Research paper

Heat of combustion studies for carbon black mixed ADN, KDN, and AP oxidizers

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Abstract

In the present study, heat of combustion (ΔH_c) values are calculated for energetic materials (EM's) pellets based on ammonium perchlorate (AP), ammonium dinitramide (ADN) and potassium dinitramide (KDN) using a bomb calorimeter unit. ADN, KDN, and AP were mixed with carbon black (CB) in various ratios for preparing EM's pellets. Two set of experiments were performed for evaluating ΔH_c for prepared pellets. In the first set of experimentation, pellets made from the mixtures of ADN, AP, and CB in different ratios were used, while in the second set of experimentation, pellets made from the mixtures of KDN, AP, and CB in different ratios were used. In all the formulations, CB acts as an organic fuel and as a catalyst, while the AP, ADN, and KDN act as oxidizer entities. The pellets were prepared using a pellet maker provided with the bomb calorimeter unit. It was observed that pure ADN/CB pellet did not burn, while pure KDN /CB pellet did not burn. Further, pure AP/CB pellet produces the highest ΔH_c as compared to other prepared EM pellets.

Keywords: ADN, KDN, AP, carbon black, heat of combustion

1. Introduction

In the recent years, intense research is focused on the development of green fuels for industrial, commercial, and for day-to-day life purposes. Conventional fuels like coal, petrol, and diesel find their applications in transportation, power production industries, mining & civil works, and in domestic purposes. However, conventional fuels lead to the production of CO, CO_2, NO_x, and soot particles upon combustion. As we know, all these entities are detrimental for human health, earth environment, and for the depletion of upper ozone layer. Hence, developments of fuels which can reduce our dependency on conventional fuels are consistently being suggested, formulated, and utilized.

Similarly, aviation and defence industries also use fuels which are noxious and have detrimental effect on the health of human and of earth. Some of the fuels which are consistently being used by rocketry and defence industries are hydrazine (N_2H_4), and ammonium perchlorate (NH_4ClO_4, AP)[1]. AP is in general used in solid rocket propulsion, while hydrazine-based chemicals used in liquid and hybrid rocket propulsion. Hydrazine is carcinogenic in nature, while AP produces chlorine-based combustion products[1,2].

In the recent years, frequency of rocket launches have been increasing considerably due to the advancement in space technology, space exploration, space tourism, cleaning space debris, and for conducting space based zero-gravity experiments. Currently, all space shuttles and rockets use solid propellants in their booster stages, as the solid propellant has the capability to produce sufficient thrust in a very short period of time[3]. A high thrust is necessary during rocket take-off as the weight of rocket is maximum and the rocket also has to defy gravity for its upward movement. Apart from this, the plume signature of AP based propellant is also very clear and dominant. Use of rockets based on AP during conflict leave the trail

of its trajectory, which will help human to locate the launch site. Hence, the development of other classes of energetic fuels which can replace AP completely or partially can reduce our dependency on AP in the coming future is important.

In an attempt to remove AP for rocket propulsion, scientific community has developed several green fuels. Some of the noteworthy developed green fuels are, a) ammonium dinitramide (ADN), b) potassium dinitramide (KDN), c) ammonium nitrate (AN), and d) hydrazinium nitro formate (HNF)[4]. These available green fuels are also known as green energetic materials (GEMs).

Out of the above mentioned four GEMs, ADN and KDN are used for the present study for calculating heat of combustion (ΔH_c) of mixed oxidizer pellets using a bomb calorimeter unit. All the three oxidizers decomposes to release free gaseous oxygen, which further reacts with fuel to form a high temperature luminous flame over the solid propellant burning surface. The decomposition mechanism of AP (NH_4ClO_4), ADN [$NH_4N(NO_2)_2$], and KDN [$KN(NO_2)_2$] can be summarized as below[2), 13),19)]:

