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Influence of humidity on the decomposition process of double base rocket propellant

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ABSTRACT

The decomposition mechanisms of the polymer cellulose nitrate (NC) which is used in double base (DB) rocket propellants, have been extensively studied, and the influence of storage temperature on the lifetime of these energetic formulations is well known. However, the impact of humidity and water on the polymer decomposition process is poorly understood. This paper studies the influence of humidity on the decomposition chemistry of NC and its impact on shelf life. Stabiliser consumption was first analysed by ageing the propellant in sealed vials at different humidity levels for 7 days at an isothermal temperature of 90 °C. Samples were also analysed using heat flow calorimetry (HFC) at isothermal temperatures of 80 °C, 90 °C, and 100 °C. The results indicates that stabiliser depletion increases with increasing water content. Life assessment calculations (AOP 48 ed2) show that increasing the absolute humidity from 6 to 22 g m^{-3} will decrease the propellant life from 11 to 6 years (25 °C equivalents). The HFC results follow the same trend as the stabiliser depletion where greater absolute humidity increases the heat flow by up to 400 %. Unlike the pass/fail criteria for stabiliser depletion, the HFC samples passed the 10-year (25 °C equivalent) life criteria (STANAG 4582). A multi-temperature (80, 90, 100 °C) kinetic analysis of the initial heat flow showed that the heat flow rate increased with increasing humidity, but the activation energy for all humidity levels remained at 131 (± 3) kJ mol^{-1}.

1. Introduction

1.1. Chemical decomposition of double base rocket propellants

The main ingredients of double base (DB) rocket propellants are the polymeric energetic binder cellulose nitrate (NC) and an energetic plasticizer such as nitroglycerine (NG) [1–3]. These two substances are nitrated esters and are chemically unstable substances because of the low bond energy R-O-NO_2 groups (about 155 kJ mol^{-1}) [4–7] they contain. The decomposition process of the NC polymer in DB rocket propellants begins with the homolytic cleavage of the –O– NO_2 bonds, producing denitrification of the polymer and a release of nitrogen oxides (NO_x) [5–10], this is known as intrinsic decomposition which cannot be prevented and therefore will always occur [11].

There are two primary mechanisms of intrinsic decomposition of the energetic polymer NC: i) hydrolysis and ii) thermolysis. Hydrolysis, as the name suggests, is catalysed by the presence of water, which promotes the hydrolytic cleavage of the -O-NO_2 bond of the NC main chain [6]. When mixed with the water in the medium, the newly separated NO_2 radicals produce nitric acid [5,12]. The acid formed exothermically reacts with the NC polymeric chains, producing more NO_2 [12]. Eqs. (1) and (2) illustrate the hydrolysis process and subsequent reaction of HNO_3 [5,6,13,14].

$$R - O - NO_2 + H_2O \overset{H^+}{\rightarrow} R - OH + HNO_3 \tag{1}$$

$$R - OH + HNO_3 \rightarrow R - CHO + NO_2 + H_2O \tag{2}$$

As the temperature increases, the rate of decomposition by hydrolysis increases, however there will be a change in the reaction mechanism, which generally occurs at a temperature of around 60 to 65 °C, where hydrolysis is no longer the dominate reaction mechanism [15–19]. This reaction mechanism is known as thermolysis and as the name implies, the intrinsic decomposition will depend on temperature. The decomposition process via thermolysis is shown in Eq. (3).

$$R - O - NO_2 \rightarrow RO^{\cdot} + NO_2 \tag{3}$$

The NO_2 gas released due to the intrinsic decomposition process of NC follows four different pathways, each with a different reaction rate

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List of abbreviations

2-NDPA	2-Nitro-Diphenylamine
2, 4-DNDPA	2, 4-dinitrodiphenylamine
AH	Absolute humidity
AOP	Allied Ordnance Publication
DPA	Diphenylamine
CHF	Critical heat flow
DB	Double base
E_a	Activation Energy
HF	Heat flow
HFC	Heat flow calorimeter
HPLC	High-performance liquid chromatography
N-NO-2DPA	N-nitroso-2-nitrodiphenylamine
NC	Cellulose nitrate
NG	Nitroglycerin
NO_x	Nitrogen oxides
STANAG	Standard Agreement
t_c	Critical time
t_d	Depletion time
WC	Water content
% w/w	Percentage by mass

coefficient k, as illustrated in Fig. 1. It shows the gases may (i) escape from the propellant as red fumes (k_1), (ii) react with stabilizing agents presents in the energetic formulation to trap them (k_2), (iii) adsorb within the DB propellant matrix (k_3), (iv) react with the NC polymer (k_4). The latest path is known as autocatalysis process [6,20–22] as the gases accelerate the decomposition reaction of NC which may result in self-ignition [23].

1.2. Stabiliser consumption

Certain substances known as (chemical) stabilisers are added to the DB propellant formulation in order to slow down the decomposition reactions of the NC polymer [14,22,24]. The function of stabilisers is to trap the NO_x resulting from the decomposition of the propellant [4, 25–28]. Stabilizers, which are generally derivatives of aromatic amines or urea, must offer good compatibility with the NC/NG present in DB rocket propellants and provide good adsorption capacity for NO_x released during decomposition [29,30].

