

## Diaminofurazan (DAF): Thermolysis and evaluation as ballistic modifier in double base propellant

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### Abstract

Diaminofurazan (DAF) is used as a precursor in the synthesis of many high performance insensitive high explosives. This paper reports the thermal studies on DAF and its evaluation as a ballistic modifier in double base propellant formulations. Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) revealed that DAF shows two-stage decomposition, whereas the kinetics of initial stage of thermal decomposition of DAF evaluated from TG data gave activation energy ( $E_a$ ) of  $67 \text{ kJ mol}^{-1}$ . The evolution of gases containing species such as CN, NH, OH and oxides of nitrogen during thermal decomposition of DAF was also revealed by hyphenated TG–FTIR data.

Evaluation of DAF as a ballistic modifier in RDX incorporated double base propellant formulations indicated that it brings down the pressure index to 0.20 compared to 0.70 for a control composition in the pressure range 6.9–8.8 MPa when used in combination with basic lead salicylate (BLS). It was observed that DAF does not have adverse effect on vulnerability and chemical stability of the propellant formulation.

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### 1. Introduction

Research is being conducted in many laboratories to design promising building blocks for the development of high density, high performance insensitive high explosives. Possible use of furazans as precursor for development of HEMs was envisaged in the literature as early as 1968 [1]. Moreover these materials could also be used as an energetic additive to modify the ballistic properties when used in nitramine based composite propellant formulation.

Nitramines like RDX and HMX have acquired prominence as energetic component of eco-friendly propellants by virtue of their positive heat of formation ( $+58.5$  and  $+75 \text{ kJ mol}^{-1}$ , respectively), superior chemical and thermal stability as well as presence of reduced pollutants in combustion products and non-smoky exhaust similar to that of double base propellants. However, the major drawback of these formulations is high-pressure index ( $n$ ) values [2,3]. Innumerable efforts made to reduce the “ $n$ ” of nitramine-based systems by conventional bal-

listic modifiers such as lead salicylate, have met with the limited success [4–6]. Search is on for lead free ballistic modifiers to be incorporated in nitramine based double base propellants. Dinitropiperazine (DNP) is reported to be used as an additive capable of reducing the pressure index value of nitramine based propellants in combination with conventional ballistic modifiers [7,8]. Compounds like diaminoglyoxime (DAG) and 3,4-diaminofurazan (DAF) have elicited interest as pressure index suppressants during recent times [9,10]. A lowering of the burning rate and pressure index value ( $n$ ) in composite propellants on incorporation of DAG and DAF is reported by Stoner and Brill [10]. They observed that, DAG and DAF thermolyse on the burning surface of the propellant to form thermally stable melamine type intermediates.

Fast thermolysis studies undertaken by Stoner and Brill [10] have also revealed the formation of large thermally stable cyclic azines along with the evolution of low molecular weight gases namely  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{HCN}$  and  $\text{N}_2\text{O}$  on decomposition of DAG and DAF. Williams et al. [9] suggested that DAG and DAF form a thermally stable cyclic azine, viz., melon (stable up to  $700^\circ\text{C}$ ) in the superficial reaction layer of the burning surface. Such thermally stable products of decomposition are thought to retard heat transfer from the gas phase to the condensed phase.

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During this work, thermal studies on DAF were undertaken by applying simultaneous thermal analysis (STA) and differential scanning calorimetry (DSC) and hyphenated TG–FTIR. During STA experiments, differential thermal analysis (DTA), thermogravimetric (TG) analysis and the derivative of TG of the sample was carried out simultaneously. The potential of DAF as a ballistic modifier for RDX incorporated double base propellant formulations was evaluated by determining strand-burning rates experimentally. The effect of DAF on sensitivity, compatibility and mechanical properties of propellant formulations was also investigated on the lines similar to DAG as reported by Talawar et al. in their previous paper [11].

## 2. Experimental

### 2.1. Materials and methods

The starting materials used in the present study are of laboratory grade and are used directly without purification. The synthesis of DAF was carried out in a Paar reactor. DAG and aqueous potassium hydroxide was maintained at 175 °C for 2 h at 2.8 MPa pressure as reported [12] to yield DAF. It was characterized by elemental analysis (Elemental Analyzer Model EA 1110, Carlo Erba Model) and IR (Perkin-Elmer FTIR spectrophotometer model 1605). The mass spectrum of DAF was recorded on a Finnigan make instrument (Model No. 1020).