$$[NH_4ClO_4 \rightarrow NH_3+HClO_4; HClO_4 \rightarrow HCl+2 O_2]$$
$$[NH_4N(NO_2)_2 \rightarrow NH_3+HN(NO_2)_2; 2HN(NO_2)_2 \rightarrow H_2O+3N_2O+ 1.5O_2; N_2O \rightarrow N_2+0.5 O_2]$$
$$[KN(NO_2)_2 \rightarrow KNO_3+N_2O; KNO_3 \rightarrow KNO_2+0.5 O_2; N_2O \rightarrow N_2 +0.5 O_2; 2 KNO_2 \rightarrow K_2O+N_2O; K_2O \rightarrow 2 K+0.5 O_2]$$
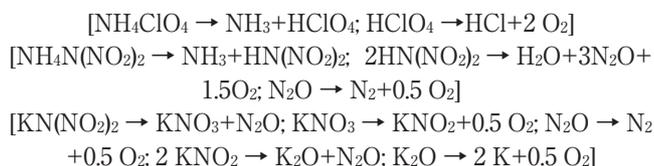
Heat of combustion (ΔH_c) is an important parameter to be studied in context with measuring the heat production capacity for newly formulated liquid and solid fuels. The heat of combustion (ΔH_c) refers the caloric equivalent of total combustion energy of propellant materials. There are several available literatures which conduct heat of combustion (ΔH_c) studies for AP based composite solid propellants[5), 6)]. However, heat of combustion studies for carbon black (CB) mixed AP, ADN, and KDN were not reported previously. The obtained results are also very exciting and throw some light on the heat capacity production of these mixed oxidizers.

Although AP mixed ADN or KDN oxidizer samples can't be completely considered as a green oxidizer, since AP is present in it, with the addition of ADN or KDN in AP crystals, the potential health hazards of AP based solid propellants on the environment and on upper ozone layer can be minimized up to some scale, which will be a one big step towards the reduction of pollution caused by AP based rockets.

In the present study, pellets prepared from AP, ADN, KDN, and CB were used for the study. Mass of prepared pellet for all the four entities in different combinations and ratios was kept less than 1 g. Heat of combustion (ΔH_c) and *%mass* consumed for different prepared pellets were calculated and discussed. AP pellet shows the highest heat of combustion (ΔH_c) values as compared to pure ADN and pure KDN pellets. However, for the mixed composition, the ΔH_c values vary greatly with pellet to pellet.

2. Experimental methodology

Initial attempts were taken to synthesize ADN and

KDN in a laboratory scale. The methodologies adopted to synthesize ADN and KDN were as described in Golofit et al.[7]. After synthesis, characterization of ADN and KDN was carried out using various analytical instruments. AP was purchased from Tamil Nadu Chlorates, Madurai, while CB of analytical grade was purchased from Sigma Aldrich, USA. Finally, all these chemicals were used to prepare pellets in different ratios for heat of combustion experiments using a bomb calorimeter unit.

This section divided into four sub-sections for clear and enhanced understanding. The names of four sub-sections are:

  a) *ADN and KDN synthesis*
  b) *Characterization of ADN and KDN*
  c) *Pellets composition and preparation*
  d) *Instrumentation*

2.1 ADN and KDN synthesis

All the starting materials for synthesizing ADN and KDN are of A.C.S. analytical reagent grade. The list of chemicals used are, sulfamic acid (Sigma-Aldrich, 99.3 %, A.C.S Reagent), potassium hydroxide (Sigma-Aldrich, 90 %, Reagent grade), ethanol (Merck, analytical reagent grade), fuming nitric acid (Merck, 100 % pure), sulfuric acid (Acros Organics, 95 %, A.C.S. Reagent), acetone (Merck, for synthesis, reagent grade), isopropyl alcohol (Sigma-Aldrich, USP, Analytical reagent), ammonium sulfate (Sigma-Aldrich, Bioxtra, 99 % pure, reagent grade), and petroleum ether (Sigma-Aldrich, A.C.S. Reagent, 40-60 °C b.p.). Preparation of KDN was completed in two steps, while preparation of ADN takes one more step after synthesizing KDN. These steps are:

