

Predicting Cylinder-Test Detonation Energy via Thermochemical and Gas-Phase Descriptors

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Abstract In this work, mechanical work potential refers to the ability of an explosive to convert chemical energy into expansion work, as quantified experimentally by cylinder-test detonation energy. A novel predictive method is introduced for the assessment of cylinder-test detonation energy (DE) in CHNOFCl energetic compounds, specifically targeting performance in the cylinder test. Utilizing four distinct decomposition pathways, the model evaluates the heat of detonation (Q), the number of moles of gaseous products (NMGP), and the average molecular weight of these gases (AMWGP) by accounting for key species such as HF, HCl, CO, N₂, H₂O, H₂, and CO₂. Initial analysis reveals a strong linear correlation between experimental DE and a composite parameter of Q , loading density (ρ_0), and NMGP, expressed as: $DE = 9.58 + 2.50 \times 10^2 Q^{0.5} (\rho_0 \times NMGP)^{0.7}$ ($R^2=0.886$). To further enhance accuracy, an improved correlation was developed by incorporating $\log(AMWGP)$ as a corrective term, yielding the refined model: $DE_{cor} = -14.7 + 8.90 \log(AMWGP) + 0.355 \times 10^2 Q^{0.5} (\rho_0 \times NMGP)^{0.7}$. The robustness and generalizability of this improved model were rigorously validated through internal and external evaluation techniques, demonstrating its reliability for predicting the mechanical work potential of diverse energetic materials.

Keywords: Cylinder test; Detonation energy; Predictive empirical regression model; CHNOFCl explosive; Decomposition pathways

1. Introduction

High-energy density materials (HEDMs) are essential components in modern aerospace and defense technologies, providing the propulsion and explosive force required for rocket systems and military applications [1]. A primary measure of an HEDM's performance is its heat of detonation, which represents the energy released per unit mass during a supersonic, shock-driven explosion [2]. This parameter, typically evaluated at the Chapman-Jouguet (CJ) state, is determined by chemical factors—such as the formation of specific detonation products—and physical factors like loading density [3]. While maximizing energy is critical, the inherent instability of high-performance HEDMs requires a careful balance between explosive power and operational safety [4].

The experimental development and characterization of new HEDMs are often hazardous, time-consuming, and expensive [5]. Traditional methods for measuring detonation heat, such as constant-temperature or adiabatic calorimetry, are frequently limited by equipment complexities or imprecise thermal control [6]. Consequently, computational tools have become indispensable for the safe and efficient screening of material candidates during early-

stage research [7]. Historically, researchers have relied on empirical correlations like the Kamlet-Jacobs equations, thermochemical codes such as CHEETAH [8] or EXPLO5 [9], and quantum chemical methods like density functional theory [10]. While effective, these methods can be computationally intensive or overly complex for rapid performance assessments.

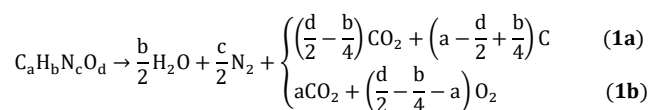
Recent advancements have focused on nitrogen-rich HEDMs, which are both high-performing and environmentally friendly, as they produce non-toxic dinitrogen (N₂) rather than harmful CO₂ or CO [11]. Compounds containing heterocyclic rings, such as tetrazole or furazan, store additional strain energy that significantly enhances detonation performance [12]. Despite these gains, challenges remain; specifically, few models can predict post-detonation behavior, such as the Jones-Wilkins-Lee (JWL) equation of state (EOS) parameters, which are critical for weapon design [13]. It is important to distinguish between the parameters within equations of state, such as the JWL equation, and the fundamental cylinder-test detonation energy of an explosive. While the JWL equation characterizes the pressure-volume relationship of detonation products, this study focuses on the direct prediction of the total energy released during detonation. Additionally, the field of inverse prediction—designing molecules to match specific explosion properties—remains underexplored but holds immense potential [14]. Detonation performance is typically characterized by parameters such as detonation velocity and the assessment of mechanical work potential [15,16]. Predicting the performance of novel energetic materials from their molecular structure and estimated crystal density allows for the efficient screening and elimination of poor candidates [17,18]. Sophisticated computer codes like CHEETAH [8] or EXPLO5 [9] utilize the equations of state of detonation products to evaluate these properties. Furthermore, various empirical correlations can also be employed to predict detonation parameters [19,20]. Given the frequent scarcity of reliable experimental data, the comprehensive assessment of detonation performance is vital for designing high-performance pure and composite energetic mixtures.

