

BURNING BEHAVIOUR OF B/KDN-MIXTURES COMPARED WITH B/KNO₃

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Abstract

Potassium dinitramide features in a high potential as effective pyrotechnic oxidiser. In this study a stoichiometric B/KDN composition and one with 30% boron are compared with the equivalent B/KNO₃ compositions concerning thermodynamic performance, shock and friction sensitivity, gas generation and particle temperatures.

Introduction

The ignition of modern gun propellants is still a challenging task that requires for new igniter compositions adapted to the single type of the propellant. The igniter has to provide a certain amount of gas of high temperature and hot small particles in a short time period. Pyrotechnic research always looks for new components which may help to improve the performance of an igniter. Recently Ammonium dinitramide (ADN) and other promising green oxidisers developed in the second part of the 20th century became cheaper by new medium scale production technologies offering also a basic access to synthesise new pyrotechnical compounds. One of these is potassium dinitramide (KDN) qualifying as stable and halogen-free oxidiser with a high oxidising potential and moderate hygroscopicity and acceptable stability data. [1]-[3].

By the elementary composition KDN is similar to potassium nitrate KNO₃ which is widely used as pyrotechnical oxidiser but KDN offers a better heat of formation, a larger gas production potential and more molar oxygen.

This study aims in a draft comparison of KDN with KNO₃ in combination with boron. B/KNO₃ is a material widely used as standard igniter when high amounts of particles should be produced.

Thermodynamic Predictions

To compare the theoretical performance data, calculations using the ICT-Thermodynamic Code [4] were performed at a loading density of $\Delta=0.1 \text{ g/cm}^3$ as a function of the boron mass fraction. Results are shown in Figure 1. Maximum pressure and temperature are predicted for a stoichiometric composition of 15% boron, which is the same mass fraction for both oxidisers. When using KDN a maximum pressure close to 90 MPa is predicted, which would be nearly twice the value of B/KNO₃. Also the maximum temperature is with 4900 K nearly 1000 K higher as that of B/KNO₃. Classical igniter mixtures of B/KNO₃ include a mass ratio of 30 : 70 to achieve a large number of hot boron particles. At this ratio the system B/KDN still features in drastically increased pressure and higher temperatures. The chemical thermodynamic calculations predict for both systems a condensed material fraction of 16 mol/kg. This indicates that B/KDN should feature in profitable pressure generation at a higher temperature level but with a similar amount of hot particles.

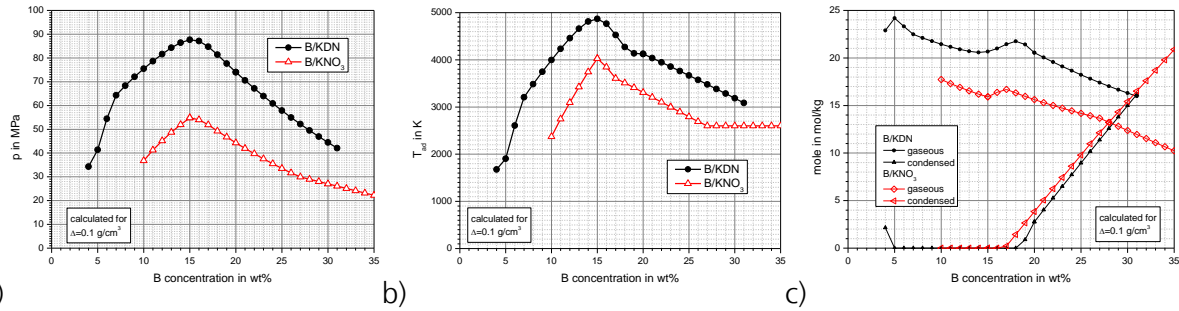


Figure 1 Comparative isochoric calculations using ICT-Thermodynamic-Code of a) pressure, b) adiabatic temperature and c) mole number of gaseous and condensed products.

