrical conductivity is low or electric spark get masked and the bridge performance is poor.Based on the formula  $E=1/2CU^2$ , under a certain capacity, the larger the firing voltage, the higher is the firing energy.

# 3.3 Effect of lead wires distance on the ignition performance

In order to investigate the effect of electrode distance on the ignition performance, three kinds of Ignition Bridge that contain1.2mg carbon each and coupled with lead styphnate as energetic material are studied. The lead wires are successively placed at a distance of 2.4mm, 3.1mm, and 4.2mm respectively the results of which are presented in Table-1. Table-1 Effectofelectrodedistanceonignitionperformanceofcarbonbridgeigniter

Electrode distancemm	Minimum all- firing voltage V	Firing energy mJ	Firing time μs
2.4	17.3	0.37	197.8
3.1	20.6	0.41	164.3
4.2	28.8	0.76	120.9

The smaller the electrode distance the lower is the minimum total ignition voltage, and longer is the ignition time. On the basis of the calculation formula of field intensity E=U/d, with a certain voltage, the smaller the polar distance the larger is the field intensity. The internal resistance gets smaller when the electrode distance reduces and the current across the carbon based is larger. When electric sparkgenerated ismore it is easy to ignite the charge. There is a critical energy for the ignition of charge,  $E = \int P dt = \int UI dt =$ the  $\int \frac{U^2}{R} dt = \int I^2 R dt$ , under the presence of a certain resistance, the smaller the voltage, the smaller is the current and the longer is the ignition time.

# 3.4 Effect of different agents on the ignition performance

The ignition performance of carbon bridge igniter with lead wires distance of 3.1 mm,

carbon filling of 1.2 mg, and with different energetic materials like lead styphnate, lead azide, lead picrate, nickel hydrazine nitrate and B+KNO3, are studied. Lead styphnate, lead azide, lead picrate and nickel hydrazine nitrate were prepared by the method reported [11] and the mixture B+KNO3 was prepared according to standard WJ- 2497-97-China. The voltage-time curves of five energetic materials are presented in Fig 7.The minimum firing voltage, maximum no-firing voltage and minimum all-firing voltage are obtained by using D-optimization method (Table-2).



Fig. 7 Voltage-time curves of five energetic materials

Table-2	D-optimization	method	results of	five	different	charges
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Agent	Minimum all-firing voltage V	Maximum no-firing voltage V	50%-firing voltage V	Minimum firing voltage V
lead styphnate	20.6	12.9	17.6	14.3
lead azide	26.1	17.5	21.4	17.2
lead picrate	42.2	25.8	36.5	26.9
nickel hydrazine nitrate	31.4	21.3	27.7	20.5
B+KNO <sub>3</sub>	38.7	23.2	33.6	23.8

On comparison of 50%-firing voltage, allfiring voltage, and the voltage-time curves of five charge agents, the order of electrospark sensitivity can be obtained as:

lead Styphnate > lead azide > nickel
hydrazine nitrate>B+KNO<sub>3</sub>>lead picrate.

# 3.5 Determination of end-to-end antistatic electricity discharge

End-to-end antistatic electricity dischargedetermination was carried out on the carbon bridge igniter coupled with lead styphnate as the energetic material. This bridge has a capacitance of 500 pF, and a series resistor of 5000  $\Omega$  is added to it, the 50%-firing voltage is 50 KV. (The end-to-end antistatic voltage of common SCB is about 20 KV). When the series resistor is 500  $\Omega$ , the end-to-end antistatic voltage of the carbon electric ignition bridge is larger than 53 KV and its performance is quite good. This is the distinct advantage of the carbon bridge igniter. The excellent antistatic performance is related to the electrical characteristics of the carbon layer and this is worthy of further studies.

#### 3.6 Safe current of the carbon bridge igniter

Carbon bridge igniter with lead wire distance of 3.1 mm and coupled with lead styphnate(<75µm) layerwas tested for safe current evaluation. The measured safe current of this bridge is only 0.38A. In order to increase its safe current, a negative temperature coefficient (NTC) thermistor(R<sub>25</sub> = 5 $\Omega$ ) was added in parallel. The NTC thermistor is used to shunt the current. It has a high sensitivity, stable property, and has quick response to temperature change. On this condition, the bridge can deal with up to 1 A of current for 5 mins without firing. With the addition of NTC thermistor the ignition performance does not change, suggesting the thermistor to be effective for the enhancement of the safety of the carbon bridge.