The reactions that occur between stabilisers and NO_x are quite complex, resulting in the formation of the nitration and nitrosation products [13,31–33]. These derivatives can have a stabilizing effect which helps to keep propellants safe during storage [34]. For example, in the case of 2-nitrodiphenylamine (2-NDPA), the reactions between this stabilizer and the decomposition gases form secondary stabilisers such as N-nitroso-2-nitrodiphenylamine (N—NO-2-NDPA), 2, 4-dinitrodiphenylamine (2, 4-DNDPA) and 2, 4′-DNDPA [35–38]. These reactions are shown in Fig. 2.

Monitoring the stabiliser consumption is one of the methods commonly used to determine the safe life of DB rocket propellants [21, 39]. AOP 48 ed2 [36] is the standard used to determine whether a DB propellant is safe to be stored. For this purpose, samples are artificially aged at temperatures from 50 to 90 °C for periods between 3.5 and 301 days (depending on the selected temperature) and the stabiliser content is measured by high-performance liquid chromatography (HPLC) [11, 36]. The pass/fail criteria established by this standard are i) Maximum decrease in effective stabilizer during ageing (% of initial level) $\leq$ 80 % w/w, and ii) Minimum percentage of effective stabilizer remaining after ageing $\geq$ 0.2 % w/w. Since the stabiliser content present in a DB rocket propellant is between 1 and 3 % w/w [40,41], the first criterion is generally used to determine the remaining shelf life.

1.3. Heat flow calorimetry (HFC)

Heat flow calorimetry (HFC) is used by construction, pharmaceutical and explosive industries. The construction industry uses HFC to estimate curing times in different types of cement and in the pharmaceutical industries, it is an essential tool for the evaluation of the compatibility of the ingredients for new drugs [42]. This technique has been employed since the late 1960s to determine the long-term stability and shelf life of NC-based propellants. HFC directly measures the heat released/absorbed from chemical reactions, therefore, the heat generated is directly proportional to the rate of decomposition of NC. Bohn [11] states that the heat generated is a sum of all the exothermic/endothermic reactions that occur during the polymer decomposition.

During decomposition, the temperature within the NC-based propellant increases to a point where ignition will occur. The autoignition process of the propellant consists of three main steps (Fig. 3): i) sustained increase in heat generation, known as the induction period, which is dependant of the stabiliser nature and concentration [24]; ii) once the stabiliser is depleted (t_d), the heat flow (HF) generated increases dramatically due to the autocatalytic decomposition of NC, this stage is known as the run-away decomposition period; iii) autocatalytic reaction reaches a critical heat flow value (CHF) where the NC polymer generates heat much faster than it can release it, potentially resulting in autoignition [43–45].

The induction period is not necessarily linear as multiple reactions

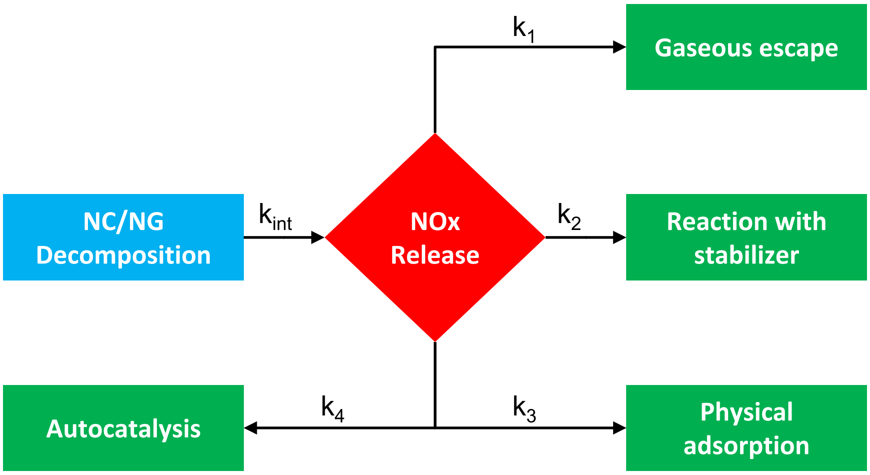

Fig. 1. Scheme for the chemical DB rocket propellant decomposition [6,13].

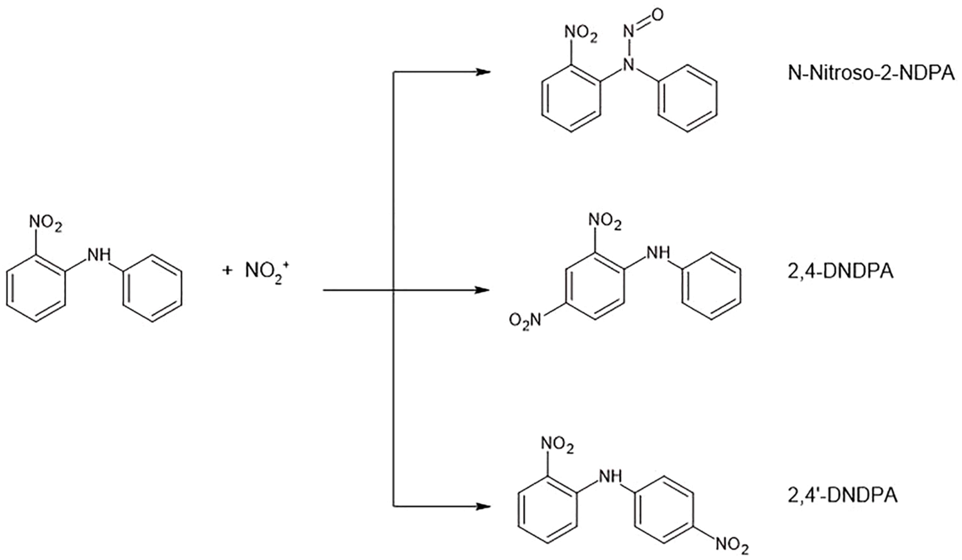

Fig. 2. Secondary stabilisers derived from 2-NDPA and nitrogen oxides [35].