Step 1: Preparation of Potassium Sulfamate

Firstly, a solution of sulfamic Acid (H_2NSO_3H) was suspended in distilled water. Afterwards, another solution was prepared with potassium hydroxide (KOH) dissolved in distilled water. Slowly and with constant stirring, complete KOH solution was poured into a suspended sulfamic acid (H_2NSO_3H) solution to obtain a neutral solution. Finally in ethanol, the prepared neutral solution was poured. Since potassium sulfamate, $K^+[NH_2SO_3^-]$ is insoluble in ethanol, it will precipitate in the form of white crystalline salt. The salt was filtered off with the help of a filter paper and a funnel.

$$KOH+H_2NSO_3H \rightarrow K^+[NH_2SO_3^-]+H_2O$$
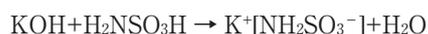
Step 2: Preparation of Potassium Dinitramide

Second step was the nitration of $K^+[NH_2SO_3^-]$ by mixed acids i.e. nitric and sulfuric acid. First step was to prepare a nitrating mixture of 95 % conc. sulfuric acid and 40 mL of 100 % conc. nitric acid (*fuming*) in the ratio of 1:4. The nitration mixture was kept at −40 °C, in an ultra-low immersion chiller. $K^+[NH_2SO_3^-]$ was added in a small portion in nitrating mixture with vigorous agitation. The reaction proceeds with the formation of dinitramide anion [$N^-(NO_2)_2$] and potassium sulfate ($KHSO_4$). The viscosity of the solution increases as the potassium sulfate ($KHSO_4$) precipitates. The amount of dinitramide anion [$N^-(NO_2)_2$]

slowly decreases as the acid is not stable in acidic solution. The reaction mechanism between $K^+[NH_2SO_3^-]$ and nitrating solution is shown below:

$$K^+[NH_2SO_3^-] \xrightarrow[T=-40\ ^oC]{H_2SO_4/HNO_3} [N^-(NO_2)_2]+KHSO_4$$
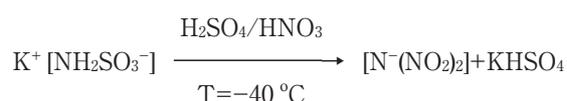
The reaction mixture was immediately poured onto a finely crushed mixture of ice and water. Afterwards, a cold solution of KOH was gradually added. The temperature was maintained in the range of $-10\ ^oC$ to $0\ ^oC$. At the neutralization point, the color of the mixture turned to characteristic green-yellow color. Neutralization process was carried out untill the solutions turned weakly basic ($pH = 8$). At this point, the neutralization was stopped and the formation of white precipitate was observed. This white precipitate was the mixture of potassium sulfate ($KHSO_4$), potassium nitrate (KNO_3), and potassium dinitramide (KDN). The precipitate was washed vigorously with acetone, as KDN was soluble while other two salts are insoluble in acetone. Finally, KDN was obtained after evaporating acetone mixed with it.

$$N^-(NO_2)_2+KHSO_4 \longrightarrow K^++[SO_3N(NO_2)_2]$$

$$K^++[SO_3N(NO_2)_2] \xrightarrow[KOH,\ T<0\ ^oC]{H_2O} [K^+][N^-(NO_2)_2]+KHSO_4+KNO_3$$
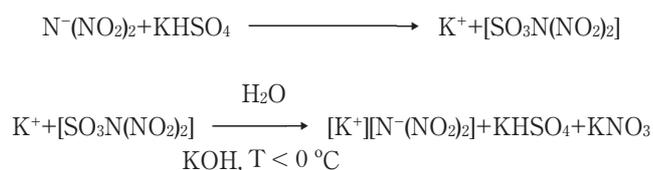
Step 3: Preparation of Ammonium dinitramide