# 3.7 Ignition performance under varying temperature and humidity conditions

The carbon bridge igniter with a lead wire distance of 3.1 mm and charged with lead styphnate (75  $\mu$ m) is stored at ahigh temperatureof 70°C and low temperature condition of -50°C. Then the samples were tested for the pulse discharges experiment. The discharge capacitor is 47 $\mu$ F, and the firing time and energy are recorded under two input voltages of 40 and 60 V. These results are presented in Table-3.

Table-3 Ignition performance of carbon bridge under 70°C and -50°C (in parentheses)

Input Voltage V	Average time Ms	Standard deviation Ms	Average energy mJ	Standard deviation mJ
40	130.5 (130.8)	4.49 (3.52)	2.05 (2.10)	0.25 (0.27)
60	123.6 (124.3)	4.67 (3.48)	2.62 (2.58)	0.20 (0.27)

Comparing the data from the Table-3 with that in Fig 5, we can see that under a certain condition, the firing time and energy under 70°C and -50°C is similar to that achieved under normal condition. Thus, a high-low temperature has no effect on the ignition performance of the carbon bridge igniter. It might be because the ignition mechanism of the carbon bridge igniter is different from the plasma ignition of SCB. The carbon bridge igniter produces electric spark and then ignites the energetic material indicating that it is less influenced by external environment.

Two experiments were performed at a constant temperature of 30°C and high humidity conditions of 95% RH. In the first case the carbon bridge is charged initially and then stored in the conditions of high humidity at 30°C. In the second case the carbon bridge is first stored in the high humidity condition and then charged later. These results are presented in Table 4.

Table-4 Ignition performance of Carbon Bridge under 30°C, 95% RH before charging and after charging (in parentheses)

Input Voltage V	Average time Ms	Standard deviation Ms	Average energy mJ	Standard deviation mJ
40	146.0 (131.7)	4.89 (6.28)	2.32(2.04)	0.33 (0.31)
60	141.5 (124.4)	3.69 (5.72)	2.95(2.55)	0.38 (0.35)

It is observed from Table-4 that the ignition time and firing energy of the charged

carbon bridge igniter at 30°C, 95% RH is larger than at normal condition, which suggests that the ignition performance of the carbon bridge degenerates at high humidity. This waning may be due the deterioration of the energetic materials with dampness. However, if the naked bridge goes through high humidity conditions and then charged the firing time and energy is almost same as with that under normal condition. Therefore, thecarbon bridge igniter canwithstand humid environment.

### 3.8 Ignition performance of different bridge The ignition performance of different ignition bridges is compared with an electrode distance

of 3.1 mm, carbon filling quality of 1.2 mg, and layered with lead styphnate (<75µm) are tested (Table-5).

Table-5 Ignition performance of different bridges

Type of ignition bridge	50%- firing voltage V	Minimum all-firing voltage V	Maximum no-firing voltage V
Carbon ignition bridge	17.6	20.6	12.9
Bridge wire ignition bridge	15.3	19.6	11.1
Semiconductor bridge	8.9	11.2	6.6

Form the results of Table-5 it is concluded that carbon ignition bridge performance is almost similar to that of bridge wire ignition bridgeHowever., at this stage it is the most insensitive as its minimum all-firing voltage is high (20.6V, electrode distance 3.1 mm) compared to SCB.. It may not be conducive to use as such, but this is just the beginning and with further improvements in the structure and morphology of carbon layer, it is envisaged that the ignition performance will be better without compromising the safety. Further research in this direction is under progress.

#### 4. Conclusion

Carbon was used as ignition components to make carbon electric ignition bridge, and its ignition performance was studied. The results are as follows:

- The carbon Ignition Bridge has a larger resistor compared with traditional bridge wire Ignition Bridge.
- (2) Within a certain range, with the increase of carbon filling quantity, minimum total ignition voltage drops before it rises determining the optimal working condition. When the electrode distance is 2.4mm, the carbon filling quantity is 1.2mg, the minimum all-firing voltage is 17.3 V.

