Pressure and Temperature Dependency of ADN-based Solid Rocket Propellants

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Abstract

Solid rocket propellants based on ammonium dinitramide (ADN) as oxidizer and glycidyl azide polymer (GAP) as binder are suitable candidates for future propellants with good performance characteristics and no hazardous impact to the environment relating to the burning products. The comparison with the actual state of the art solid propellant, based on hydroxyl-terminated polybutadiene (HTPB) and ammonium perchlorate (AP), reveals that ADN-based propellants, especially in combination with an energetic binder, result in non-suitable burning rates (*r*) and pressure sensitivities (*n*) for civil applications.

In a previous work **Fehler! Verweisquelle konnte nicht gefunden werden.**, propellant formulations of ADN/GAP, ADN/HTPB and AP/GAP, AP/HTPB were produced and investigated to comprehend the differences in the combustion mechanism. In this work a detailed characterization of the pressure- and temperature-depended burning behavior was done in a Crawford-type bomb (2 – 200 MPa; -40 °C – 50 °C).

For keeping the number of experiments low and to gather empirical knowledge, design of experiment was used.

Keywords: Combustion behaviour, Solid rocket propellants, Design of experiment, ADN, AP

1 Introduction

Solid rocket propellants typically consist of a mixture of granules of a solid oxidizer (AP, AN, ADN) placed in a polymeric binder combined with energetic compounds (HMX, RDX), metallic additives (Al, Mg) plasticizers, stabilizers and / or burn rate modifiers [1].

Today, HTPB (hydroxyl-terminated polybutadiene, binder) and AP (ammonium perchlorate, oxidizer) are widely used in solid propellants. These propellants are well known for their good performance characteristics, mechanical properties and the wide operating temperature range. But the contamination of the environment by the combustion products of perchlorate is also well known and documented [2]. For this reason, the future propellants should keep the performance characteristics and the mechanical properties, but replace the components, which lead through the burning to a hazardous contamination of the environment. One oxidizer, which has the potential to fulfil the criteria, is ADN. In combination with non-energetic binders like HTPB, specific impulse values comparable to systems based on HTPB/AP could be reached. Pressure exponents higher than 0.7 for HTPB/ADN formulations [3] make them ineligible for the majority of potential applications. Another approach is the use of GAP as an energetic binder. GAP is classified as a high-nitrogen content polymer and due to its availability, good binder properties and low detonation sensitivity, it is a suitable polymer for solid propellants [4], [5]. Usually, GAP/ADN propellant formulations, which are reaching similar specific impulse values as comparable systems based on HTPB/AP, feature a very high burning rate in the operation range between 2 and 20 MPa. The pressure exponent is typically ranging from 0.3 to 0.7 [6], [7], [8]. ADN-based propellants in combination with an energetic binder result in non-suitable burning rates for civil applications.

2 Experimental Procedure

2.1 Materials

In summary, four formulations of solid composite propellants have been investigated. The main differences are the used oxidizer and binder, the oxidizer-binder ratio was kept constant (Table 1).

Labelling	HTPB	GAP [%]	ADN [%]	AP [%]	Ratio Oxidizer/Binder
GADN_27_73		27.0	73.0		2.70
HADN_27_73	27.0		73.0		2.70
GAP_27_73		27.0		73.0	2.70
HAP_27_73	27.0			73.0	2.70

Table 1 Composition of the investigated solid propellants with different oxidizers and binders.

The labelling of the samples is chosen that the important information is immediately identifiable. The first letter stands for the used binder (H=HTPB; G=GAP). The further letters label the oxidizer (ADN, AP), followed by the mass percentage of binder (first number) and oxidizer (second number) of the investigated formulations.

The produced solid composite propellants include ADN or AP prills with particle sizes of 176 µm (ADN) or 200 µm (AP). The selected curing system for the energetic binder (GAP) is a combination of three isocyanates (Desmodur N 100, Desmodur N 3400, and Desmodur XP 2617) for a comprehensive NCO/OH ratio of 0.9. Increasing the reaction rate, the catalyst dibutyltin dilaurate (D22) was added. For the curing of the non-energetic binder formulations, one isocyanate (IPDI) and the same catalyst (DBTL, D22) were used. Overviews of the components are listed in Table 2.