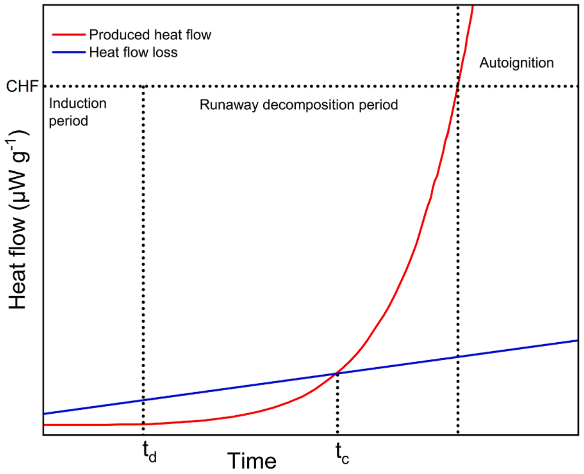

Fig. 3. Propellant self-ignition stages [43].

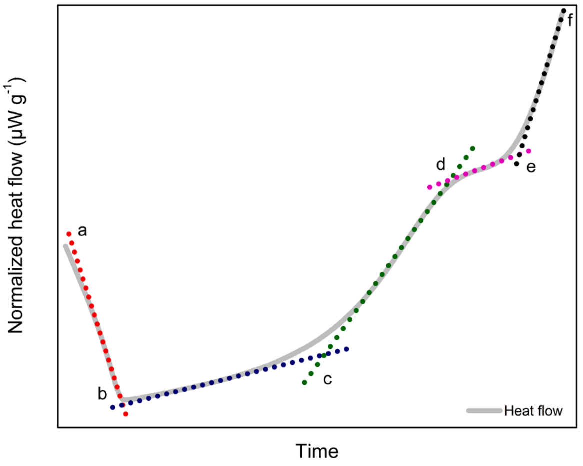

Fig. 4. DB rocket propellant heat flow measurement (Data taken from HFC test at 90 °C).

are involved which will affect the heat flow. Such reactions will depend on the nature of the stabilisers present in the formulation. For example, when diphenylamine (DPA) and its derivatives such as 2-Nitro-DPA (2-NDPA) are used to stabilise NC-based propellants, the overall HF signal follows a five-stage process as illustrated in Fig. 4 [46,47]. The initial part of the HF curve presents a first maximum (point a) which is associated with the reaction between the oxygen present inside the sample ampoule and the energetic formulation. Once point a is reached, the signal starts to decrease until it reaches the first minimum (point b). According to Wilson et al. and Jelisavac et al. [48,49], the b-c part of the HF curve is the result of a constant NC polymer decomposition rate accompanied by stabiliser consumption. Once the primary stabiliser is consumed, the generated HF could present an inflection point (point d). Section c-d is caused by the stabilising effects of the secondary stabiliser products from the reaction between the stabiliser and the released NO_x [6,13]. Because the ability to scavenge NO_x decreases as the number of nitroso and/or nitro groups in the original stabiliser molecule increases, the secondary products are less effective stabilisers than main stabilisers [48,50–52], whereby the generated HF starts to increase significantly (point e). Once the secondary products are consumed, the NO_x released during the intrinsic decomposition will start to react with the NC polymer, resulting in the uncontrolled increase of the generated HF [11,22,46]. This is known as autocatalysis (point f).

STANAG 4582 [53] is the standard used to determine the service life of NC-based propellants. As per AOP 48 ed2, this standard tests if an NC propellant, stored at temperatures equivalent to an isothermal storage at 25 °C, will remain chemically stable for a minimum of 10 years [15,53]. The failure criterion determines that a propellant is chemically stable if the maximum HF, in the experimental part between the time corresponding to a heat release of 5 J/g and the defined time, does not exceed a limit calculated from the following equation [15,53]:

$$HF = HF_{71}\exp\left[\frac{E_{a1}}{R}\left(\frac{1}{T_{71}} - \frac{1}{T_m}\right)\right] \tag{4}$$

where HF is the heat flow generated, HF_{71} is the heat flow limit at 71 °C (39 μW g^{-1}), E_{a1} is the activation energy for heat generation caused by thermal decomposition of propellants at temperatures higher than 60 °C (120 kJ mol^{-1}), R is the gas constant (8.3143 J K^{-1} mol^{-1}), and T_m is the temperature of measurement (K).