- (3) The order of electro-spark sensitivity of ignition bridge layered with five kinds of energetic material is lead styphnate>lead azide>nickel hydrazine nitrate>B+KNO<sub>3</sub>>lead picrate.
- (4) The carbon bridge igniter has a strong static electricity protection capability.
   The mechanism of ignition in the carbon bridge igniteris worth for further studies.

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# *E*LECTRICAL POWER FROM NUCLEAR ENERGY: AN UP-TO-

### **DATE OVERVIEW**

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#### **1. Introduction**

Of all power producing processes, nuclear energy is probably the most well known. In the United States, about 100 nuclear reactors produce 20 percent of the electricity needs. Around the world, there are between 400 and 500 reactors producing nearly 20 percent of the world's electricity. Historically, there have been two main types of reactors—pressurized water reactors (PWR) and boiling water reactors (BWR). Both types use energy from nuclear fission of fissile nuclei such as uranium -235 to heat water that will generate steam to turn a turbine that runs a generator, sending the electricity out to the public. In the PWR, the steam does not come in contact with the radioactive material as it does in the BWR.Today, in addition to the PWR and BWR, there are technologies being researched within the power industry to make the process safer, cleaner, and more efficient.

In cases where stringing electrical lines proves difficult, for instance, in remote areas nuclear radiation sources are used to produce electrical or thermal power. These sources can be used to power spacecraft and satellites, the lights on ocean buoys, and remote weather stations. They can also be used to generate electrical power for consumer use as is done in a nuclear reactor.

Waste from nuclear fission reactors produce radiations. There are other radioactive materials that produce radiations too. This radiation has tremendous energy. Radioactive decay is the process in which an unstable atomic nucleus loses energy by emitting ionizing particles and radiation. Energy is released by a radioactive nucleus during its decay. The radioactive nucleus releasing energy during its decay is called parent nuclide and the decay product is called daughter nuclide.

The energy difference of the parent and daughter nuclides can be written as Q:

Q = (Kinetic energy after the decay - Kinetic energy before the decay) $= (rest mass before x C^2) - (rest mass after x C^2)$ 

where 'C' is the velocity of light.

Nuclear decay energy is usually quoted in terms of the energy units - MeV (million electron volts) or keV (thousand electron volts).

Types of radioactive decay includesgamma rays, beta decay (decay energy is divided between the emitted electron and the neutrino which is emitted at the same time) and alpha decay. The decay energy can be calculated from the mass difference *dm* between the parent and the daughter atom and particles.

#### 2. Atomic Batteries - Energy from Radioactivity

The nucleus <sup>60</sup>Co decays into <sup>60</sup>Ni. The mass difference dm is 0.003 amu. The radiated energy is approximately 2.8 MeV and the half life of <sup>60</sup>Co is 5.27 year. From this data the radiation power for  ${}^{60}$ Co works out to be 17.9 W/g. It is relatively long lasting, low powerdensity and high energy power supply. The family of devices that convert these radiations to electrical power is known as Atomic Batteries. This conversion is classified into two main types: thermal and non-thermal. Thermal conversion uses the energy of the radiation to heat a target, which is then converted to electricity using a thermocouple or thermoelectric materials. Non thermal converters do not depend on the thermal energy of radiation. Here radiation is used to induce charge which is then converted to electricity.

These batteries have been employed to enable compact and high energy capacity power generators for applications ranging from implantable cardiac cardiacpacemakers to space stations [1,2]. Atomic batteries can be used for high energy applications typically with low power density and 20% efficiency at best. The cost analysis shows Sr-90 and Cs-137 batteries to be very promising.

Radiation power in *W/g* for several isotopes is as follows:

<sup>60</sup>Co: 17.9, <sup>238</sup>Pu: 0.57, <sup>137</sup>Cs: 0.6, <sup>241</sup>Am: 0.1, <sup>210</sup>Po: 140 (T=136 d), <sup>90</sup>Sr: 0.9

To compare their performances, one considers the power and energy density of various types of energy storage devices. Such a plot is known as a Ragone plot [2,3]. Figure 1 presents a Ragone plot of atomic batteries made of some commonly used radioactive materials and compares them to commonly used batteries. The sloped lines are constant-time lines. The numbers for atomic batteries are calculated as shown in the previous section, assuming an efficiency of 0.1. This shows that atomic batteries are high energy density and relatively low power density devices.