Component	Class	Supplier
ADN	Oxidizer	Synthetized at EUB, prilled at FOI and ICT
AP	Oxidizer	SNPE, Japan
GAP 06S12	Binder	Eurenco, Sweden
Polyvest EP HT	Binder	Evonik, Germany
Desmodur N 100 / 3400	Curing Agent	Covestro AG, Germany
Desmodur XP 2617	Curing Agent	Covestro AG, Germany
IPDI	Curing Agent	Evonik, Germany
Dibutyltin dilaurate (DBTL, D22)	Catalyst	Merck, Germany

Table 2 Chemicals used in experimental work.

All the propellants discussed in this paper were produced with the ARV-310 Thinky Mixer, a planetary centrifugal bladeless kneader, “under vacuum” (~1000 Pa), in order to minimize air inclusions induced by the mixing process in the slurries.

2.2 Design of Experiments

Design of Experiment is a strategy to gather empirical knowledge, i.e. knowledge based on the analysis of experimental data and not on theoretical models [9], [10]. Building a design means carefully choosing a small number of experiments that are to be performed under controlled conditions for a better understanding of the pressure- and temperature-dependent burning behaviour of the investigated solid rocket propellants. For this reason, a response surface method (RSM) for optimization was chosen. The goal of RSM is to generate a map of response (burning rate) in the form of a 3–D rendering graph. The used design consists of two factors (pressure and temperature) and exhibits in total 5 levels for each factor (T: -40, -20, 0, +23, +40 °C; p: 2, 4, 7, 10, 13, 20 MPa). For each formulation, 16 runs were performed. An example for the performed experimental design (formulation: HADN_27_73) is shown in Table 3.

Run	**Factor 1** T [°C]	**Factor 2** p [MPa]	**Response** r [mm/s]
1	23	7	13.90
2	0	10	16.62
2	-20	4	5.92
3	-40	13	13.92
4	40	13	25.64
5	0	10	17.36
6	-40	7	9.07
7	-20	20	22.34
7	40	20	31.14
7	-20	20	21.66
8	-40	4	5.02
8	0	10	15.88
9	-40	13	14.20
10	0	3	4.69
11	0	10	15.95
11	40	3	9.78

Table 3 Design of experiment for the formulation: HADN_27_73

To generate the design of experiment and for the evaluation of the data, the software DESIGN-EXPERT 11 from Stat-Ease, Inc. was used.

2.3 Experimental Setup

For the pressure- and temperature-dependent characterization, samples were tested as strands in a Crawford bomb between 2 and 20 MPa nitrogen pressure and between -40 °C and +40 °C. The investigated solid propellant is placed as strands in vertical position in the high pressure vessel. The strand is protected against surface burning by mantle insulation. The ignition is done electrically at the upper end. The combustion rate is recorded with the aid of three wire probes, which are arranged across the strand at two intervals of 50 mm.

3 Results and Discussion

The procedure for creating a map of response will be demonstrated using the results of the temperature- and pressure-dependent burning rate measurements of the formulation: HADN_27_73. The used RSM design is shown in Table 3. The centerpoint (0 °C, 10 MPa) was replicated 3 times to provide enough power for the analysis. These points, along with all others, were performed in random order. For all examined formulations, a quadratic model was suggested; in which both factors (temperature, pressure) have a significant influence on the burning rate. The suggested quadratic model for the formulation HADN_27_73 is presented in the following equation:

$$r = 0.1366 + 0.06582 \cdot T + 1.983 \cdot p + 0.004863 \cdot T \cdot p + 0.000232 \cdot T^2 - 0.03751 \cdot p$$

Source	Sum of Square	df	Mean Square	F-value	p-value
Model	829.07	5	165.81	266.39	<0.0001
A-Temperature	180.41	1	180.41	289.85	<0.0001
B-Pressure	637.44	1	637.44	1024.08	<0.0001
AB	9.99	1	9.99	16.04	0.0025
A^2	0.42	1	0.42	0.67	0.4331
B^2	21.63	1	21.63	34.74	0.0002
Residual	6.22	10	0.62		
Lack of Fit	4.53	5	0.91	2.68	0.1516
Pure Error	1.69	5	0.34		
Cor Total	835.29	15			