The working potential of an energetic compound is determined by its heat of detonation, detonation velocity, and the volume of gaseous products [9]. The relative contribution of these parameters depends on the specific conditions under which the detonation occurs, with gaseous products and heat being most critical in closed or semi-closed environments. Among the various tests used to determine blasting and brisance capacity, the cylinder test provides a standard

measure of hydrodynamic performance. This test involves an explosive charge within a tightly fitting copper tube, where the radial motion of the wall is captured via streak camera techniques. The kinetic energy transferred to the copper wall in this fixed geometry provides a direct method for expressing explosive performance [16]. For CHNO energetic compounds, several studies have attempted to introduce simple correlations for predicting cylinder wall velocities or [21–24]. Regarding compounds with the general formula CHNOFCl, reliable predictions of detonation heat, pressure, velocity, and related performance parameters have been achieved by assuming four specific decomposition pathways based on oxygen balance, as demonstrated in previous studies employing this thermochemical framework [25,26]. CHNOFCl compounds were selected in this study because they represent a distinct and practically important subgroup of high-energy density materials for which thermochemical behavior can be analyzed with a consistent decomposition framework. However, we do not assume that the mere presence of fluorine or chlorine necessarily increases cylinder-test detonation energy. Their contribution depends strongly on the molecular composition and on the nature of the final detonation products. In particular, the energetic role of halogens may become more pronounced in metal-containing systems, where the formation of stable metal fluorides or chlorides can affect the overall energy release. The present work is therefore focused specifically on pure and composite CHNOFCl formulations, for which a reliable predictive correlation can be developed and validated. This work aims to introduce a simple and reliable method for predicting the cylinder-test detonation energy of CHNOFCl energetic compounds. One limitation of several previously reported simple correlations is their relatively low prediction accuracy for some energetic compounds. To address this issue, the present work proposes an improved thermodynamic correlation designed to reduce the deviation between predicted and experimental detonation energies. The proposed formulation aims to provide a more reliable estimation of cylinder-test detonation energy for CHNOFCl energetic materials while maintaining the simplicity required for practical applications. This new approach represents a significant advancement in the assessment of various pure and composite CHNOFCl formulations. A direct numerical comparison with thermochemical codes such as CHEETAH could further support model evaluation; however, access to the CHEETAH software was not available in the present study. Therefore, the proposed correlation is evaluated primarily using available experimental cylinder-test detonation energy data and established thermodynamic relationships, which also highlights the usefulness of the present method when specialized thermochemical software is not accessible.

2. Theory

When describing the behavior of $C_aH_bN_cO_d$ explosives, Kamlet and Jacobs [27] proposed a specific model for how these materials break down. They assumed that every bit of available oxygen in the molecule goes toward creating water and carbon dioxide, completely skipping the formation of carbon monoxide. Based on this logic, the final products of the explosion are simply H_2O , N_2 , CO_2 and either C (graphite) or O_2 depending on the explosive's oxygen balance, as shown below:



Equations (1a) and (1b) are designed to handle underoxidized and overoxidized explosives, respectively. Kamlet and Jacobs [27]

originally used these specific product sets to estimate the detonation pressure and velocity for $C_aH_bN_cO_d$ explosives with loading densities above 1.0 g/cm^3 . However, later research revealed that this method struggles with accuracy when the loading density drops below that threshold, leading to significant deviations in the results [28,29].

To address these limitations for more complex $C_aH_bN_cO_dFeCl_f$ explosives, researchers suggested using four distinct decomposition pathways to better predict performance across a broader range of densities [26]. This approach assumes that all nitrogen is converted to N_2 , fluorine to HF, and chlorine to HCl. Meanwhile, a portion of the oxygen forms H_2O , and carbon is prioritized to form CO rather than CO_2 . The four specific pathways used to determine these detonation products are outlined as follows **2a**, **2b**, **2c**, **2d** [26].

For clarity, the decomposition reactions used in this work are expressed using the general molecular formula $C_aH_bN_cO_dFeCl_f$. Depending on the oxygen balance of the compound, four decomposition regimes are considered, each producing the principal detonation products HF, HCl, CO, N_2 , H_2O , H_2 , and CO_2 . The stoichiometric coefficients in Eqs. (2a–d) were derived to satisfy elemental mass balance for carbon, hydrogen, nitrogen, oxygen, fluorine, and chlorine. To illustrate the application of the proposed decomposition scheme, representative calculations are provided for both a pure energetic compound and a composite formulation.

As an example of a pure compound, consider RDX ($C_3H_6N_6O_6$). Using the general molecular representation $C_aH_bN_cO_dFeCl_f$ and the decomposition pathways adopted in this work, the detonation products can be approximated as CO, H_2O , and N_2 under oxygen-balanced conditions. A simplified stoichiometric representation is



From this reaction, the total number of moles of gaseous products and their average molecular weight can be calculated and subsequently used to determine the thermodynamic parameters required in the proposed correlation.