Two separate solutions of KDN and ammonium sulfate $[(NH_4)_2SO_4]$ were prepared in distilled water. The solutions were mixed with each other in a separate beaker. As both chemicals interact with each other, cation exchange reaction starts and NH_4^+ of $(NH_4)_2SO_4$ replaced with K^+ of KDN, and ammonium dinitramide $[NH_4N(NO_2)_2]$ formed. Formed ADN was in dissolved state with water and the solid precipitate formed was of $KHSO_4$. Isopropyl alcohol

was added to the solution and $KHSO_4$ was filtered off. The remaining solvent was evaporated under reduced pressure in rotary evaporator untill the dry moist solid obtained. The slight yellow color moist solid obtained after evaporation again treated with isopropyl alcohol and then poured in petroleum ether. ADN precipitates as a needle-like crystals with yellow to white in color. The equation to obtain ADN can be shown below:

$$K^+[N^-(NO_2)_2]+[(NH_4)_2SO_4] \xrightarrow{H_2O} NH_4^+[N^-(NO_2)_2]+ K_2SO_4$$
Cation exchange reaction
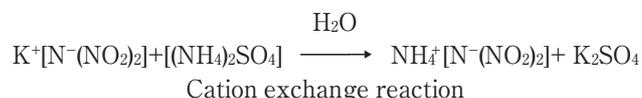
2.2 Characterization of ADN and KDN

ADN and KDN were characterized using the following analytical instruments:

a) **Differential Scanning Calorimetry (DSC) and Thermal Gravimetry (TG):** Simultaneous Thermal Analyzer (*Make*: *NETZSCH*, *Germany*, *Model No*. *STA Model 409 PG luxx*) was used to obtain the DSC and TG thermo grams of ADN at the heating rate of $10\ ^oC$ /min. DSC was used to determine the melting point (m.p.) temperature and decomposition temperature (d.t.), while TG was used to determine the percentage mass loss during decomposition with increase in temperature of synthesized ADN and KDN crystals.

b) **UV-Spectrophotometer :** UV-spectrophotometer (*Make*: *Perkin Elmer*, *Model No*. *Lambda 25*, *USA*) was used to obtain UV-spectrum of ADN and KDN. UV-spectrum provides the wavelength at which peak absorbance was observed for particular crystal.

c) **Carbon-Hydrogen-Nitrogen-Sulphur (CHNS) analyzer:** CHNS analyzer (*Make*: *Elementar*, *Model No*. *Vario EL III*, *Germany*) was used to obtain the percentage content of the various elements present in ADN and KDN crystals. CHNS analysis was used to determine the purity of the synthesized compounds.

Obtained results from STA, UV-spectrophotometer, and

Table 1   ADN data from various analytical instruments.

Sample	DSC				TG		UV-spectrum		CHNS	
	m.p. [ºC]	Ref.[8] [ºC]	d.t. [ºC]	Ref.[8] [ºC]	Mass loss [mass %]	Ref.[9]	Absorbance peak	Ref.[7]	Elements	[%]
ADN	50	93	190	192	98 % in between 160 to 260 ºC	99 % in between 140 to 200 ºC	213 nm and 284 nm	212 nm and 285 nm	C H N S	0.11 5.35 31.0 1.28

Table 2   KDN data from various analytical instruments.

Sample	m.p. [ºC]	Ref.[10] [ºC]	d.t. [ºC]	Ref.[10] [ºC]	Mass loss [mass %]	Ref.[11]	Absorbance peak	Ref.[7]	Elements	[%]
KDN	129	130	220	225	40 % in between 180 to 240 ºC	35 % in between 200 to 240 ºC	212 nm and 286 nm	212 nm and 285 nm	C H N S	0.11 0.04 16.67 0.17

CHNS are summarized in Tables 1 and 2. All the obtained results are compared with previously published articles[7)-11)] for the accuracy. The comparisons gave us confidence that the obtained ADN and KDN are pure in nature and further research can be carried out with the obtained synthesized samples.

From the obtained results Tables 1 and 2, it can be stated that the obtained ADN and KDN are pure and can be utilized for further studies. Details of all the obtained data has provided in Tables 1 and 2 were previously reported and discussed in details in Ref.[12)-14)].