Table 4 ANOVA for the performed measurements and results of the formulation HADN_27_73

An interaction of the two factors could be detected. The results of the analysis of variance for the formulation: HADN_27_73 is shown in Table 4. P-values less than 0.05 indicate model terms that are significant. In this case, the overall model with the terms: A (temperature), B (pressure), the interaction between both and B^2 are significant model terms. For a better description of the pressure- and temperature-dependent burning rate, the term A^2 was also included in the model

Also the model F-value of 266.39 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. The Lack of Fit F-value of 2.68 implies the Lack of Fit is not significant relative to the pure error. The diagnosis of the residuals showed no abnormality. Therefore, the model is statistically solid.

The procedure of the implementation of the design of experiment was identical for all of the four formulations. The resulting response surface graphs are shown in Figure 1. Each colour represents a combination of the input factors (temperature and pressure) that produces similar response (burning rate). The performed measurements are shown as dots. The dark red dots are design points above the predicted value and the bright red dots the points below the predicted value. The number of replicates at this set of conditions was set to 4.

As expected, the maximum burning rate for all formulations occurs at +40 °C and 20 MPa. The fastest burning rate can be reached with an ADN/GAP propellant at the mentioned conditions (41.57 mm/s). Replacing the energetic binder GAP by HTPB reduces the maximum burning rate to 31.7 mm/s. The PDL for this formulation increased from 2 MPa to 3 MPa. This fact was taken into account in a customized design of experiment. The combination of GAP and AP as oxidizer reveals lower burning rates in the examined range of pressure and temperature. At +40 °C and 20 MPa, a burning rate of 26.61 mm/s was measured. AP as an oxidizer combined with the inert binder HTPB is showing the lowest burning rates compared to the other formulations, with the maximum burning rate at 5.42 mm/s and the lowest value at -40 °C and 2 MPa with 2.47 mm/s.