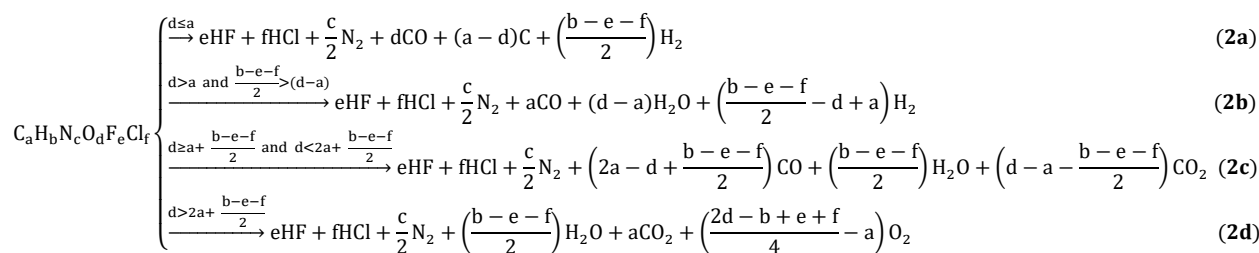
As an example of a composite formulation, consider a mixture consisting of 60 wt% RDX ($C_3H_6N_6O_6$) and 40 wt% TNT ($C_7H_5N_3O_6$). The effective elemental composition of the mixture is first determined from the weighted contributions of each component, and the resulting empirical formula is then treated within the same $C_aH_bN_cO_dFeCl_f$ decomposition framework. Based on the overall oxygen balance of the mixture, the appropriate decomposition pathway is selected and the stoichiometric amounts of gaseous products (e.g., CO, H_2O , N_2 , CO_2 , and H_2) are calculated. These values are then used to determine the number of moles of gaseous products and the average molecular weight required for the cylinder-test detonation energy correlation. By incorporating a more comprehensive set of detonation products, Eq. (2) offers several distinct advantages over traditional models:

For $C_aH_bN_cO_d$ explosives, the products defined in Eq. (2) yield a significantly more accurate heat of detonation than those in Eq. (1) [26].

The model in Eq. (2) also provides superior predictions for detonation pressure and velocity, particularly for explosives with loading densities below 1.0 g/cm^3 , where standard models often fail [26,30].

Unlike the classic Kamlet and Jacobs [27] method, this approach is versatile enough to handle both ideal and non-ideal pure or composite explosives containing fluorine and chlorine ($C_aH_bN_cO_dFeCl_f$), ensuring reliable performance metrics for halogenated systems [26,30].

To evaluate these performance metrics experimentally, the cylinder test is used to measure the hydrodynamic work potential of an



explosive. In this setup, a 25.4 mm diameter explosive charge is housed in a precision-fitted copper tube; once initiated, a streak camera captures the rapid expansion of the cylinder wall [16]. This expansion provides a direct look at how kinetic energy is transferred to the surrounding metal, which can occur either head-on (normal) or sideways (tangential) depending on the geometry [2].

Because the equation of state for the detonation products influences energy transfer, the effective energy often varies between these two geometric cases. The cylinder test tracks radial wall velocities at specific intervals—typically 5–6 mm and 19 mm—to distinguish between head-on and tangential explosive energy. By the time the cylinder reaches its breakup point, terminal velocities are roughly 7–10% higher, signaling that about half of the total cylinder-test detonation energy has been transferred to the metal. Ultimately, the cylinder-test detonation energy per unit volume is calculated simply as the square of the wall velocity at a 19 mm displacement.

3. Results and discussion

Several factors influence the measured cylinder-test detonation energy during a cylinder test, which can be categorized as follows:

1. Heat of Detonation – The heat of detonation (Q) represents the fundamental energy release of the reaction and is defined as:

$$Q \cong - \frac{[\sum_i \Delta_f H^\theta(\text{Products})_i - \Delta_f H^\theta(\text{c})]}{\text{Formula weight of explosive}} \quad (3)$$

In this equation, $\Delta_f H^\theta(\text{c})$ represents the condensed heat of formation for the explosive reactant, while $\Delta_f H^\theta(\text{Products})_i$ refers to the heat of formation for each resulting product, such as H_2O , CO_2 , and N_2 . The resulting heat of detonation can vary depending on whether water is formed as a gas or a liquid [27], with the notation $Q[\text{H}_2\text{O}(\text{g})]$ specifically indicating the gaseous state [2]. Naturally, explosives with a higher intrinsic energy content release more heat during detonation, which in turn boosts the kinetic energy transferred to the cylinder wall.