2.3 Pellets composition and preparation

Pellets were prepared using AP, ADN, KDN, and CB. There preparations have been divided into two groups. In the first group (*Group-A*), AP, ADN, and CB were used, while in second group (*Group-B*), AP, KDN, and CB were used. Total composition was kept 100 % in both groups. Out of 100 % composition, 20 % composition was kept constant for CB, while the rest 80 % was divided among oxidizers, i.e. in between AP and ADN, or in between AP and KDN. The mass of the prepared pellets was kept < 1 g using pellet maker provided with the bomb calorimeter unit. The composition of the prepared pellet in percentage is provided in Table 3.

Table 3 Composition of the prepared pellets using AP, ADN, KDN, and CB.

Sample No.	Group-A			Group-B		
	AP [%]	ADN [%]	CB [%]	AP [%]	KDN [%]	CB [%]
1	0	80	20	0	80	20
2	10	70	20	10	70	20
3	20	60	20	20	60	20
4	30	50	20	30	50	20
5	40	40	20	40	40	20
6	50	30	20	50	30	20
7	60	20	20	60	20	20
8	70	10	20	70	10	20
9	80	0	20	80	0	20

2.4 Instrumentation

Bomb calorimeter (*Make*: *Modern scientific instrument*, *New Delhi*) was used to determine the heat of combustion (ΔH_c) values for prepared pellets. To calibrate the bomb calorimeter, pellet of benzoic acid (*standard*) in 400 psi oxygen atmosphere was combusted. The water equivalent (W) of calorimeter was obtained as 2369 cal·$^{\circ}$C^{-1} by repeating the experiment for three times. It was calculated using the following equation[15)]:

$$W = [(Q \times m) + e]/T$$

Where,

Q = *Heat of combustion of the standard benzoic acid sample*=6319 cal·g^{-1}
m = *Mass of benzoic acid sample* [g] = 0.66 g
T = *Temperature rise* [$^{\circ}$C] = 1.77°C
e = *Correction for nichrome wire (*24 cal *for* 10 cm*)*

The heat of combustion (ΔH_c) of pellets was determined by the same procedure as adopted for above measurement. However, the equation for determining the heat of combustion of pellets (Q_c) was used as given below[15)]:

$$Q_c = \{[(W \times T) - e]/m\}$$

Percentage mass consumed (%m consumed) was also calculated using the following equation given below:

$$\%m \text{ consumed} = [(M_{\text{final}} - M_{\text{initial}})/M_{\text{final}}] \times 100$$
$$= (\Delta m/M_{\text{final}}) \times 100$$

3. Results and discussion
3.1 Heat of Combustion studies for Group-A

Heat of combustion values (ΔH_c) values along with other details of pellets used in Group-A is provided in Table 4.

From Table 4, it can be observed that there are variations in the ΔH_c values for pellets of different composition. ADN/CB pellet does not combusted, while AP/CB pellet combusted with ΔH_c value of 1498.2 cal·g^{-1}. However, with the addition of 10 % of AP in ADN/CB pellets, the pellets combustion starts. Further, it can be noticed that with the increase of AP percentage in ADN/CB pellets, the ΔH_c values continues to decrease. The

Table 4 Heat of combustion values for Group-A.

S. no.	AP [%]	ADN [%]	CB [%]	ΔT_{max} [$^{\circ}$C]	M_{initial} [mg]	M_{final} [mg]	Δm [mg]	[%m] consumed	Heat of combustion [cal·g^{-1}]
1	0	80	20	*NC	−	−	−	−	−
2	10	70	20	0.40	680	004	676	99.41	1358.2
3	20	60	20	0.42	750	011	739	98.53	1294.6
4	30	50	20	0.52	940	014	926	98.51	1284.9
5	40	40	20	0.52	960	021	939	97.81	1258.2
6	50	30	20	0.57	880	023	857	97.38	1507.2
7	60	20	20	0.61	948	029	919	96.94	1499.0
8	70	10	20	0.62	972	031	941	96.81	1486.4
9	80	0	20	0.56	980	035	945	96.42	1498.2

*NC = Not Combusted

lowest ΔH_c value of 1258.2 cal·g^{-1} was obtained for AP/ADN (40/40) pellet. Although, with the further increase of AP in ADN/CB pellets, the ΔH_c values start to increase and it values remains close to about 1500 cal·g^{-1} for three AP/ADN ratios of 50/30, 60/20, and 70/10. Finally, AP/CB pellet combusted with ΔH_c value of 1498.2 cal·g^{-1}.