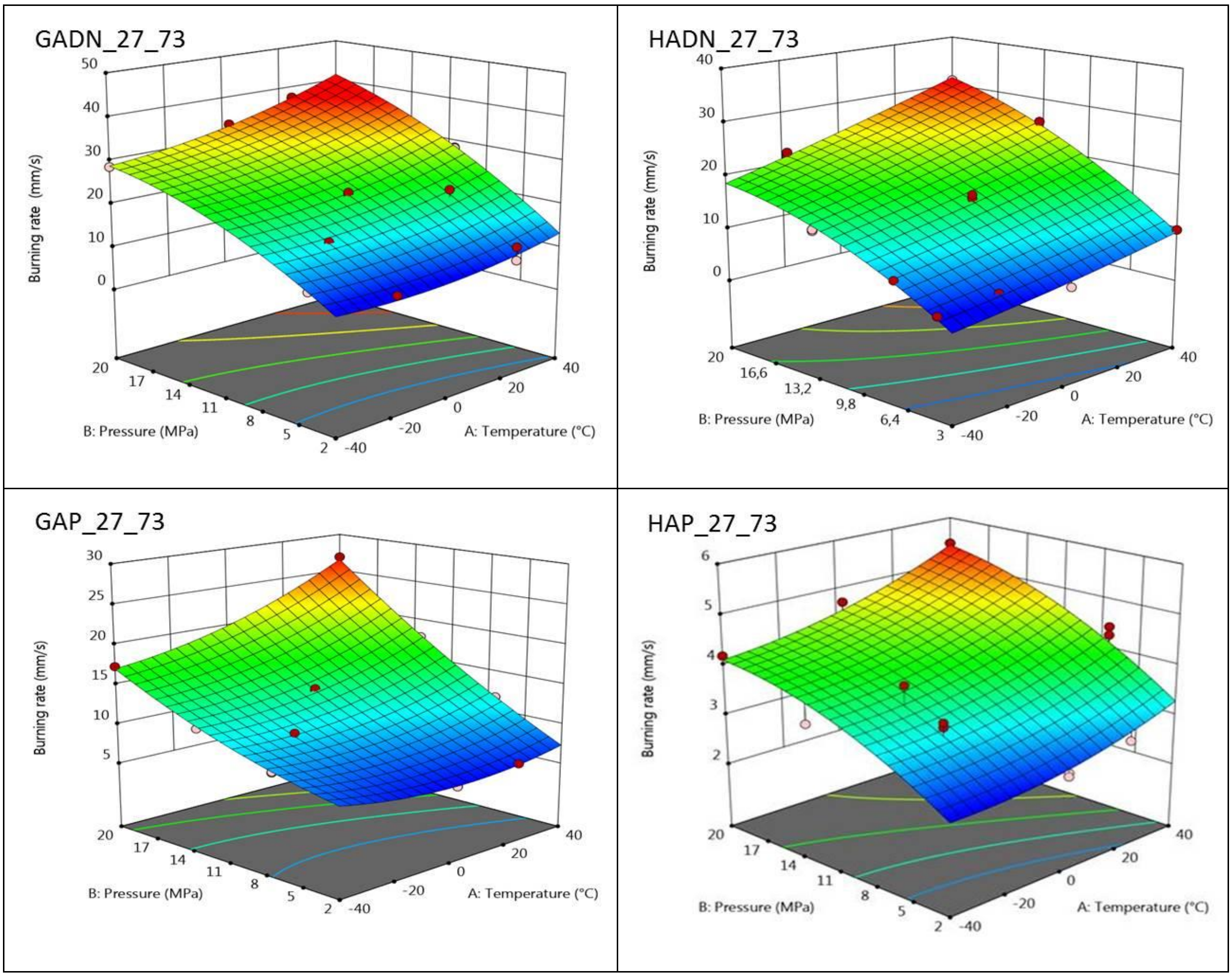

Figure 1 Response surface plot for the formulations: GAP/ADN, HTPB/ADN, GAP/AP, and HTPB/AP.

A common approach to evaluate models is to plot predicted against actual values and compare slope and intercept parameters against the 1:1 line. The plot could be also seen as a visualization of the ANOVA table (Table 4; HADN_27_73).