The equation is based on the fact that heat generation rate of 39 μW g^{-1} at 71 °C causes a temperature increase of about 1.5 °C in the centre of the propellant loaded into the 230 mm gun cartridge. For rocket propellants, the same effect is achieved by a heat generation rate of 2.6 μW

g^{-1} at 50 °C in 1000 mm propellant grain [15,53]. Therefore, for a temperature of 90 °C, the maximum HF is 350 μW g^{-1} according to Eq. (4).

During the manufacturing of rocket propellant, the environment conditions and in particular the relative humidity are not controlled. To assess the shelf life of propellant, many standards [6,21] have been published but the humidity is not a factor which is taken into consideration despite the potential presence of water, an hydrogen donor, which can react with NO_2 to form a Lewis acid and accelerates the kinetic decomposition of the NC polymer [12,54]. During manufacture, an environmental seal is added to the rocket motor to keep the moisture out. The seal can deteriorate over time, allowing water to enter the motor [55–57].

This paper will assess the influence of humidity on the decomposition chemistry of NC-based propellants and its impact on shelf life. Samples of DB propellant will be exposed to different humidity conditions (from 6 to 22 g m^{-3}) and artificially aged at 90 °C. The shelf life of the DB propellant will be investigated by analysing the evolution of the heat generated using a HFC (STANAG 4582) and by monitoring the evolution of the stabiliser by HPLC (AOP 48 ed2).

2. Material and methods

In this study, an extruded double base (EDB) propellant, Propellant A consisting of nitrocellulose 5–57 % w/w, nitroglycerine 19–46 % w/w, 2-nitrodiphenylamine 1–8 % w/w, and copper oxide 0–3 % w/w was investigated. The propellant is estimated to be 15 years old at <20 °C storage. The propellant sample used for this experiment was obtained from a propellant billet (ø 40 mm x 38 mm) as shown in Fig. 5. The propellant was cut, sieved (4 mm), and preconditioned at 25 %, 50 %, 75 %, and 95 % relative humidity (RH) using a Nuve TK 120 test cabinet for an interval of 48 h at standard pressure and 25 °C. The 3 ml HFC glass vials (propellant loading density 0.83 g cm^{-3}) were sealed with a rubber septum and aluminium crimp caps and inserted in a HFC or aged in an oven. Table 1 shows the equivalent value of the absolute humidity.

The DB rocket propellant sample ageing, for stabiliser depletion, was carried out using an oven at 90 °C. Each moisture level had a set of 7 samples that were removed daily to monitor the depletion of the stabiliser. For HPLC analysis, approximately 0.5 (±0.001) g of propellant was extracted with acetonitrile (125 ml) for 4 h using an orbital shaker. To precipitate out the NC, a 25 ml 2 % aqueous solution of $CaCl_2$ was added. The precipitate was allowed to settle for 1 h. The supernatant liquid was then filtered through a 0.2 μm nylon filter and transferred into an HPLC vial. The chromatographic conditions used are shown in Table 2.

The HFC tests were performed isothermally at temperatures of 80, 90, and 100 °C for 15, 7, and 2 days respectively using a TAM-IV microcalorimeter system from TA instruments. The calorimeter was calibrated at each temperature and the baseline was recorded before and after the test. For both tests, one sample with a corresponding replicate was used.

Table 1
Relative and absolute humidity conditions (25 °C and standard pressure).

Relative humidity (RH) %	Absolute humidity (AH) g m^{-3}	Water mass inside 3 ml vials mg
25	6	3.1
50	12	6.1
75	17	8.7
95	22	11.2

Table 2
HPLC conditions for stabiliser depletion analysis.

Instrument	Waters Alliance 2695
Module Column	Kinetex 5μ XB-C18 100Å @ 30 °C
Mobile phase	40% Acetonitrile, 60% H_2O +0.1% formic acid @ 1.5ml/min
Detector	Waters 996 PDA @ 254 nm
Injection Vol	10 μl

3. Results and discussion

The results from the stabiliser analysis are shown in Fig. 6, where the ageing time is reported as equivalent time of storing the propellant at 25 °C, which is calculated using Eq. (5).

$$t = t_{25}\exp\left[\frac{1}{R}\left(E_{a1}\left(\frac{1}{T_m}-\frac{1}{T_{60}}\right)+E_{a2}\left(\frac{1}{T_{60}}-\frac{1}{T_{25}}\right)\right)\right] \tag{5}$$

where t is the time of measurement, t_{25} is the time of storage at 25 °C for 10 years, E_{a1} is the activation energy for heat generation caused by thermal decomposition of the NC-polymer present in the propellants at temperatures higher than 60 °C (120 kJ mol^{-1}), T_m is the temperature of measurement (K), T_{25} is the storage temperature (298.15 K), and R is the gas constant (8.3143 J K^{-1} mol^{-1}).