Experimental

Synthesis

KDN was synthesized from surplus ADN prills (without coating) by dissolving in acetonitrile and adding the equimolar amount of KOH in methanol. Ammonia was removed by vacuum and KDN was slowly recrystallized twice from anhydrous acetonitrile.

Compositions

To compare B/KDN with B/KNO₃, for each oxidiser two compositions one with 15 and one with 30% of boron were prepared. 15% of boron is the stoichiometric composition with the highest predicted temperature. A mass fraction of 30% boron is a classic mixture ratio of B/KNO₃ igniter compositions in order to achieve a good particle ratio of hot particles.

Species \ Samples	unit	B82	B83	B84	B85
B	wt%	15	30	15	30
KDN	wt%	85	70	-	-
KNO₃	wt%	-	-	85	70
Oxygen balance	wt%	-0.5	-39.6	0.3	-38.9

Table 1 Investigated compositions.

Set-Up

To characterize the gas production rate of the mixtures an especially designed mini bomb (volume 50 ml) was applied [5]. 350 mg of the mixture were filled into a perforated casing that was fixed inside the mini bomb. The closed mini bomb was equipped with a pressure transducer (Kistler 6221A) and electrical ignition was performed by a percussion cap (DM 1520, Dynamit Nobel) achieving a maximum pressure of 50 kPa which was negligible with respect to the significantly higher pressure produced by the igniter mixtures.

To investigate the combustion as a function of pressure the mixtures were measured inside the ICT optical bomb. This chimney-type window bomb allows the observation of the reaction of energetic materials at moderate pressure up to 18 MPa under different atmospheres and is equipped with four windows that can be adapted to various spectral ranges. In this case, it was pressurized with nitrogen at constant levels between 1 and 13 MPa. The samples were provided as bulk material inside a plastic tube. For ignition, a melting wire was used.

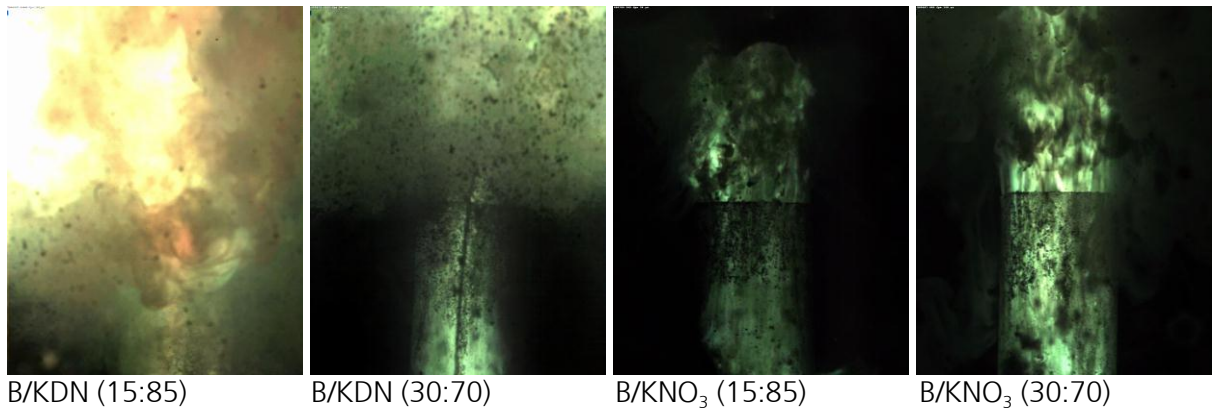


Figure 2 B/KDN and B/KNO₃ compositions reacting in plastic tubes at 1 MPa in the ICT window bomb.

Measuring Techniques

For visible observations a digital colour high-speed video camera (Motion Pro X3) with up to 8000 fps was used to characterize the reaction zones. A macro lens offers a reproduction scale of 1:1 and more.