DSC curves were obtained by using Perkin-Elmer differential scanning calorimeter (DSC-7). The sample cups were of aluminum close pan and the temperature range employed was 30–600 °C with a heating rate of 10 °C/min in nitrogen atmosphere. Thermal decomposition of DAF was studied thermogravimetrically at the heating rate of 10 °C/min, by using thermal analysis system of Mettler Toledo make (TG/SDTA-8551) in nitrogen atmosphere at a purge rate of 20 ml/min. The sample holder was made up of alumina open cup and instrument was calibrated using standard sample Indium and FTIR was calibrated using Polystyrene. The temperature range employed was 30–600 °C (with a sample mass of 1–2 mg). The gaseous decomposition products were characterized by FTIR (Bruker make – equinox 55) in conjunction with TG. Nitrogen flow at the rate of 20 ml/min was used to carry out evolved gases from TG furnace to FTIR detector through hot tube. The gases were detected by FTIR detector and the gas temperature was kept as high as possible (about 180 °C) to avoid condensation of gases.

RDX based double base propellant formulations (Table 1) were prepared by replacing 10% NC by RDX and processed by

standard solventless extrusion technique [13]. Incorporation of the ingredients was carried out for 3 h. RDX, basic lead salicylate (BLS) and DAF were added during the kneading stage. After drying of the propellant paste in a steam heated hot oven maintained at 50 °C for 6–8 h it was passed through steam heated over rollers maintained at 80 °C. A minimum of 30 passes was required to obtain a good gelatinized sheet. Discs were punched out of these propellant sheets and were then loaded in the press basket, which was also maintained at 80 °C by steam heating. The propellant was extruded in form of strands (3 mm × 150 mm) at an extrusion pressure of 50 kg/cm<sup>2</sup>. The details of the propellant formulations are presented in Table 1.

Impact sensitivity was determined by a standard “Fall Hammer” set-up according to the ‘Bruce Staircase’ approach [14] whereas friction sensitivity was assessed on a Julius Peters apparatus [15] by incrementally increasing the load from 0.2 to 36 kg, till there was no ignition/explosion in five consecutive test samples. Stability aspects were studied based on the evolution of gaseous nitrogen oxide during heating of propellant sample, by applying both qualitative (Abel’s heat test) and quantitative (Bergmann and Junk test) methods as per standard procedure [16]. The calorimetric value of propellant composition was determined in Julius Peters adiabatic bomb calorimeter. The burn rates of propellants at different pressures were determined in indigenously fabricated Crawford Bomb strand burner equipment [17]. Mechanical properties of propellant formulations were determined on Universal Testing Machine (Instron-1185).

## 3. Results and discussion

### 3.1. Thermolysis

DSC of DAF is depicted in Fig. 1. DAF undergoes two-stage decomposition in the temperature range of 170–228 °C ( $T_{\max}$  220 °C) and 228–250 °C ( $T_{\max}$  at ~230 °C). DTA of DAF (Fig. 2) exhibited an endotherm due to phase transition (melting) at 180 °C followed by exothermic decomposition in the temperature range of 235–257 °C with a  $T_{\max}$  at 252 °C. In TGA (Fig. 3), the weight loss corresponding to the first and second

Table 1  
Percentage composition of various propellant ingredients in control composition (C)

Ingredients	Percentage
Nitrocellulose (NC)	49.5
Nitroglycerine (NG)	30.5
RDX	10
Diethyl phthalate (DEP)	7.0
Carbamite	3.0

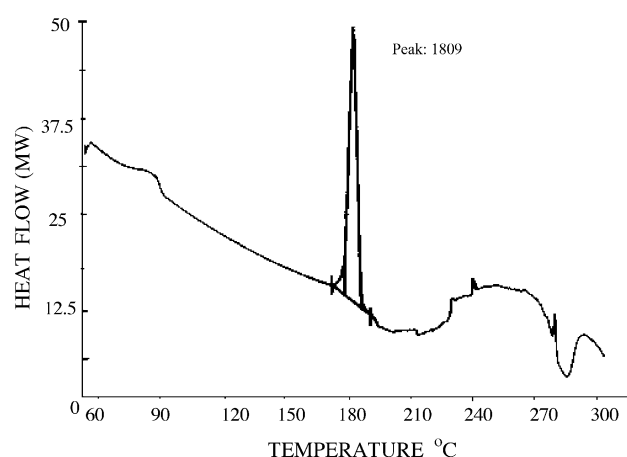


Fig. 1. DSC of DAF.