Therefore, samples aged at 90 °C for 3.43 days are equivalent to storing the propellant at 25 °C for 10 years. Using the equivalent storage time allows the assessment of DB rocket propellant safe life under the criteria established by AOP 48 ed2 [36]. From Fig. 6, it can be seen that increasing the concentration of water increases the rate of stabiliser depletion. The water is catalysing the decomposition reaction of the NC polymer present in the DB propellant. After 5 years equivalent of storage

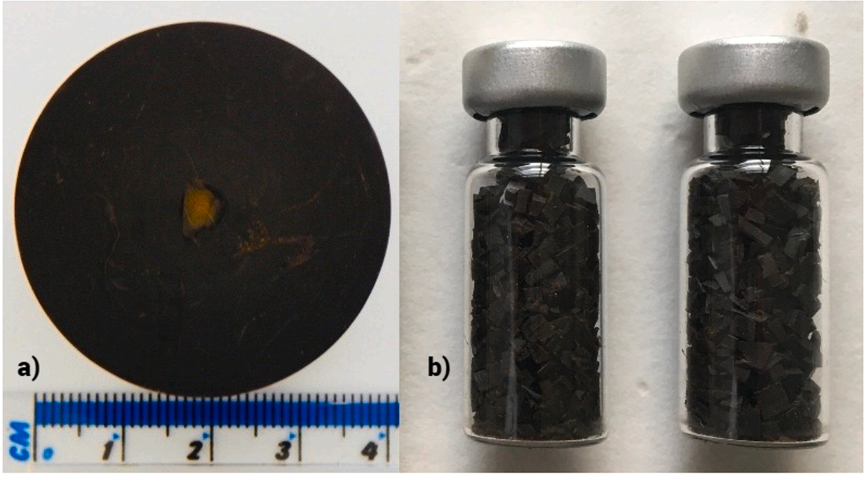

Fig. 5. Propellant sample preparation (a) propellant billet. (b) Cut < 4 mm and loaded into 3 cm^3 HFC vials with rubbery septum and aluminium crimp caps.

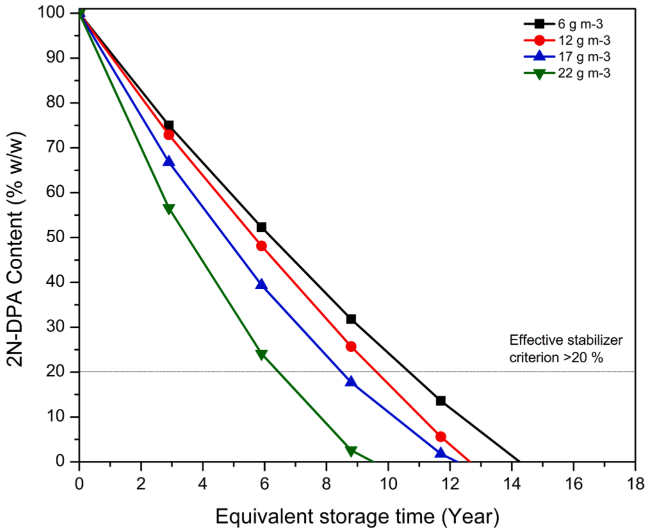

Fig. 6. The influence of absolute humidity on the DB propellant stabiliser depletion rates at 90 °C (equivalent years at 25 °C).

at 25 °C, all sample sets have sufficient stabiliser content to be safely stored, but it is noticeable that the samples with higher moisture content have consumed more than 50 % of the total stabiliser. Only the 6 g m^{-3} water test passed the 10-year life criterion set by AOP 48 ed2, and will be safe to use for 11 years. Samples with 22 g m^{-3} water failed the criteria after 6 years, a reduction of 5 years compared to the lowest water content.

The stability of the samples analysed in the HFC at 90 °C was determined according to STANAG 4582 [53]. The test times are the same as those of AOP 48 ed2, and therefore the equivalent storage times are the same and the heat generated in the test ran should not exceed 350 μW g^{-1} [15,53]. The 90 °C HFC data are plotted against the equivalent storage time as shown in Fig. 7 *(see supplementary data for 80 °C and 100 °C HFC curves)*. Unlike the pass/fail criteria for stabiliser depletion, the HFC samples pass the STANAG 4582 criteria for all humidity conditions. It should be noted that, with the exception of the 22 g m^{-3} absolute humidity sample which shows a strong increase in generated heat flow after 10 years, the other samples show that they can be safely used after a period exceeding 18 years of storage at 25 °C. The difference in pass/fail results between stabiliser consumption and HFC is because: i) considering the self-heating model presented in Section 1.2, the stabiliser consumption failure criterion occurs before the end of the induction stage and ii) the HFC failure criterion is past the induction stage within the runaway decomposition period.

Previously, it was mentioned that both AOP 48 ed2 and STANAG 4582 use the same temperatures and activation energies to evaluate the stability of DB rocket propellants. In Fig. 8, the signal generated by the HFC is overlayed with the stabiliser depletion curve obtained at 90 °C and 22 g m^{-3} water content. It is evident that, when the primary stabiliser concentration is no longer effective (6 years equivalent), the HF dramatically increases. In other words, the self-heating of the NC occurs after the concentration of the primary stabiliser has reached an ineffective level. The onset of rapid decomposition from the autocatalytic decomposition of NC is delayed by the concentration of the secondary stabiliser which is a by-product of the reactions between the primary stabiliser and the NO_x released by the NC and can act as stabiliser itself. According to Schroeder et al., Lussier and Gagnon [26,31], the consumption of the main stabiliser generates derivatives, such as 2, 4-DN-DPA, which will assume the role of secondary stabiliser. The secondary stabiliser presence helps to delay the onset of rapid decomposition of the autocatalytic decomposition of NC polymer. The stabiliser depletion failure criteria do not take into account for these secondary stabiliser products when calculating effective stabiliser concentration.