From Table 4, it can also be observed that the final residual mass of the pellets continuously increases with increase in AP percentage. The reason for such behavior was because of the gaseous combustion products from pure ADN[8), 9)]. While, with the percentage increment of AP in ADN/CB, some condensed/ solid decomposition products are formed which lead to less %m consumed.

3.2 Heat of Combustion studies for Group-B

Heat of combustion values (ΔH_c) values along with other details of pellets used in Group-B is provided in Table 5.

From Table 5, it can be observed that ΔH_c values for KDN/CB based pellets are continuously increases with percentage increment of AP in KDN/CB pellets. The lowest ΔH_c value of 623.09 cal·g^{-1} was obtained for KDN/CB pellet, while the highest ΔH_c value of 1503.52 cal·g^{-1} was obtained for AP/CB pellet. In Table 4, the obtained ΔH_c value for the same composition of AP/CB pellet was 1498.2 cal·g^{-1}, which is 5.32 cal·g^{-1} less than 1503.52 cal·g^{-1}. There are always some variations in the experimentally obtained values for the same experiments if it performed for several times or repeatedly. These variations are generally expressed in percentage error (%$_{error}$) as:

$$\%_{error} = [X_1 - X_2/(X_1 + X_2)/2] \times 100$$

Where,

$X_1 = \Delta H_c$ for AP/CB as obtained in Table 4.
$X_2 = \Delta H_c$ for AP/CB as obtained in Table 5.

By putting the values of X_1 and X_2 in the above equation, the obtained %$_{error}$ between the two obtained ΔH_c values comes out to be 0.33. The reasons for such variations in results are may be due to instrumental errors, environmental errors, observational errors, or theoretical errors. In the present case, the percentage variation in the two obtained results is not much high.

For AP/KDN/CB pellets, the highest ΔH_c value of 1257.77 cal·g^{-1} was obtained for AP/KDN (70/10)/CB based pellet, while the lowest ΔH_c value of 755.73 cal·g^{-1}

was obtained for AP/KDN (10/70)+CB based pellet. From Table 5, it can also be observed that with the increase of AP percentage in KDN crystals, %m consumed also increases. The reason for this lies on the decomposition mechanism of KDN[14)]. In first step decomposition, KDN decompose to form 60 % potassium nitrate (KNO$_3$) i.e. 40 % decomposition completes. In second step decomposition, 60 % KNO$_3$ decomposes to form 40 % potassium nitrite (KNO$_2$), i.e. 20 % decomposition completes. KDN decomposes at 200 ℃ to form KNO$_3$, while KNO$_3$ decomposes at 600 ℃ to form KNO$_2$. Finally, KNO$_2$ decomposes at 700 ℃ to form K$_2$O. Hence, in the case of KDN/CB pellet, 60 % decomposition completed, i.e. KNO$_2$ remains in the residual mass. Thus, with the increment of AP percentage and decrement of KDN percentage in AP/KDN/CB pellets, the %m consumed constantly increases since less KNO$_2$ was present in the final residual mass.

The variation of %m consumed and ΔH_c produced for both Group-A and Group-B is depicted in Figure 1 and 2. For studying the variations in %m and ΔH_c values for both groups, *least square method* was used to determine the *best curve fit equation* in the form of $y = mx + c$, and co-efficient of determination (R^2). Both the best curves fit equation and R^2 values for the both groups are presented in the Figures 1 and 2.