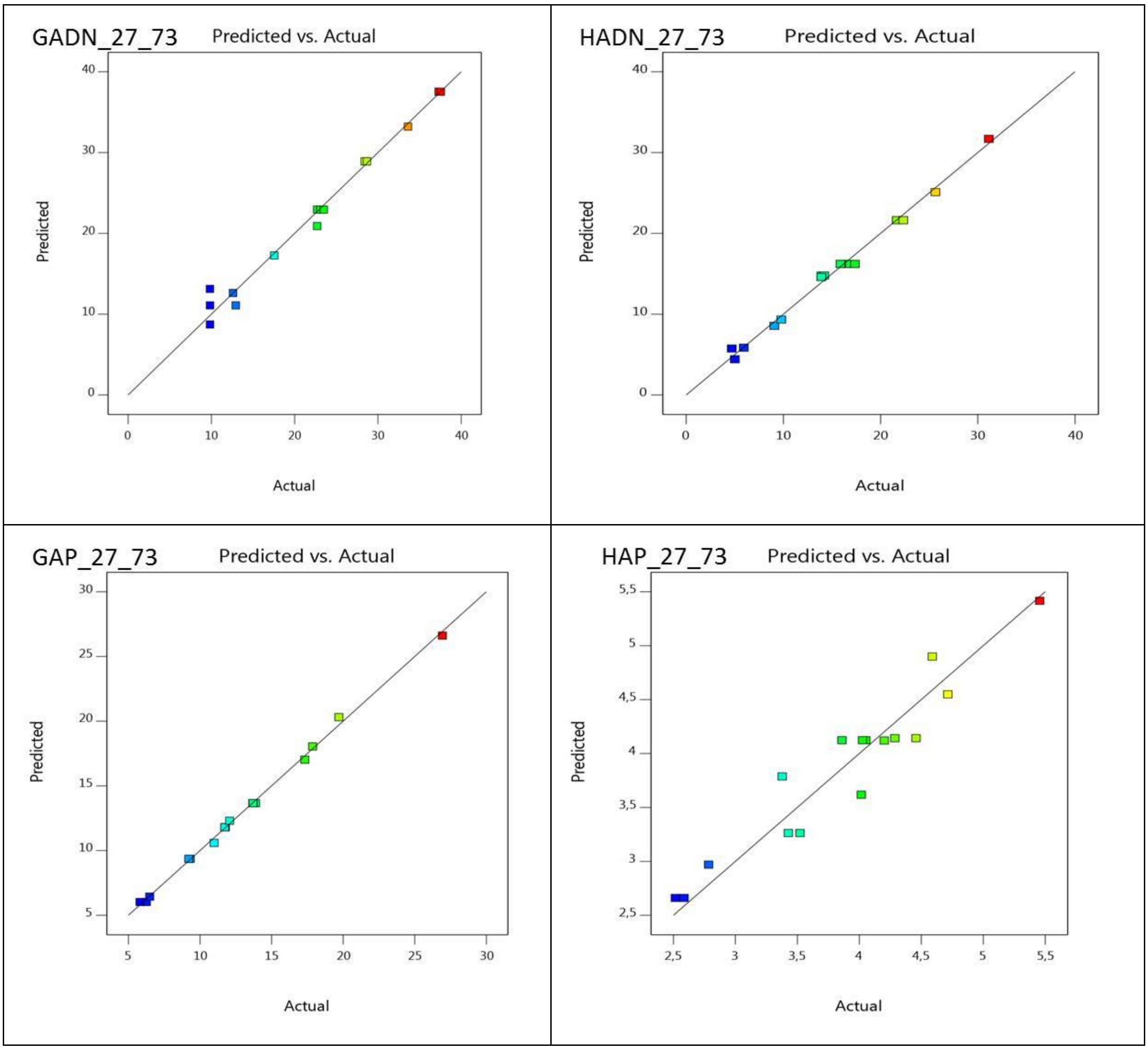

Figure 2 Predicted vs. Actual Plot for the formulations: GAP/ADN, HTPB/ADN, GAP/AP, and HTPB/AP.

For the formulations: GAP/ADN, HTPB/ADN and GAP/AP the models are very accurate. There's a strong correlation between the model's predictions and its actual results. The goodness of fit leads to a high coefficient of determination (R^2) in all three cases (GADN_27_73: R^2 = 0.9845; HADN_27_73: R^2 = 0.9925; GAP_27_73: R^2 = 0.9981). Noticeable is the scattering around the regression for the GADN_27_73 formulation at low burning rates (10 – 15 mm/s), which occurs at low pressures and/or temperatures. In this range, the model will be adapted in the near future by further measurements. The only exception is the formulation with AP as oxidizer and HTPB as binder. The R^2 is lower compared to the other formulations (HAP_27_73 R^2 = 0.9155). The measured burning rates scatter around the diagonal line over the whole, examined pressure and temperature range. One possible explanation is that measurement inaccuracies have a greater influence on slow-burning propellants.

Summary

The combustion behaviour of GAP/ADN, HTPB/ADN and GAP/AP, HTPB/AP propellants was studied in a Crawford bomb. Samples were tested at pressures of 2, 4, 7, 10, 13 and 20 MPa under nitrogen and in a temperature range from -40 to +40 °C. With the help of statistical experimental design, the interaction between influencing factors (pressure, temperature) and target variables (burning rate) is determined with a high accuracy by 16 measurements for each formulation. For all examined formulations, a quadratic model was suggested with a strong correlation between the model's predictions and its actual results.

Abbreviation

ADN	Ammonium dinitramide
AP	Ammonium perchlorate
GAP	Glycidyl azide polymer
HTPB	Hydroxyl-terminated polybutadiene
Al	Aluminium
Mg	Magnesium
ICT	Fraunhofer Institut für Chemische Technologie
n	Pressure exponent
r	Burning rate
EUB	EURENCO Bofors
PDL	Pressure Deflagration Limit
ROI	Region of interest
RSM	Response Surface Method
R^2	Coefficient of determination

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