As previously discussed, five different steps (from a to f, Fig. 4) were observed in the HF curves generated for the sample heated at 90 °C with 17 g m^{-3} of water present. The data contained between these intervals, have a quasi-linear behaviour. Table 3 summarises these five stages identified during the decomposition of the NC polymer present in DB rocket propellant.

In the region b-c (Table 3), the decomposition reaction is a first order so the corresponding HF curves obtained for the HF curve can be plotted for all the experiments as a function of time, as shown in *Fig. 9.(a)*. The limits of the b-c segment have been calculated using a Python® code (supplement files).

It can be observed in Figs. 9.(b),(c) and (d) that, as the absolute humidity increases, the onset time of point b decreases and the generated HF increases. The water appears to increase the rate at which the remaining oxygen in the vial reacts with the NC present in the propellant, resulting in the accelerated formation of NOx and increasing the heat generated [46,58]. Likewise, when the water contained in the samples increases, the b-c reaction rate increases to the point where the effective stabiliser concentration is reduced, meaning that the curve will be shorter and steeper.

So far, it has been shown that the presence of water with NC polymer has a significant effect on the HF curves. Despite the complexity of the

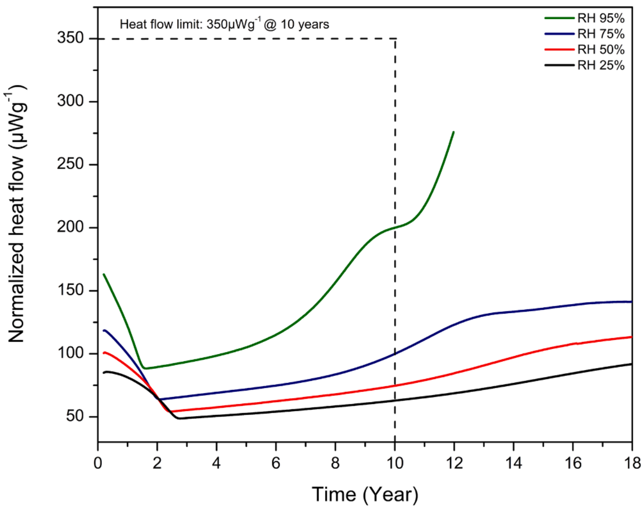

Fig. 7. Influence on DB propellant heat flow (HFC) at 90 °C (equivalent years at 25 °C).

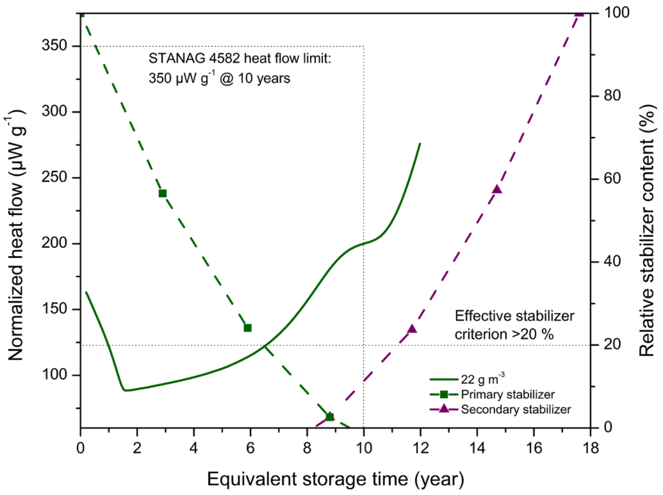

Fig. 8. Stabiliser depletion and HF at 90 °C, 22 g m^{-3} AH (equivalent years at 25 °C).

Table 3
Description of the different HFC stages of a DB rocket propellant decomposition.

Stage	Description
a-b	Stage where the remaining oxygen interacts with the propellant.
b-c	Region where propellant decomposition is accompanied by the depletion of the main chemical stabiliser.
c-d	Stage where the heat flow increases due to the depletion of the main stabiliser.
d-e	Zone where propellant decomposition is followed by the consumption of secondary stabilisers.
e-f	Stage of considerable increase in decomposition rate (autocatalysis)

reaction mechanisms accompanying the decomposition of DB rocket propellants, this can be described using a first-order kinetic process [59, 60]. Therefore, the following equation is used to evaluate the reaction rate constants:

$$\ln|\Delta HF| = -k\cdot t \tag{6}$$

where *HF* is the generated heat flow, *k* is the reaction rate constant, and *t* is time.

The reaction rate constant *k* for all the samples is given in Table 4. To further understand the role of water in the decomposition of these energetic formulations, the Arrhenius kinetics and the effective activation energy (E_a) can be determined [61,62]. Eq. (6) only establishes the dependence of the rate constant *k* on temperature, neglecting the effects of other variables, such as water, that could influence the reaction. Work by Waterman, Li et al. and Zhao et al. [63–65] have developed models based on the Arrhenius equation that takes into account the combined effect of temperature and water in the system on the reaction rate. The general model from these works is shown below:

$$\ln|k| = -\frac{E_a}{RT} + \ln|A| + [C\cdot WC] \tag{7}$$

where *A* is the frequency factor, *C* is the humidity coefficient, and *WC* is water content (% w/w).