2. Loading density- The loading density (ρ_0) is another critical factor for both pure and composite explosives, as higher densities significantly enhance performance metrics like detonation velocity and pressure [2]. Materials with high energy density are particularly effective because they combine a large energy content with a compact mass, maximizing the overall cylinder-test detonation energy.

3. The number of moles of gaseous products per gram of explosive- Furthermore, the number of moles of gaseous products per gram of explosive ($NMGP$) plays a vital role in determining cylinder-test detonation energy [2]. As the $NMGP$ increases, the work potential of the explosive expansion grows, leading to higher measured energy values.

The calculated values for $Q[\text{H}_2\text{O}(\text{g})]$ and $NMGP$ for various explosives with known experimental data are summarized in Table 1, while Table 2 provides the measured cylinder-test

detonation energy at the CJ condition for these materials. In the present study, Q denotes the heat of detonation expressed as the magnitude of the energy released during the detonation reaction and is therefore treated as a positive quantity in the proposed correlation. All descriptor values used in the correlation and reported in Table 2 were calculated using the positive magnitude of Q . Although some entries in the dataset correspond to the same chemical compound at different loading densities, they were retained as separate samples because detonation energy in the cylinder test is influenced not only by chemical composition but also by the initial density of the explosive. Variations in density can modify the state of the detonation products, the pressure history, and the resulting expansion work, leading to measurably different performance even for the same molecular structure. For this reason, formulations with identical composition but different densities were treated as distinct thermodynamic states rather than as duplicate chemical entries. The same consideration applies to composite formulations, whose effective detonation behavior depends on both composition and formulation-specific physical properties. Therefore, the dataset was constructed to reflect practically relevant explosive states rather than only unique molecular identities.

As illustrated in Figure 1, a clear linear correlation exists between the measured cylinder-test detonation energy and the optimal combination of $Q[\text{H}_2\text{O}(\text{g})]$, ρ_0 and $NMGP$, which can be expressed as follows:

$$DE = 9.58 + 2.50 \times 10^2 Q^{0.5} (\rho_0 \times NMGP)^{0.7} \quad (4)$$

In this equation, DE represents the cylinder-test detonation energy measured in 10^{13}J/m^3 . The R^2 value for Eq. (4) is 0.886, indicating a relatively strong correlation between the experimental data and the calculated parameters.

While the correlation in Eq. (4) is respectable, there is still room to improve its predictive reliability. Past research suggests that the average molecular weight of gaseous products ($AMWGP$) is a key factor that significantly influences detonation performance [2]. To incorporate this, the multiple linear regression (MLR) method was employed to introduce $\log(AMWGP)$ as an additional independent variable. The dataset was analyzed using the QSARINS software platform, a recognized tool for developing high-quality models [31,32].

To ensure the model is both accurate and capable of handling new data, we followed strict machine learning protocols by splitting the dataset: 70% was used for training the model, while the remaining 30% was set aside for independent validation. This strategy helps prevent "overfitting"—where a model is too tailored to its initial data—and ensures it can reliably predict the performance of unseen energetic compounds. Using this MLR approach, the

Table 1. Parameters used in calculations.