NIR-spectra were recorded with a Plane Grating Spectrometer PGS-NIR 2.2 (Carl ZEISS GmbH) in the wavelength range from 1 to 2.17 μm . As optical entrance, a glass fibre was used. Under the applied experimental conditions the field of view was about 10 mm in diameter. This only allowed the determination of time history of overall temperatures. The evaluation of NIR emission spectra used the ICT-BaM code to model spectra of gaseous reaction products, soot and continuum radiation. The procedure compares each experimental spectrum with a calculated one using a least-squares fit-method to determine parameters like temperature or concentration paths. It is described in detail in [6]. For the recent application the continuum radiation from 1.0 to 2.1 μm was regarded as grey-body emission. Potassium lines were omitted. The evaluation simultaneously results in time profiles of intensity and temperature.

Experimental Results and Discussion

Sensitivity on Shock and Friction

Impact sensitivity and friction sensitivity tests were performed according to NATO STANAG 4487 and NATO STANAG 4489 procedures with the BAM drop hammer and Friction sensitivity tester made by the former company Julius Peter (Berlin). The value reported is the smallest load under which deflagration has been noticed at least one time in six consecutive tests.

For all compositions the friction tests show very insensitive behaviour. The B/KDN compositions are more sensitive to shock than B/KNO₃. But the materials are still manageable. Also one should keep in mind that the samples are pure particle mixtures, whose sensitivity might be improved by granulation using an appropriate additive agent.

Species \ Samples	unit	KDN	B82	B83	B84	B85
Shock	Nm	50	2.5	2.5	25	25
Friction	N	>360	>360	>360	>360	>360

Table 2 Shock and friction sensitivity of the investigated compositions.

Closed Vessel

The mini-bomb test qualifies excellent to compare the kinetics of gas production rate and pressure generation. The pressure traces of these tests are presented in Figure 3. Both B/KDN compositions start 0.6 ms after ignition. That is 0.2 and 0.3 ms faster than B/KNO₃ with 15% and 30% of boron, respectively. The stoichiometric B/KDN composition reaches a peak pressure of about 2.8 MPa after about 1 ms. The composition with 30% of boron is somewhat later (at about 1.5 ms) with a maximum pressure of 2.5 MPa. The maximum pressure of the B/KNO₃ compositions is about 1.6 MPa and was achieved after 2 and 2.5 ms. This indicates that B/KDN compositions are sufficiently fast to be used as igniter compositions. The ratio of the maximum pressures of B/KDN and B/KNO₃ samples are about the same as predicted in Figure 1a indicating that under ballistic conditions the reactions run according to the thermodynamic calculations.