The E_a can be calculated using the points obtained previously during the linearization process of the generated HF curves between b and c at various temperatures with different water content. The linear fit b-c is

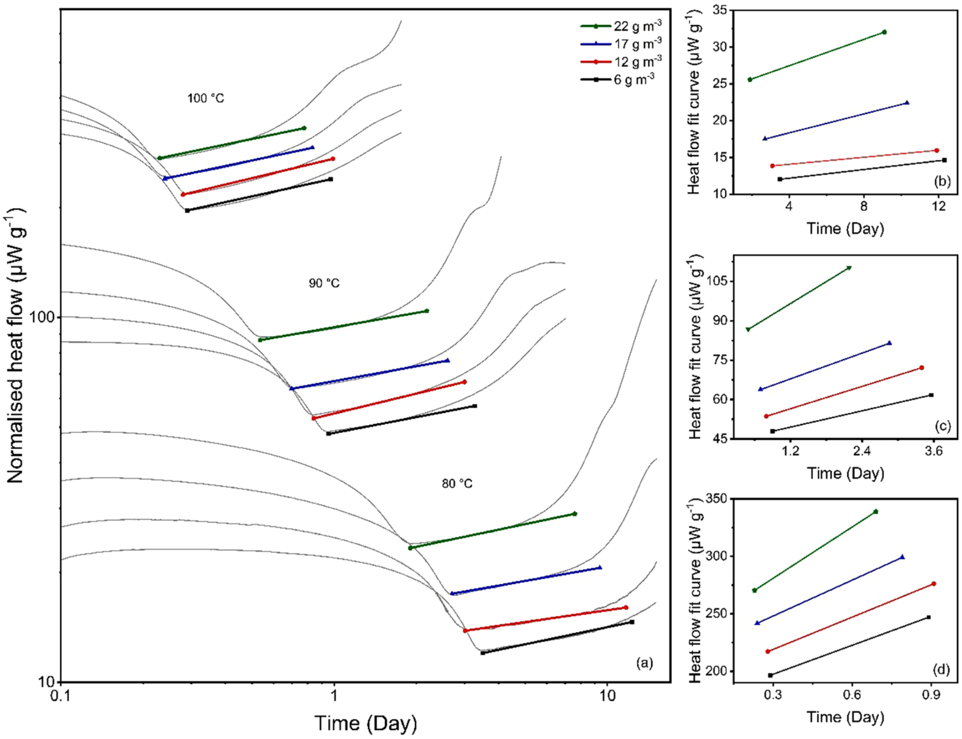

Fig. 9. Influence of absolute humidity on (a) log-log HFC curves at 80, 90 and 100 °C, with stage b-c linear fitted curves. (b-d) Linear HFC curves at 80, 90 and 100 °C, with stage b-c linear fitted curves.

Table 4
Time, heat and heat flow differences in the constant decomposition region b-c.

T °C	Water content g m^{-3}	Linear fit 1st minimum μW g^{-1}	Initial time (point b) Day	Δ Time Day	Δ Normalized heat J g^{-1}	Δ Normalized heat flow μW g^{-1}	K s^{-1}
80	6	0.1x+11.7	3.5	11.5	11.7	4.3	0.4
	12	0.3x+12.9	3.1	8.8	13.3	6.1	0.7
	17	0.7x+15.7	2.7	7.6	14.0	4.9	0.6
	22	1.1x+21.6	1.9	7.2	19.2	6.4	0.9
90	6	5.2x+43.2	0.9	2.6	12.8	13.6	5.2
	12	7.1x + 47.9	0.8	2.7	14.6	19.1	7.0
	17	8.2x + 57.9	0.7	2.2	14.9	17.4	7.9
	22	13.9x + 79.7	0.5	1.7	19.7	22.8	13.4
100	6	84x+144.5	0.3	0.6	13.0	50.4	84.0
	12	91.7x+194.7	0.3	0.6	14.9	59	98.3
	17	104.1x+241.6	0.2	0.6	15.2	57.3	95.5
	22	150.5x+235	0.2	0.5	19.9	68.5	197.0

used because propellant decomposition is taking place steadily and primary stabiliser depletion is occurring at the same time. Table 4 shows the different values obtained using the proposed methodology. As can be seen in the table, both heat and HF increase as the water content of the samples increases. If the HF at b-c is just influenced by the reaction of the primary stabiliser, the normalised HF should be equivalent across the different temperatures; but this is not the case. The likely cause of this phenomenon is the initial reaction with the water and oxygen in the HFC vial altering the subsequent decomposition chemistry.

As shown in Fig. 10, using the differences in the heat flows at 80, 90, and 100 °C, the Arrhenius curves are obtained for different water content. The plot shows a good log-linear relationship between the temperature and the reaction rate constant; therefore, E_a can be obtained from the slope of the linear regression performed, obtaining a value of $E_a = 131 \pm 3.1$ kJ mol^{-1}, which remains constant over the range of temperatures used in the experiments.