From the obtained R^2 values from Figures 1 and 2, it can be interpreted that more than 90 % of the observed variations for three curves, i.e. %m curves for Group-A and B, and ΔH_c curve for Group-B can be explained by the model's input. While for ΔH_c curve for Group-A, only 56 % of the observed variations can be explained by the model's input. This is because of the high variations in ΔH_c values of AP/ADN based pellets.

4. Conclusion

Development of green energetic materials (GEMs) for rocket propulsion is getting much attraction nowadays because of the increase in frequency of rocket launch every year. Present work is an attempt to quantify the heat production capacity of AP, ADN, and KDN- based pellets in order to use them as possible or partial replacement of AP in composite solid propellants. Some of the important conclusions that can be drawn from the present study are summarized below:

a) AP/CB pellet has the highest ΔH_c value of 1500

Table 5　Heat of combustion values for Group-B.

S. no.	AP [%]	KDN [%]	CB [%]	ΔT_{max} [℃]	$M_{initial}$ [mg]	M_{final} [mg]	Δm [mg]	[%m] consumed	Heat of combustion [cal·g^{-1}]
1	0	80	20	0.26	957	556	401	41.90	623.09
2	10	70	20	0.31	945	389	556	58.83	755.73
3	20	60	20	0.33	931	380	551	59.18	814.80
4	30	50	20	0.36	897	332	565	62.98	924.01
5	40	40	20	0.39	950	304	646	68.00	947.27
6	50	30	20	0.45	954	295	659	69.07	1092.29
7	60	20	20	0.48	982	267	715	72.80	1133.52
8	70	10	20	0.54	998	115	883	88.47	1257.77
9	80	0	20	0.61	947	40	907	95.77	1503.52
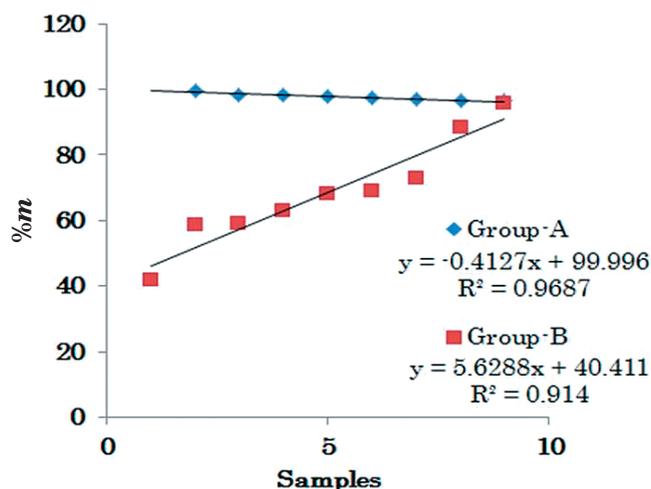
Figure 1   [%*m*] for Group-A and Group-B.
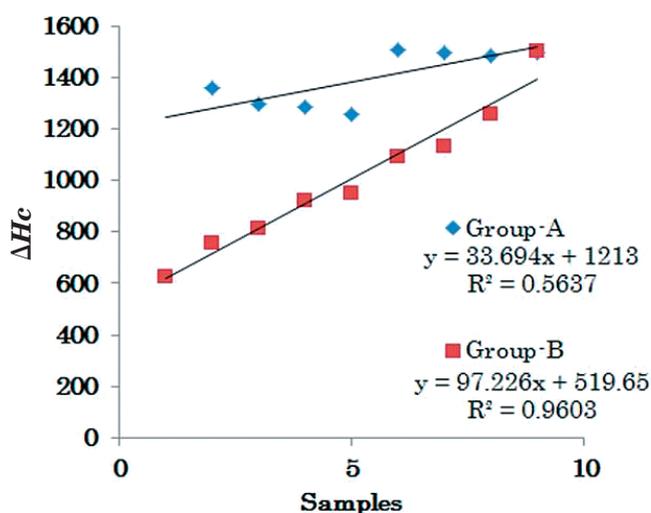
Figure 2   [ΔH_c] for Group-A and Group-B.