Fig. 1 Ragone plot for various batteries including Atomic batteries.

[Adopted from Ref. 4].

Currently, radioisotope power generators are being developed for realizing safe, compact, high energy capacity and long lifetime batteries. These find applications in remote wireless sensor microsystems ranging for environmental health monitoring to structural health monitoring[5,6].They are also employed in a variety of industrial applications including electron capture devices for gas chromatography.

# 3. Nanomaterials turn nuclear energy directly into electricity

Materials that directly convert radiation from nuclear materials not into heat but into electricity could produce a new era of spacecraft and even Earth-based vehicles powered by high-powered nuclear batteries, say US researchers.LiviuPopa-Simil, former Los Alamos National Laboratory nuclear engineer and founder of private research and development company LAVM and CludiyMuntel, of Alabama A&M University, US, say transforming the energy of radioactive particles into electricity is more effective. The materials they are testing would extract up to 20 times more power from radioactive decay than thermoelectric materials. Tests of layered tiles of carbon nanotubes packed with gold and surrounded by lithium hydride under way. Radioactive particles that slam are into the gold push out a shower of highelectrons. These electrons pass through energy carbon nanotubes and pass into the lithium hydride from where they move into would be best used to create electricity using a radioactive material, because they could be embedded directly where radiation is greatest. But they could also harvest power directly from a fission reactor's radiation.Devices based on the material could be small enough to power anything from interplanetary probes to aircraft and land vehicles, he adds.

A paper on the new nuclear power materials was presented on 25 March, at the Materials Research Society Spring Meeting 2008, San Francisco, California, US [7].

#### 4. Radioisotope Thermoelectric Generators

thermoelectric A radioisotope electrical generator (RTG, RITEG) is an generator that uses an array of thermocouples to convert the heat released by the decay of suitable radioactive material into electricity by the Seebeck effect[8]. An RTG has no moving parts. RTGs and nuclear power reactors use very different nuclear reactions. Nuclear power reactors use controlled nuclear fission in a chain reaction. Chain reactions do not occur in RTGs, so heat is produced at an unchangeable, though steadily decreasing rate that depends only on the amount of fuel isotope and its half-life. An accidental power excursion is impossible.

RTGs are usually the most desirable power source for unmaintained situations that need a few hundred watts (or less) of power for durations too long for fuel cells, batteries, or generators to provide economically, and in places where solar cells are not practical. The RTG electricity can be used for powering scientific instruments and communication to Earth on the probes [9].

RTGs were developed in the US during the late 1950s by Mound Laboratories in Miamisburg, Ohio under contract with the United States Atomic Energy Commission. The first RTG launched into space by the United States was SNAP 3 in 1961, aboard the Navy Transit 4A spacecraft. One of the first terrestrial uses of RTGs was in 1966 by the US Navy at uninhabited Fairway Rock in Alaska. RTGs were used at that site until 1995.

In the past, small "plutonium cells" (very small <sup>238</sup>Pu-powered RTGs) were used in implanted heart pacemakers to ensure a very long "battery life" [10]. As of 2004 about 90 are still in use. They were used with Pioneer 10, Pioneer 11, Voyager 1, Voyager 2, Ulysses, Cassini, New Horizonsandthe Mars Science Laboratory. RTGs were used to power the two Viking landers and for the scientific experiments left on the Moon by the crews of Apollo 12. RTGs were also used for the Nimbus, Transit and LES satellites.

In addition to spacecraft, the Soviet Union constructed many unmanned lighthouses and navigation beacons powered by RTGs [11]. Powered by strontium-90 (<sup>90</sup>Sr), they are very reliable and provide a steady source of power. There are approximately 1,000 such RTGs in Russia. All of them have long exhausted their 10-year engineered life spans. They are likely no longer functional, and may be in need of dismantling.