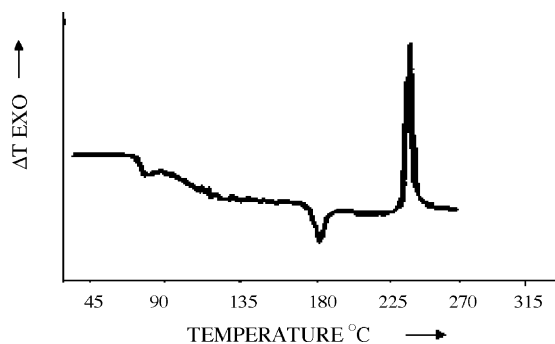


Fig. 2. DTA of DAF.

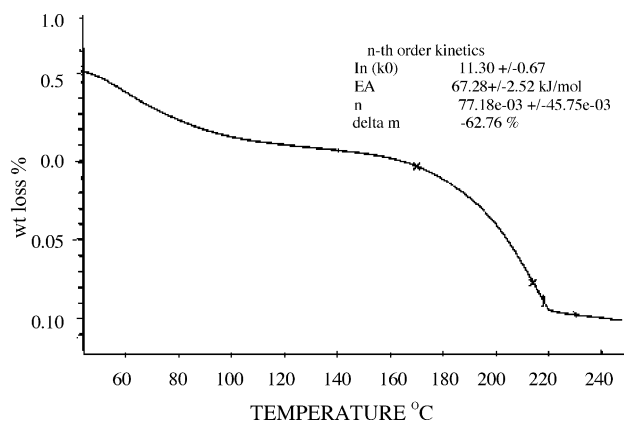


Fig. 3. TG of DAF.

stages of decomposition was of the order of 62 and 14%, respectively. The activation energy of 67 kJ mol<sup>-1</sup> obtained from the experimentally determined TG data by applying Coats–Redfern equation [18] is also in agreement with calculated bond dissociation energy of C–N bond [19,20]. The thermal decomposition of DAF lead to the evolution of gases containing species such as CN (2358 cm<sup>-1</sup>), NH<sub>2</sub> (3743 cm<sup>-1</sup>), OH, (3258 cm<sup>-1</sup>) and oxides of nitrogen as revealed by hyphenated TG–FTIR data (Fig. 4).

### 3.2. IR and mass spectrum

The IR spectrum of DAF (Fig. 5) shows peak at 3158, 2668 and 1420 cm<sup>-1</sup> corresponding to OH, CH, C=N. The mass spectrum of DAF (Fig. 6) exhibited molecular ion with a mass/charge

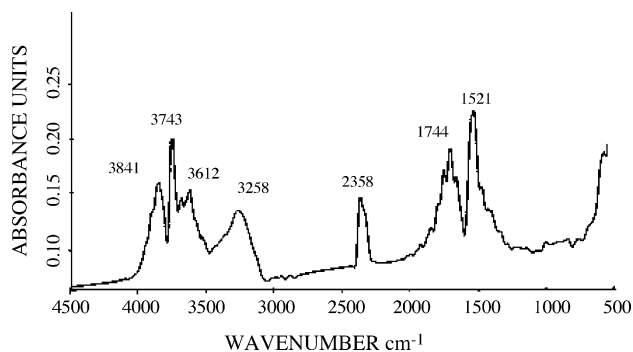


Fig. 4. TG–FTIR of the DAF.

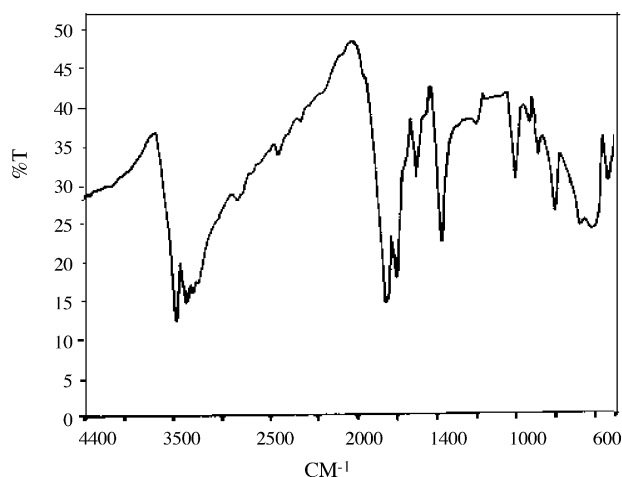


Fig. 5. IR spectrum of DAF.

(*m/z*) ratio of 100, in high abundance and its fragmentation pattern also indicates of the loss of 2 NH<sub>2</sub> and subsequently OH (*m/z* at 70 and 55, respectively).