Explosive	Formula	MGPGE (mol/g) ^a	AMWGP (g/mol) ^a	Q[H ₂ O(g)] (kJ/g) ^{b,c}
BTF	C ₆ N ₆ O ₆	0.0357	28.01	-5.03
Comp A-3 (RDX/Wax 91/9)	C _{1.87} H _{3.74} N _{2.46} O _{2.46}	0.0497	20.1	-3.66
Comp B, Grade A(RDX/TNT/Wax 63/36/1)	C _{2.03} H _{2.64} N _{2.18} O _{2.67}	0.0444	22.53	-3.83
Comp C-4 (RDX/Di(2-ethylhexyl)sebacate/Polyisobuthylene/Motor oil 91/5.3/2.1/1.6)	C _{1.82} H _{3.54} N _{2.46} O _{2.51}	0.0479	20.89	-3.8
FEFO	C ₅ H ₆ N ₄ O ₁₀ F ₂	0.0344	29.65	-5.02
HMX	C ₄ H ₈ N ₈ O ₈	0.0405	24.68	-5.01
HNS	C ₁₄ H ₆ N ₆ O ₁₂	0.04	23.68	-3.12
LX-04-1 HMX/Viton A (85/15)	C _{1.55} H _{2.58} N _{2.30} O _{2.30} F _{0.52}	0.0425	23.55	-3.99
LX-07 (HMX/Viton A 90/10)	C _{1.42} H _{2.62} N _{2.43} O _{2.43} F _{0.35}	0.0418	23.92	-4.33
LX-09-1 (HMX/pDNPA/FEFO 93.3/4.4/2.3)	C _{1.43} H _{2.74} N _{2.59} O _{2.72} F _{0.02}	0.041	24.41	-4.83
LX-10-1 (HMX/Viton A 94.5/5.5)	C _{1.410} H _{2.663} N _{2.579} O _{2.579} F _{0.156}	0.0412	24.26	-4.64
LX-11 (HMX/Viton A 80/20)	C _{1.61} H _{2.53} N _{2.16} O _{2.16} F _{0.70}	0.0431	23.2	-3.65
LX-14-0 (HMX/Estane 5702-F1 95.5/4.5)	C _{1.52} H _{2.92} N _{2.59} O _{2.66}	0.0427	23.4	-4.49
LX-17-0 (TATB/Kel-F 800 92.5/7.5)	C _{2.29} H _{2.18} N _{2.15} O _{2.15} F _{0.2} Cl _{0.054}	0.0444	22.11	-2.01
NM	CH ₃ NO ₂	0.0491	20.35	-3.93
PBX-9010 (RDX/Kel-F 90/10)	C _{1.39} H _{2.43} N _{2.43} O _{2.43} Cl _{0.09} F _{0.26}	0.0403	24.79	-4.5
PBX-9404-3 (HMX/NC/CEF 94/3/3)	C _{1.40} H _{2.75} N _{2.75} O _{2.69} Cl _{0.03} P _{0.01}	0.0406	24.62	-4.73
PBX-9501 (HMX/Estane/BDNPA-F 95/2.5/2.5)	C _{1.47} H _{2.86} N _{2.60} O _{2.69}	0.042	23.82	-4.87
PBX-9502 (TATB/Kel-F 95/5)	C _{2.3} H _{2.23} N _{2.21} O _{2.21} Cl _{0.083} F _{0.13}	0.0451	21.9	-2.02
Pentolite 50/50 (PETN/TNT 50/50)	C _{2.33} H _{2.37} N _{1.29} O _{3.22}	0.0416	24.03	-3.72
PETN	C ₅ H ₈ N ₄ O ₁₂	0.0348	29.29	-5.79
Tetryl	C ₇ H ₅ N ₅ O ₈	0.0418	23.93	-3.61
TNT	C ₇ H ₅ N ₅ O ₆	0.044	21.51	-2.62

^aCalculated Descriptors (NMGP, AMWGP): $\pm 1 - 2\%$ (derived from chemical stoichiometry and decomposition pathway assumptions).

^bHeats of formation for explosives were obtained from [34]

^cHeat of Detonation (Q): ± 100 kJ/kg (typical for calorimetric measurements).

Table 2. Comparison between experimental and calculated cylinder-test detonation energy (10^{13} J/m³) for 25 pure and composite explosives using the refined Eq. (5)

Explosive	ρ_0 (g/cm ³) ^a	Measured DE $\times 10^{13}$ (J/m ³) ^b [34]	Calculated log (AMWGP)	Calculated $10^2 Q^{0.5}(\rho_0 \times NMGP)^{0.7}$	Calculated $DE_{cor} \times 10^{13}$ (J/m ³)	Deviation
BTF	1.859	11.5	1.447	33.59	10.10	-1.4
Comp A-3 (RDX/Wax 91/9)	1.65	8.9	1.303	33.22	8.69	-0.21
Comp B, Grade A(RDX/TNT/Wax 63/36/1)	1.717	8.5	1.353	32.29	8.80	0.3
Comp C-4 (RDX/Di(2-ethylhexyl)sebacate/ Polyisobuthylene/Motor oil 91/5.3/2.1/1.6)*	1.601	9.0	1.320	32.30	8.51	-0.49
FEFO	1.59	8.0	1.472	29.30	8.80	0.8
HMX*	1.891	10.5	1.392	37.05	10.85	0.35
HNS	1.0	4.1	1.374	18.56	4.12	0.02
HNS*	1.4	6.0	1.374	23.49	5.87	-0.13
HNS*	1.65	7.5	1.374	26.35	6.89	-0.61
LX-04-1 HMX/Viton A (85/15)*	1.865	9.5	1.372	33.87	9.54	0.04
LX-07 (HMX/Viton A 90/10)	1.865	10.0	1.379	34.88	9.95	-0.05
LX-09-1 (HMX/pDNPA/FEFO 93.3/4.4/2.3)	1.84	10.5	1.388	36.00	10.43	-0.07
LX-10-1 (HMX/Viton A 94.5/5.5)	1.865	10.4	1.385	35.74	10.31	-0.09
LX-11 (HMX/Viton A 80/20)	1.875	9.0	1.365	32.84	9.11	0.11
LX-14-0 (HMX/Estane 5702-F1 95.5/4.5)	1.835	10.2	1.369	35.64	10.14	-0.06
LX-17-0 (TATB/Kel-F 800 92.5/7.5)	1.9	6.9	1.345	25.11	6.18	-0.72
NM	1.128	5.1	1.309	26.16	6.23	1.13
PBX-9010 (RDX/Kel-F 90/10)*	1.787	9.0	1.394	33.64	9.65	0.65
PBX-9404-3 (HMX/NC/CEF 94/3/3)	1.84	10.2	1.391	35.38	10.24	0.04
PBX-9501 (HMX/Estane/BDNPA-F 95/2.5/2.5)	1.84	10.2	1.377	36.76	10.61	0.41
PBX-9502 (TATB/Kel-F 95/5)*	1.895	7.1	1.340	25.41	6.25	-0.85
Pentolite 50/50 (PETN/TNT 50/50)	1.7	8.1	1.381	30.20	8.31	0.21
PETN	1.77	10.1	1.467	34.20	10.49	0.39
Tetryl	1.73	8.2	1.379	30.21	8.30	0.1
TNT	1.63	7.0	1.333	25.59	6.25	-0.75
RMSE						0.54