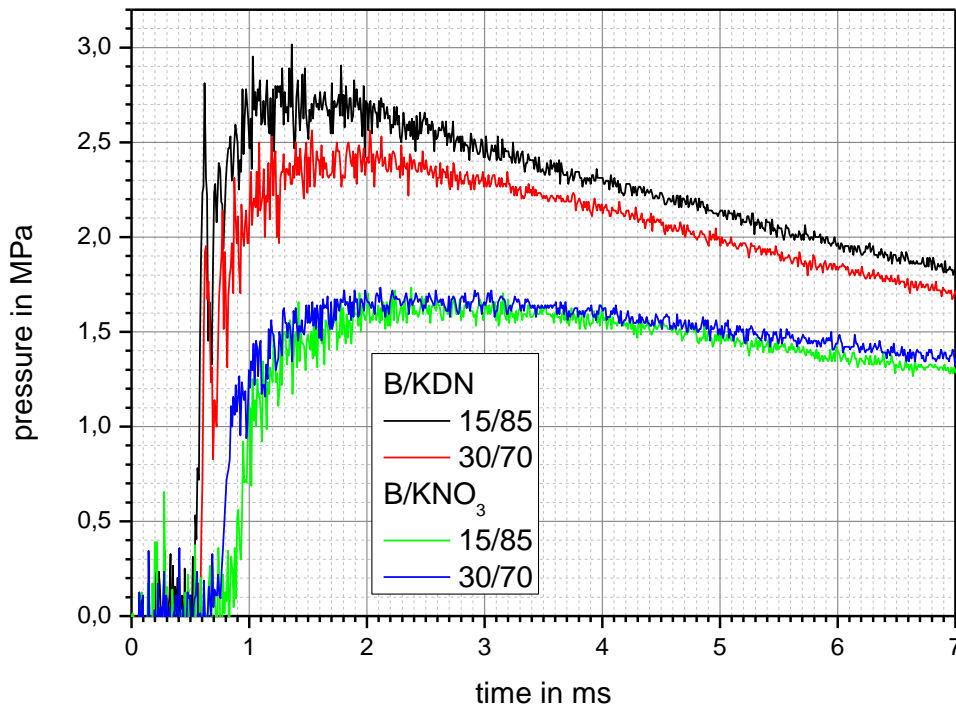


Figure 3 Pressure traces of the sample combustion inside the mini-bomb.

Spectroscopy and Temperatures

As expected the spectra of all compositions feature in the same lines (mainly K) and systems (BO) of gaseous species overlapped by a continuum emission with a maximum in NIR range. Figure 4 compares typical spectra from all compositions. The spectral intensity of the samples is normalized to the intensity at 1 μm . Only the strongest potassium line at 768 nm of the B/KNO₃ samples shows a self-absorption effect. It is obvious that the BO-system from 0.4 to 0.65 μm of B/KDN is stronger compared to the intensity of this line and also to the continuum emission.

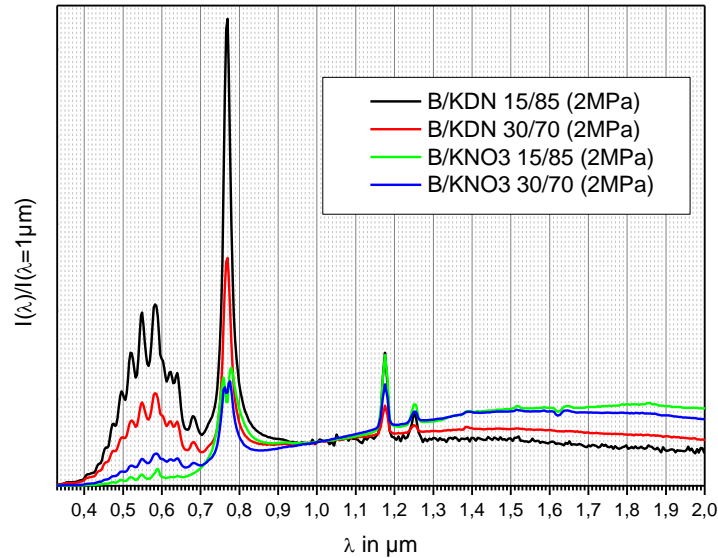


Figure 4 Spectra of the samples burning at 2 MPa (related to intensity at 1 μm).

Omitting the potassium lines at 1.17 and 1.25 μm the continuum could be described with very high accuracy using Planck's equation for grey body emission to determine the emission temperature of the continuum. In general, this continuum emission is generated by hot condensed surfaces. Considering the optical set-up it can mainly be attributed to detached particles in the igniter flame plume. Figure 5 presents the so measured temperature history of all compositions burning at 7 MPa. All compositions show their temperature maximum shortly after ignition. B/KDN features in higher temperature maxima than B/KNO₃ samples but cool down faster than B/KNO₃. In general the absolute values are significantly lower than might be expected when comparing with the isochoric calculations in Figure 1b. Also isobaric calculations at 7 MPa result in drastically higher values, listed in the legend of Figure 5.