cal·g^{-1} as compared to other pellets. This result shows that AP can produced the high temperature gaseous combustion products. However, specific impulse (I_{sp}) and thrust (F) of any rocket depends on host of other parameters too namely. molecular weight (MW) of combustion products, combustion products temperature (T_c), nozzle design parameters, propellant grain structure, oxygen balance (OB), heat of formation (ΔH_f) of oxidizer, propellant composition, etc[16]. Hence, only high temperature combustion products will not fulfilled the criteria for a high I_{sp} of rocket. Since, MW of combustion products of ADN is less, OB of ADN is high, and ΔH_f of ADN is also more as compared to AP. Hence, instead of having low ΔH_c values for ADN based pellets, it will show promising good ballistic properties than AP based composite solid propellants.

b) ADN/CB pellet does not combusted, while KDN/CB pellet combusted. The reason for not burning of ADN pellet was because of the presence of ammonium nitrate (AN) in its crystal, as while storage ADN slowly decomposes into AN. Since, both AN and ADN undergoes condensed phase combustion mechanism, further AN combustion

releases lots of moisture during its combustion[17]. Because of such reasons, ADN crystals cannot support its combustion up to 400 psi. However, with further increase in pressure, ADN/CB pellets may support its combustion.

c) KDN in itself cannot be used an oxidizer entity because of low heat of formation, high MW combustion products, and low flame temperature. Hence, for the propulsion purposes, AN mixed KDN is generally used[13],[18]. The reasons for burning of KDN/CB pellet are because of its less hygroscopic behavior, along with low amount of presence of potassium nitrate (KNO$_3$) in KDN crystals. KNO$_3$ decomposition is above 600 °C, while KDN decomposition is around 200 °C[13]. Since, KNO$_3$ is not present or may be in less quantity, and hence, KDN/CB pellet combusted easily.

d) With the addition of AP in ADN/CB pellets, the ΔH_c values increases upto 1507 cal·g^{-1} for AP/ADN ratio of 50/30. With further increase of AP in ADN/CB, the ΔH_c values remains hovering at around 1500 cal·g^{-1}. Hence, AP mixed ADN in the ratio of 50/30 can be used for obtaining the high specific impulse propellant samples with minimal hazardous effects on the environment.

e) With addition of AP in KDN/CB pellets, the ΔH_c values increases continuously. The lowest ΔH_c value of 623.09 cal·g^{-1} was obtained for KDN/CB pellet, while AP/KDN (70/10)+CB pellet shows the ΔH_c value of 1257.77 cal·g^{-1}. Since KDN, cannot be directly utilized in composite solid propellants, and hence AP/KDN in the ratio of 90/10 to 70/30 can be utilized for achieving slightly good ballistic properties with less hazardous effects on the environment.

List of Abbreviations:

ADN:	*Ammonium Dinitramide*
AP:	*Ammonium Perchlorate*
CB:	*Carbon Black*
CHNS:	*Carbon Hydrogen Nitrogen Sulfur*
DSC:	*Differential Scanning Calorimetry*
d.t.:	*Decomposition Temperature*
e:	*Correction for nichrome wire*
EM:	*Energetic materials*
GEM:	*Green Energetic Materials*
KDN:	*Potassium Dinitramide*
m.p.:	*Melting Point*
m:	*Mass of benzoic acid sample*
M_{final}:	*Final mass of the pellet after experiment*
$M_{initial}$:	*Initial mass of the pellet before experiment*
Δm:	*Difference between initial and final mass*
TG/DTG:	*Thermal Gravimetry-Differential Thermal Gravimetry*
ΔT:	*Temperature rise* (°C)
Q:	*Heat of combustion of the standard benzoic acid sample*
Q_c:	*Heat of combustion of pellets*
W:	*Water Equivalent*

ΔH_c: *Heat of Combustion*
ΔH_f: *Heat of Formation*
%*m* consumed: *Percentage mass consumed*
%$_{error}$:   *Percentage error*

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