^aLoading Density (ρ_0): ± 0.01 g/cm³.^bDetonation Energy (Experimental): $\pm 3 - 5\%$ (reflecting measurement errors in cylinder expansion).

*Test set

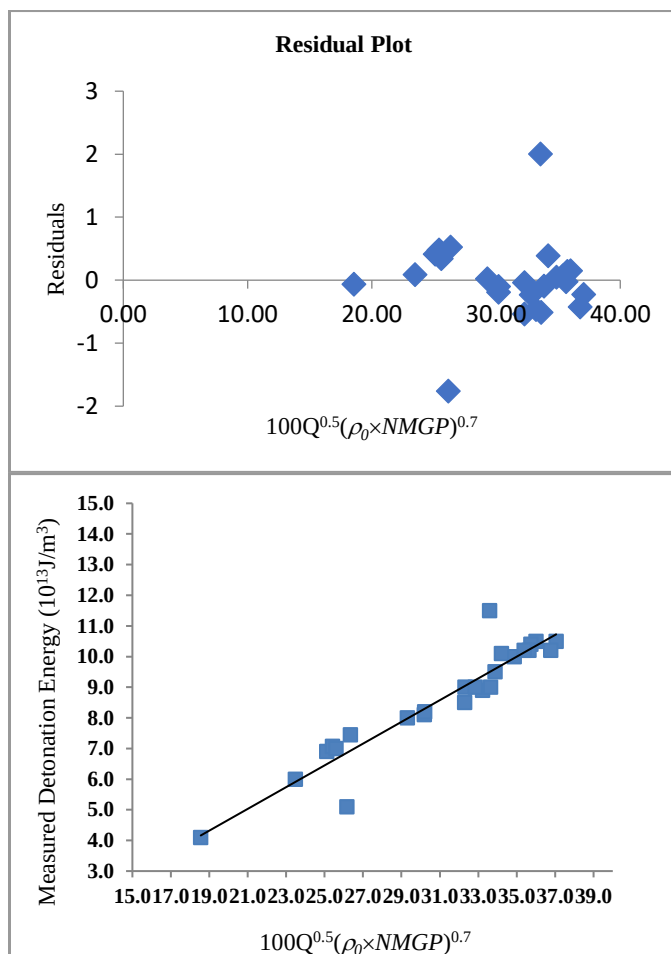


Figure 1. Comparison of measured cylinder-test detonation energy versus the model descriptor $100Q^{0.5}(\rho_0 \times NMGP)^{0.7}$ for 25 pure and composite explosives according to Eq. (4). The main plot shows the linear correlation between the experimental data and the structural parameters, where the solid line represents the regression fit ($R^2 = 0.886$). The inset displays the residual plot, showing the distribution of errors relative to the descriptor values, confirming the model's reliability and the absence of systematic bias across the investigated range.

final relationship between DE and the combined parameters of $\log(AMWGP)$ and the previous energy term was established as follows:

$$DE_{cor} = -14.7 + 8.90\log_{10}(AMWGP) + 0.355 \times 10^2 Q^{0.5}(\rho_0 \times NMGP)^{0.7} \quad (5)$$

In this expression, DE_{cor} represents the corrected cylinder-test detonation energy, measured in units of 10^{13}J/m^3 .

The statistical robustness of the proposed correlation was evaluated using comprehensive regression diagnostics. For the training set of 18 samples, the model yielded a coefficient of determination (R^2_{train}) of 0.9165 and an adjusted R^2 of 0.9054, indicating that the selected descriptors account for over 90% of the variance in the experimental cylinder-test detonation energy. The overall significance of the regression is supported by an F-statistic of 82.33 ($P = 8.17 \times 10^{-9}$), while the residual standard error of 0.6056 demonstrates a high degree of fit between the calculated and experimental values.