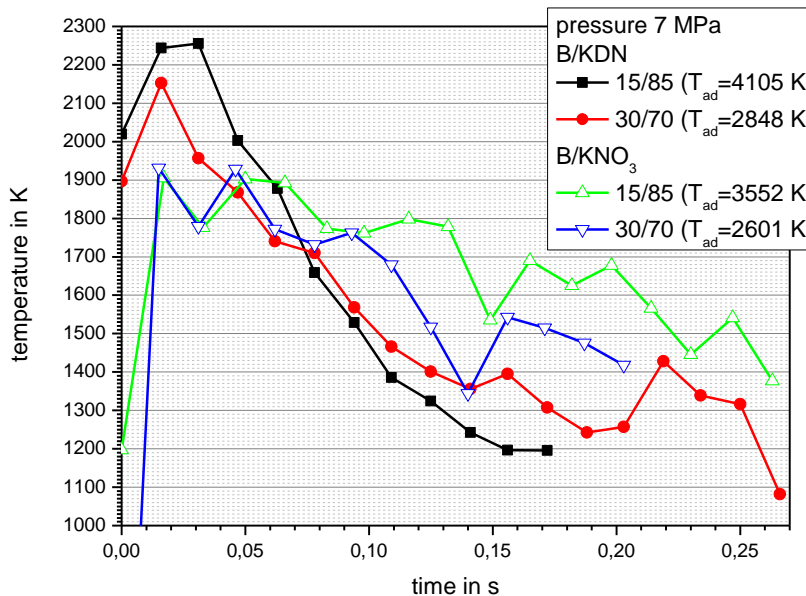


Figure 5 Temperature history of the compositions burning at 7 MPa.

For other pressure levels this was similar. The maximum temperatures of all samples vary between 1800 and 2550 K (comp. Figure 6). Although in most cases the maximum temperatures of the B/KDN compositions are higher than those of B/KNO₃, no clear trend is obvious. Interestingly the boiling or decomposition point of boron trioxide (B₂O₃) is specified between 1770 K [7] and 2520 K [8] which is exactly the range of our measured continuum temperatures. This suggests that the particle temperature is dominated by the boiling boron

oxide that covers the burning oxide particles. The selected measuring techniques did not allow measuring the gas temperature that might be significantly higher, as also indicated by the spectra of gaseous BO in Figure 4.

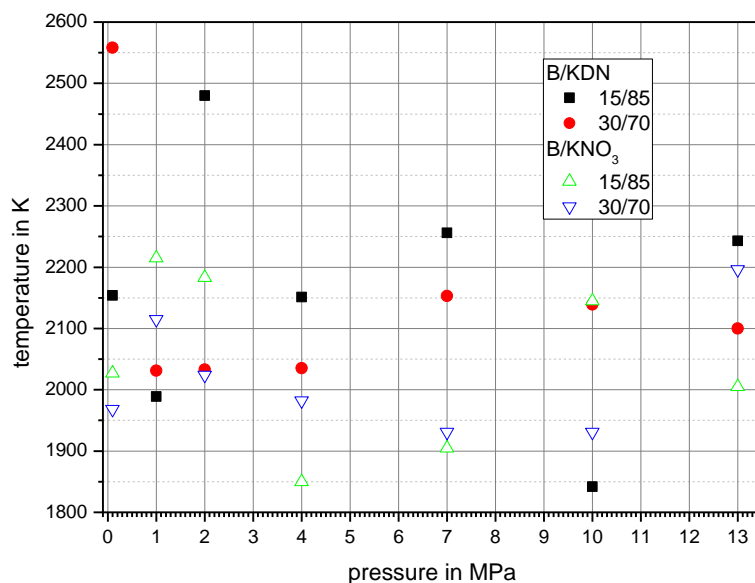


Figure 6 Maximum emission temperatures of hot boron particles measured in the plume of the compositions.

Conclusions

In combination with boron, KDN offers an interesting potential as igniter composition that promises a faster pressure increase with a similar particle to gas ratio as B/KNO₃ including particles with a high temperature level. This temperature level is only slightly higher than that of KNO₃ but significantly lower than predicted by thermo-chemical calculations in particular at increased pressure. This may be explained by the boiling or decomposition point of boron oxide that covers the burning particles.

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