Because of the shortage of plutonium-238, a new kind of RTG assisted by subcritical reactions has been proposed [12]. In this kind of RTG, the alpha decay from the radioisotope is also used in alpha-neutron reactions with a suitable element such as beryllium. Although the number of fissions produced in the RTG is very small (making their gamma radiation negligible), because each fission reaction releases almost 30 times more energy than each alpha decay (200 MeV compared to 6 MeV), up to a 10% energy gain is attainable, which translates into a reduction of the <sup>238</sup>Pu needed per mission. The idea was proposed to NASA in 2012 for the yearly NASA NSPIRE competition, which translated to Idaho National Laboratory at the Centerfor Space Nuclear Research (CSNR) in 2013 for studies of feasibility [13]. However, the essential design has not changed.

RTG have been proposed for use on realistic interstellar precursor missions and interstellar probes [9]. An example of this is the Innovative Interstellar Explorer (2003–current) proposal from NASA[14].A RTG using <sup>241</sup>Am was proposed for this type of mission in 2002.This could support mission extensions up to 1000 1000 years on the interstellar probe, because the power output would be more stable in the longterm than plutonium. Other isotopes for RTG were also examined in the study, looking at traits such as watt/gram, half-life, and decay products.An interstellar probe proposal from 1999 suggested using three advanced radioisotope power source (ARPS) [15].One mission proposed using the electricity to power ion engines, calling this method radioisotope electric propulsion (REP).

#### 4.1 Design of RTGs

An RTG consists of a sturdy container of a radioactive material (the fuel). Thermocouples are placed in the walls of the container, with the outer end of each thermocouple connected to a heat sink. Radioactive decay of the fuel produces heat which flows through the thermocouples to the heat sink, generating electricity in the process.

A thermocouple is a thermoelectric device that converts thermal energy directly into electrical energy using the Seebeck effect. It is made of two kinds of metal (or semiconductors) that can both conduct electricity. The principle of a thermocouple involves two plates, each made of a different metal that conducts electricity. Joining these two plates to form a closed electrical circuit while keeping the two junctions at different temperatures produces an electric current. Each of these pairs of junctions forms an individual thermocouple.. In an RTG, the radioisotope fuel heats one of these junctions while the other iunction remains unheated and is cooled by the

space environment or a planetary atmosphere.They are connected to each other in a closed loop. If the two junctions are at different temperatures, an electric current will flow in the loop. Thermocouples, though very reliable and long-lasting, are very inefficient. However, efficiencies above 10% have never been achieved and most RTGs have efficiencies between 3–7%.

Studies have been done on improving efficiency by using other technologies such as generation of electricity from heat i.e., thermoelectric materials. For space missions the thermoelectric materials that have included to date are silicon– germanium alloys, lead telluride and tellurides of antimony, germanium and silver (TAGS). Achieving higher efficiency would mean that less radioactive fuel is needed to produce the same amount of power, and therefore a lighter overall weight for the generator. This is a critically important factor in spaceflight launch cost considerations.

The other next method is the use of a thermionic converter. It is an energy conversion device which relies on the principle of thermionic emission. It achieve can efficiencies between 10-20%, but requires higher temperatures than those at which standard RTGs run. Some prototype <sup>210</sup>Po RTGs have thermionics, and potentially other used extremely radioactive isotopes could also provide power by this means, but short half-lives make these unfeasible.

Another alternative isby using thermo-photovoltaic cells. These cells work by the same principles as a photovoltaic cell. except that they convert infrared light emitted by a hot surface rather than visible light into electricity. Thermophotovoltaic cells have slightly higherefficiency than thermocouples and can be overlaid on top of thermocouples, potentially doubling efficiency. Systems with radioisotope generators simulated by electric heaters have demonstrated efficiencies of 20%[16], but have not been tested with actual radioisotopes. Some theoretical thermophotovoltaic cell designs have efficiencies up to 30%, but these have yet to be built or confirmed.

Dynamic generators can provide power at more than 4 times the conversion efficiency of RTGs. NASA and DOE have been developing a nextgeneration radioisotope-fueled power source called the Stirling Radioisotope Generator (SRG) that uses free-piston Stirling engines coupled to linear alternators to convert heat to electricity. SRG prototypes demonstrated an average efficiency of 23%. Greater efficiency can be achieved by increasing the temperature ratio between the hot and cold ends of the generator. The use of noncontacting moving parts, non-degrading flexural bearings, and a lubrication-free and hermetically sealed environment have demonstrated no appreciable degradation over years of operation. Experimental resultsdemonstrate that an SRG could continue running for decades without maintenance. Vibration can be eliminated as a concern by implementation of dynamic balancing

or use of dual-opposed piston movement. Potential applications of a Stirling radioisotope power system include exploration and science missions to deep-space, Mars, and the Moon.