The individual contribution of each descriptor was also statistically verified. The results show that both $\log(AMWGP)$ ($P = 0.016$) and

the composite thermochemical term ($P = 8.49 \times 10^{-9}$) are statistically significant at the 95% confidence level. To ensure the reliability of the model, descriptor intercorrelation and variance inflation factor (VIF) values were analyzed, confirming that multicollinearity does not adversely affect the stability of the coefficients. Furthermore, an analysis of standardized residuals and leverage values indicated that the model is free from influential outliers that could bias the results. The use of a two-descriptor linear model with 18 training samples provides a favorable observation-to-parameter ratio, which minimizes the risk of overfitting and ensures that the correlation remains physically interpret and generalizable to new energetic formulations.

To avoid any possibility of data leakage during model development, the formulation of the correlation and the determination of its coefficients were carried out exclusively using the training subset of the data. The dataset was first divided into training and external test sets using the random selection procedure implemented in the QSARINS software [31,32]. All steps related to model construction, including the identification of the composite descriptor structure and the estimation of the coefficients appearing in Eqs. (4) and (5), were performed using only the training compounds. The external test set was not involved in any stage of parameter adjustment or descriptor evaluation and was used solely for independent validation of the final correlation. This workflow ensures that the predictive performance reported for the model reflects genuine external predictivity rather than information leakage from the validation data. The inclusion of the $AMWGP$ as a corrective parameter can be rationalized by considering the thermodynamic behavior of detonation products during expansion [33]. The molecular weight of the gaseous products influences the density, expansion characteristics, and thermodynamic response of the detonation products, which in turn affect the mechanical work delivered during the detonation process. In particular, variations in the average molecular weight may influence the slope of the detonation product isentrope and the efficiency with which chemical energy is converted into expansion work. Therefore, incorporating $AMWGP$ into the correlation provides an indirect representation of detonation product thermodynamics that is not captured by simpler composition-based parameters. The logarithmic form was adopted as an empirical scaling term that improves the agreement between calculated and experimental detonation energies while maintaining the simplicity of the proposed predictive empirical regression model.

It should be noted that the present correlation is intended as a simplified predictive tool based on thermodynamic parameters derived from decomposition pathway analysis. More sophisticated prediction approaches for energetic materials include empirical detonation descriptors such as the Kamlet–Jacobs equations [27], cylinder-test-based correlations (e.g., Short, Kamlet, and Finger [22]), Doherty-type cylinder energy models [21], and advanced thermochemical codes such as CHEETAH [8] or EXPLO5 [9]. These methods typically require detailed thermochemical databases, extensive experimental calibration, or specialized computational tools. In contrast, the correlation proposed in this work aims to provide a rapid and practical estimate of cylinder-test detonation energy using a limited set of easily calculated parameters. A comprehensive quantitative benchmarking against these models was beyond the scope of the present study and may be considered in future work. While the thermochemical approach of Fotouhi-Far et al [25], demonstrated the utility of decomposition pathway analysis for predicting cylinder wall velocities of CHNOFCl compounds, the modified correlation developed in this work extends these thermodynamic parameters to directly predict cylinder-test detonation energy with a simplified model, avoiding the need for

complex velocity-scaling calculations.

The proposed thermodynamic correlation is developed for energetic compounds whose primary elemental composition falls within the CHNOFCl system. PBX-9404, which is included in the dataset, contains chlorine as part of its formulation and therefore remains within this compositional framework. Although a trace amount of phosphorus may be present in the formulation, its concentration is very small relative to the dominant CHNOCl constituents. Consequently, phosphorus was neglected in the decomposition treatment, and the calculations of Q , $NMGP$, and $AMWGP$ were performed using the principal CHNOFCl composition. Owing to the very small phosphorus fraction, its effect on the predicted cylinder-test detonation energy is considered negligible within the accuracy of the present correlation.

The experimental values of cylinder-test detonation energy at the specified loading density and the heats of formation used in this study were obtained from the compilation reported by Dobratz and Crawford [34], which are cited in Tables 1 and 2. The empirical formulas of the explosives as well as the thermochemical descriptors reported in Table 1, including $NMGP$, $AMWGP$, and Q , were calculated from the molecular formulas of the pure explosives using the decomposition schemes and thermodynamic relations described in this work and in the cited references. For composite formulations, the parameters were determined by considering a 100 g basis for the mixture composition. The mass percentages of the energetic components, binders/plasticizers, and other constituents were used to determine their elemental contributions, from which the effective empirical composition of the formulation was derived and subsequently used to calculate $NMGP$, $AMWGP$, and Q according to the same procedure applied for pure explosives.