### 3.3. Evaluation of DAF in double base propellants

#### 3.3.1. Thermophysical properties

Abel heat test results for nitramine formulations containing DAF were found to be well within the acceptance limit of not less than 10 min for change in colour of standard paper. The Bergmann and Junk (B & J) test results also established compatibility of DAF with other propellant ingredients as brought out by volume of nitric oxide (NO) evolved (2–2.4 cm<sup>3</sup>/5 g) on heating of sample at 120 °C which was less than the upper limit of 10 cm<sup>3</sup>/5 g sample. The incorporation of DAF in propellant formulations led to increase in impact energy for explosion (1.08–1.48 J), rendered it less vulnerable to friction stim-

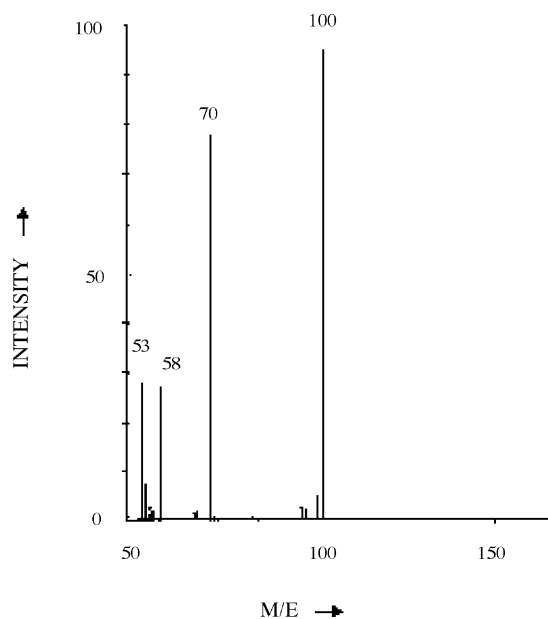


Fig. 6. Mass spectrum of DAF.

Table 2  
Results of impact and friction sensitivity tests of DAF containing formulations

Propellant composition	Impact energy (J)	Impact sensitivity ( $h_{50\%}$ ) (cm)	Friction sensitivity (kg)
Control composition (C)	0.88	44.0	24.0
C + DAF 4 parts	1.08	54.0	28.8
C + DAF 6 parts	1.16	58.0	28.8
C + DAF 4 + BLS 2	1.20	60.0	28.8
C + DAF 6 + BLS 2	1.24	62.0	32.4

Table 3  
Mechanical properties of DAF incorporated double base propellant formulations

Properties	Control (C)	C + DAF 4 parts	C + DAF 6 parts
Tensile strength (kg/cm <sup>2</sup> )	145	117	109
Elongation (%)	15	16	18

Table 4  
Burn rates of DAF based formulations

Propellant composition	Burn rate, mm/s at pressure MPa				$n$ value over pressure range MPa		
	3.5	5	7	9	3.5–0	5–7	7–9
Control (C)	4.4	4.5	6.8	8.3	0.62	0.63	0.79
C + DAF 4	4.1	5.2	6.3	8.2	0.66	0.57	1.04
C + DAF 6	4.0	5.0	6.3	8.5	0.62	0.68	1.19
C + BLS 2 + DAF 4	6.6	8.0	9.0	9.5	0.54	0.35	0.21
C + BLS 2 + DAF 6	6.4	7.6	8.7	9.2	0.48	0.40	0.22

uli (insensitive up to 28–36 kg) than control (Table 2). It also brought down the tensile strength (TS) as shown in Table 3.

### 3.3.2. Burning rate

The strand burner results revealed that incorporation of 2–4 parts of DAF over 100 parts composition by weight did not have any significant effect on the burning rate and pressure index of RDX incorporated propellant throughout the pressure range of 3.4–8.8 MPa. However, a combination of DAF (4 parts) with 2 parts of BLS over 100 parts of formulations resulted in burning rate enhancement to the extent of 14% (at 8.8 MPa) and brought down “ $n$ ” value as well (Table 4). The mix brought down the “ $n$ ” value to 0.21 as against 0.79 for the control in the pressure region of 6.9–8.8 MPa. However, the burning rate and  $n$  value realized with the composition were not remarkably different from those obtained with BLS alone.

## 4. Conclusions

Simultaneous thermal analysis and DSC pattern indicated two-stage decomposition of DAF involving endothermic process followed by exothermic process. The thermal analysis studies in conjunction FTIR of evolved gases suggest that initial decomposition of DAF is accompanied with the rupture of the C–NO bond.

DAF revealed its potential as a ballistic modifier in combination with BLS in RDX incorporated double base propellant. However, this trend is indicative and detailed investigations are necessary to understand the effect of the combination of DAF with BLS in reducing the pressure index.

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