#### 4.2 Criteria for selection of isotopes

The radioactive material used in RTGs must have several characteristics like its half-life must be long enough so that it will release energy at a relatively constant rate for a reasonable amount of time. The amount of energy released per time (power) of a given quantity is inversely proportional to half-life. Therefore typical halflives for radioisotopes used in RTGs are several decades, although isotopes with shorter half-lives could be used for specialized applications. Energy release per decay is proportional to power production per mole and alpha decays in general release about 10 times as much energy as the beta decay of <sup>90</sup>Sr or<sup>137</sup>Cs. Radiation must be of a type easily absorbed and transformed into thermal radiation, preferably alpha radiation. Isotopes must not produce significant amounts of gamma, neutron radiation or penetrating radiation in general through other decay modes or decay chain productsConsidering the above criteria the number of possible fuels would be fewer than 30 atomic isotopeswithin the entire table of nuclides. <sup>238</sup>Pu, <sup>244</sup>Cm and <sup>90</sup>Sr are the most used isotopes even though other isotopes such as <sup>210</sup>Po, <sup>147</sup>Pm, <sup>137</sup>Cs, <sup>144</sup>Ce, <sup>106</sup>Ru, <sup>60</sup>Co, <sup>242</sup>Cm, <sup>214</sup>Am and isotopes of thulium have also been studied.

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Plutonium-238 has a half-life of 87.7 years, reasonable power density of 0.54 watts per gram, and exceptionally low gamma and neutron radiation levels. It needs less than 2.5 mm of lead shielding to block the radiation. No shielding is needed in a <sup>238</sup>Pu RTG, as the casing itself is adequate to block the radiation.  $^{238}$ Pu has become the most widely used fuel for RTGs, in the form of plutonium(IV) oxide (PuO<sub>2</sub>).

Unlike the other RTG fuels,  $^{238}$ Pu must be specifically synthesized and is not abundant as a nuclear waste product. At present only Russia has maintained consistent  $^{238}$ Pu production, while the USA restarted production at ~1.5 kg a year in 2013 after a ~25-year hiatus.

are the only countries with declared production of <sup>238</sup>Pu in quantities useful for RTGs. <sup>238</sup>Pu is produced at typically 85% purity and its purity decreases over time.

Strontium-90 has been used by the Soviet Union in terrestrial RTGs. <sup>90</sup>Sr decays by  $\beta$  emission, with minor  $\gamma$  emission. While its half life of 28.8 years is much shorter than that of <sup>238</sup>Pu, it also has a much lower decay energy; its power density is only 0.46 watts per gram. Because the energy output is lower it reaches lower temperatures than <sup>238</sup>Pu, which results in lower RTG efficiency. <sup>90</sup>Sr is a high yield waste product of nuclear fission and is available in large quantities at a low price.

Some prototype RTGs first built in 1958 by the US Atomic Energy Commission, have used polonium-210. This isotope provides phenomenal power density (pure <sup>210</sup>Po emits140 W/g) because of its high decay rate, but has limited use because of its very short half-life of 138 days. A half-gram sample of <sup>210</sup>Po reaches temperatures of over 500 °C (900 °F).

Americium-241 is a potential candidate isotope with a longer half-life than <sup>238</sup>Pu: <sup>241</sup>Am has a half-life of 432 years and could hypothetically power a device for centuries. However, the power density of <sup>241</sup>Am is only 1/4 that of <sup>238</sup>Pu. and <sup>241</sup>Am produces more penetrating radiation through decay chain products than <sup>238</sup>Pu and needs more shielding. Even so, its shielding requirements in an RTG are the second lowest of all possible isotopes. With a current global shortage of <sup>238</sup>Pu,<sup>241</sup>Am is being studied as next alternative RTG fuel. The advantage of <sup>241</sup>Am over <sup>238</sup>Pu is that it is produced as nuclear waste and is nearly isotopically pure. Prototype designs of<sup>241</sup>Am RTGs expect 2-2.2 W<sub>e</sub>/kg for 5-50 W<sub>e</sub> RTGs design, putting <sup>241</sup>Am RTGs at parity with <sup>238</sup>Pu RTGs within that power range [7].