When the rate constant k is plotted against the water content regardless of temperature (Fig. 11), a log-linear increase in reaction rate constant is observed with increasing water content which is also seen in Fig. 10. The data shown that, in the temperature ranges used in the tests, there is a good correlation between the k and the water content in the samples, so the value obtained for the moisture constant C is 0.025 ± 0.0003 cm^3 g^{-1}. After substituting the averaged value of the moisture constant C in Eq. (7), the equation for the reaction rate is as follows:

$$\ln|k| = -\frac{131}{RT} + \ln|A| + [0.025 \cdot WC] \tag{8}$$

Work by Bohn, Ticmanis et al. and Volk [15,66,67] reported that the E_a for thermolysis is 120–160 kJ mol^{-1} at temperatures ≥60 °C, while hydrolysis is the dominant reaction at temperatures <60 °C, E_a 60–80 kJ mol^{-1}. The activation energy obtained for the DB propellant studied in this paper (131 kJ mol^{-1}) indicates that the dominant decomposition reaction should be thermolysis. However, the rate of reaction increases with increasing absolute humidity, which is indicative of hydrolysis. The propellant samples tested were completely sealed during ageing, meaning the decomposition reaction chemistry is influenced by the autocatalytic decomposition reaction; unlike a swept experiment where the decomposition products are removed from the propellant and which examines the intrinsic decomposition reactions of hydrolysis and thermolysis [68]. Water is a key variable in a sealed experiment where the secondary reaction mechanism of autocatalysis becomes a crucial factor in the storage life for the double base propellant studied in this paper.

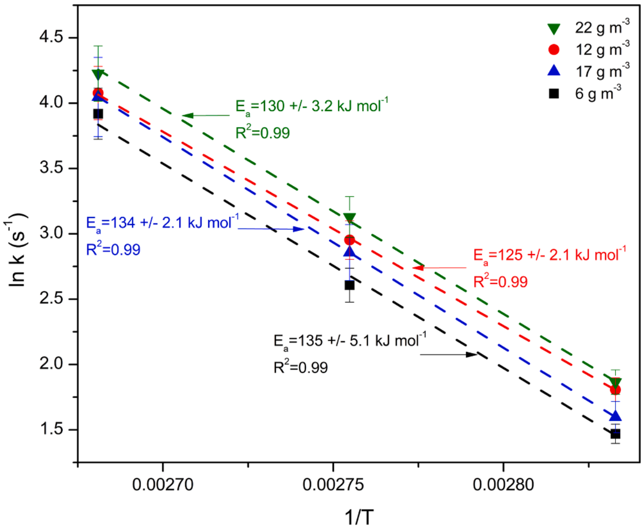

Fig. 10. Influence of absolute humidity on Arrhenius curves of HFC region b-c.

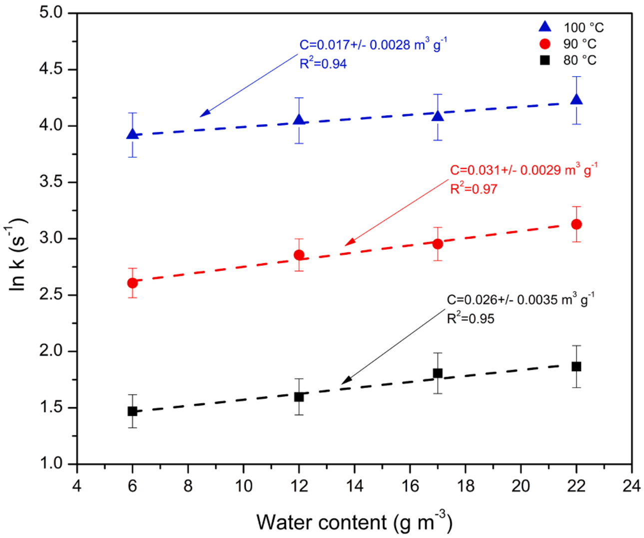

Fig. 11. Relationship between reaction rate constant and water content at different temperatures.

4. Conclusion

Stabilizer content and HF measurements showed that humidity/water significantly reduces the life of NC-based propellants. As the moisture content of the propellant increases from 6 to 22 g m^{-3}, the rate of the stabiliser depletion increases resulting in the shortening of the life of DB propellants from 11 to 6 years. The results obtained with the HF show that, over a 10-year at 25 °C equivalent period, the HF generated in the 22 g m^{-3} samples increases by more than 400 % compared to the 6 g m^{-3} samples. Despite the noticeable increase, all the samples pass the STANAG 4582 criteria, but this may become an issue for another propellant.

Modelling the HF curves has allowed the transition between different stages of the decomposition process of NC polymer to be more accurately determined. This model was used to calculate the Arrhenius kinetics of HF for the initial stage of NC decomposition of the main stabiliser (b-c) with 1st order kinetics. From the data obtained for HF in the range of 80–100 °C and due to the nature of the test, it is observed that the main decomposition mechanism is autocatalysis and that it is stimulated as the water content in the samples increases.

This paper has shown that it is important to consider more than just temperature when evaluating the safe life of NC propellants. Other environmental factors such as water/humidity should be considered. Further work in the area is ongoing to quantify the influence of water across a range of temperatures and NC propellant types.

CRediT authorship contribution statement

Alonso Romero Jabalquinto: Investigation, Writing – original draft. **Nathalie Mai:** Conceptualization, Supervision, Writing – review & editing. **Yahaya Mohammed:** Investigation. **Philip P Gill:** Supervision, Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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