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### **REPORT ON THERMANS 2016**

The Twentieth National Symposium & Workshop on Thermal Analysis (THERMANS-2016) was held at Indian Institute of Technology (Banaras Hindu University), Varanasi during January 18-22, 2016.

There was overwhelming response to the symposium and workshop. In all there were 200 registered participants from academic and research institutions with a significant percentage of student and research scholar participants.

Prof. D. Giri, Head of the Department of Physics, IIT (BHU) welcomed the participants of this symposium. Dr. Shyamala Bharadwaj, Chairperson of the Organizing Committee of the Symposium gave brief introduction to the Symposium highlighting the salient features of the three day technical program which covered a wide range of topics in Thermal Analysis.

The symposium was inaugurated by Dr. K. L. Ramakumar, Director, Radiochemistry & Isotope Group, BARC. He pointed out the active role played by thermal analysis techniques in characterization of materials for specific purposes. He also emphasized the fact that thermal analysis will have a greater role to play in the coming years as the Department of Atomic Energy is taking on the challenging tasks pertaining to PFBR, AHWR, CHTR fuel development, materials problems for ADS, SOFC, thermo-chemical water splitting for production of hydrogen using nuclear heat etc. Dr. Kannan, President, ITAS gave an account of the activities of the Indian Thermal Analysis Society. He acknowledged the financial support from BRNS and the enthusiasm of local organizers from various universities and other national laboratories.

Prof. G.V.S. Sastry, Director, IIT (BHU) in his Presidential address, talked about the several collaborative projects between Department of Atomic Energy and IIT (BHU) and the role of thermal analysis in solving several scientific challenges encountered during those projects.

The proceedings of the symposium containing the lectures from experts were released by Dr. K. L. Ramakumar and were distributed to the delegates. A Souvenir was brought out by the Indian Thermal Analysis Society on this occasion and was released by Prof. G.V.S. Sastry.

Shri. Deepak Tyagi, Secretary, THERMANS 2016 announced the names of winners of several awardees. The Awards were distributed by the distinguished dignitaries present at the Inaugural Function. SETARAM-ITAS Calorimetry Excellence Award was shared between Dr. K. Nagarajan of IGCAR, Kalpakkamand Dr. G. Suresh Kumar of CSIR-IICB, Kolkata. For his outstanding contributions in the field of thermal analysis, the NETZSCH-ITAS Award 2016 was conferred on Dr. Ratikanta Mishra of BARC. Dr. A.M. Banerjee from BARC was selected for the TA Instruments-ITAS Young Scientist Award 2016. Dr. R. Ramani of DMSRDE, Kanpur was conferred the Metler Toledo Thermal Analysis Award 2016. Dr. M. D. Karkhanavala Memorial Essay Contest 2016 was won by Shri. S. Paulose. SRF, VSSC, Thiruvananthapuram. Dr. Gurdip Singh Award for Best Thesis in Thermal Analysis 2016 was given to Dr (Ms.). D. Bhowmick of CSIR-IICB, Kolkata.

The Inaugural Function ended with a vote of thanks proposed by Dr. Salil Varma, Convenor of THERMANS 2016.



Inaugural function of THERMANS 2016. From right to left: Dr. Salil Varma (Convenor, THERMANS- 2016), Dr. S. Kannan, President, ITAS), Prof. G.V.S. Sastry (Director, IIT(BHU) Varanasi),K. L. Ramakumar(Director, Radiochemistry and Isotopes Group, BARC), Dr. Shyamala Bharadwaj (Chairperson, Organizing Committee, THERMANS 2016) and Prof. D. Giri (Head, Department of Physics IIT(BHU) Varanasi).

The Symposium had 9 technical sessions, 1 instrumentation session and 11 invited lectures. One of the invited lectures was from Prof. R. Novakovic of CNR-IENI, Genova, Italy. More than 150 research papers were presented at the symposium in both oral and poster sessions. ITAS awarded cash and merit certificates for best papers presented in both oral and poster sessions. In order to encourage the young researchers in the field of thermal analysis, the oral presentations were restricted to research scholars below the age of 35.

Prof. B. N. Dwivedi, Department of Physics, IIT (BHU), Varanasi presented an interesting Evening Talk on "Physics of Sunshine". This was followed by another thought provoking Evening Talk by Dr. B.N. Jagatap Director, Chemistry Group, BARC on "Scientific Innovations".

In the THERMANS 2016 workshop, there were 60 research scholars and student participants. There were 10 invited lectures by eminent scientists on various aspects of thermal analysis. Various topics on the application of thermal analysis in determination of phase diagrams, in the areas of electrochemistry, catalysis and analytical chemistry were dealt with. Department of Physics, IIT (BHU) Varanasi, arranged for practical demonstration of some of the thermo analytical techniques to the students.

#### **BOOK REVIEW**



#### Inorganic Hydrazine Derivatives Synthesis, Properties and Applications

Edited by K. C. Patil, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India and Tanu Mimani Rattan, Department of Physics, Sri Sathya Sai Institute of Higher Learning, Prasanthi Nilayam, India Published by John Wiley & Sons Pvt. Ltd. UK (2014)

The chemistry of hydrazine and its derivatives has attracted a lot of attention since 1950's. The importance of these compounds stems from a variety of factors, which include high energy density, reactivity and their ready availability. So it is not surprising that hydrazine and their derivatives find use as fuels, reducing agents, additives and as specialty chemicals. Entrants to this research field have to acquire a quick birds' eye view of the chemistry. Because applications of these compounds range from space research to laboratory scale organic synthesis, it is difficult to get all the information readily in one place. So in spite of their relevance, not many books are available on this specialized topic. The most authoritative source of information, apart from the primary literature, became available in 1984 when Eckart Walter Schmidt brought out an excellent treatise. This massive tome on "Hydrazine and its derivatives: preparation, properties, applications" came out in a second edition in 2001 by the same author with almost double the number of pages (2200). Fourteen years have passed without any authoritative book in this area although the chemistry surrounding hydrazine has grown by leaps and bounds. So the current book "Inorganic Hydrazine Derivatives: Synthesis, Properties and Applications" edited by K.C. Patil and Tanu M. Rattan is most welcome. It is not surprising that the book is dedicated to E. W. Schmidt

It is probably the only book on this very important molecule which gives the researcher an accelerated start to the chemistry of hydrazine in about 250 pages. The book is a compendium of five chapters edited by K. C. Patil and Tanu Rattan and authored by three scientists including the editors. All of them have extensive experience in the area of hydrazine chemistry having spent their research careers almost completely working with hydrazine and their derivatives. In a nutshell, the book is an excellent introduction to this unique molecule and their inorganic derivatives.

The book is organized in a very logical and convenient way, according to the type of compounds formed by hydrazine. If you are not sure about the type of compound, then reading the first chapter is a must which gives you a clear idea of what each chapter is talking about. But if, for example you know that you are interested in metal hydrazine complexes, you can go directly to the relevant chapter. This makes it a very handy reference tool. Apart from summarizing a large body of data on hydrazine compounds, the book quickly brings the reader up to date with the current state of affairs. A special feature of this monograph is that the authors deal with methods to generate inorganic nanomaterials using hydrazine derivatives.

The strength of the book lies in the fact that it deals not only with synthesis and properties of the inorganic derivatives of hydrazine, it also deals with several characterization techniques. Since these molecules are often used as propellants and explosives, the thermal characterization of key molecules are given. For those dealing with these molecules in the industry, ready access to these details would be important especially if they are working in quality control and trouble-shooting. As the authors have characterized several of these molecules using spectroscopy and single crystal X-ray crystallography, they also provide molecular structures of these species. This provides insight into the chemistry of these molecules.

In summary, this book is for those who are interested in a quick summary of hydrazine and the new developments in the use of hydrazine. The book by Patil and Rattan will be quite invaluable for those who plan to start research work in this area. For those who are in the industry and chemical plants where hydrazine derivatives are used, this book is a must because in a very brief form, a large number of compounds are described. Very interestingly, this book is available on iTunes, Kindle and in the traditional hardback paper format!

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