Although the present work yields an empirically optimized correlation, its descriptors originate directly from fundamental chemical processes governing detonation. The terms $NMGP$ and $AMWGP$ encode the expected decomposition chemistry: oxygen balance determines the extent of oxidation, which in turn defines the number and molecular weight of gaseous products. Heavier detonation products, particularly those involving halogens, increase the effective molecular weight of the expanding gases and thus alter momentum transfer and expansion work. Conversely, oxygen-deficient systems generate more reducing species with lower effective gas yields, reducing the work-producing fraction of the energy. By expressing these chemical pathways in quantitative descriptor space, the model connects decomposition chemistry to delivered mechanical energy, thereby advancing chemical understanding rather than solely improving curve fitting.

To ensure the statistical independence of the validation procedure, the division of the dataset into training and test subsets was performed using the random selection functionality implemented in the QSARINS software package [31,32]. This procedure randomly assigns samples to the training and external validation sets while maintaining an appropriate distribution of the data. In the present study, the available dataset was divided into 18 training samples and 7 test samples. It should be noted that some formulations correspond to the same explosive composition evaluated at different loading densities; however, each entry represents a distinct thermodynamic state because cylinder-test detonation energy depends on the loading density as well as the chemical composition. The random selection implemented in QSARINS therefore provides an unbiased partition of the dataset for model development and external validation, allowing the predictive capability of Eq. (5) to be evaluated on samples not used in model construction.

The positive coefficient associated with $\log_{10}(AMWGP)$ in Eq. (5) reflects the thermodynamic contribution of product gas composition to the total detonation work. While a higher number of moles

($NMGP$) generally drives pressure through volume generation, the $AMWGP$ term accounts for the momentum and kinetic energy density of the expanding front. Heavier gaseous species, such as Cl_2 or CO_2 compared to H_2O or N_2 , maintain higher momentum during the adiabatic expansion phase of a cylinder test. From a molecular-kinetic perspective, for a given heat release (Q), heavier molecules possess a lower average velocity but contribute significantly to the dynamic pressure exerted on the cylinder wall due to their higher mass-to-volume ratio at the CJ state. Thus, $AMWGP$ acts as a corrective factor that captures the enhanced work-performing capability of high-density gaseous products during the late-stage expansion of the detonation products.

3.1. Regression analysis of two descriptors given in Eq. (5)

A statistical analysis of the two descriptors derived from Eq. (5) was conducted using 18 training samples, with the detailed results summarized in Table 3. The regression analysis highlights several key relationships within the dataset, specifically demonstrating that both descriptors possess significant statistical weight. This significance is reflected in their small standard errors relative to their coefficients, suggesting that these variables exert a consistent and reliable influence on the predicted cylinder-test detonation energy. For these descriptors, the P-values are well below the standard 0.05 threshold, allowing the model to confidently reject the null hypothesis and confirming that each variable contributes meaningfully to the model's predictive accuracy. Furthermore, the 95% confidence intervals are notably narrow, which reinforces the precision and reliability of the estimated coefficients. Collectively, these metrics—low P-values and tight confidence intervals—provide robust evidence that these descriptors have a measurable impact on detonation performance. This statistical foundation not only validates the model's strength but also pinpoints the specific molecular features that most heavily drive the energy behavior of diverse pure and composite explosives.

3.2. Validation of the predictive performance and robustness of the improved model

Table 4 provides a comprehensive validation of the new model, utilizing both internal and external techniques to confirm its reliability and generalizability. Predictions generated via the QSARINS software show a high R^2 (exceeding 0.6) and a nearly identical Q^2_{LOO} (leave-one-out cross-validation), proving the model is both accurate and resistant to overfitting. Further testing through Leave-Many-Out (LMO) cross-validation—involving 2000 iterations with 25% of the data excluded each time—yielded a strong Q^2_{LMO} of 0.8210, reinforcing the model's stability. Additional precision metrics, such as a low RMSECV (0.7044) and MAECV (0.4770), alongside Y-scrambling results ($R^2_{YS} = 0.1095$ and a negative Q^2_{YS}), demonstrate that the model captures genuine structural relationships rather than chance correlations.

External validation using an independent test set further confirmed the model's predictive power beyond the initial training data. The model achieved an R^2_{ext} of 0.9482, explaining nearly all variance in the unseen compounds, while an R^2_m (test) of 0.7454 indicates that predictions remain balanced and are not skewed by outliers. Significantly, the Concordance Correlation Coefficient ($CCC_{ext} = 0.9509$) and various external scores (including Q^2_{F1} , Q^2_{F2} , and Q^2_{F3} ranging from 0.8773 to 0.9293) exceed recommended thresholds, ensuring the model remains reliable across diverse chemical structures.

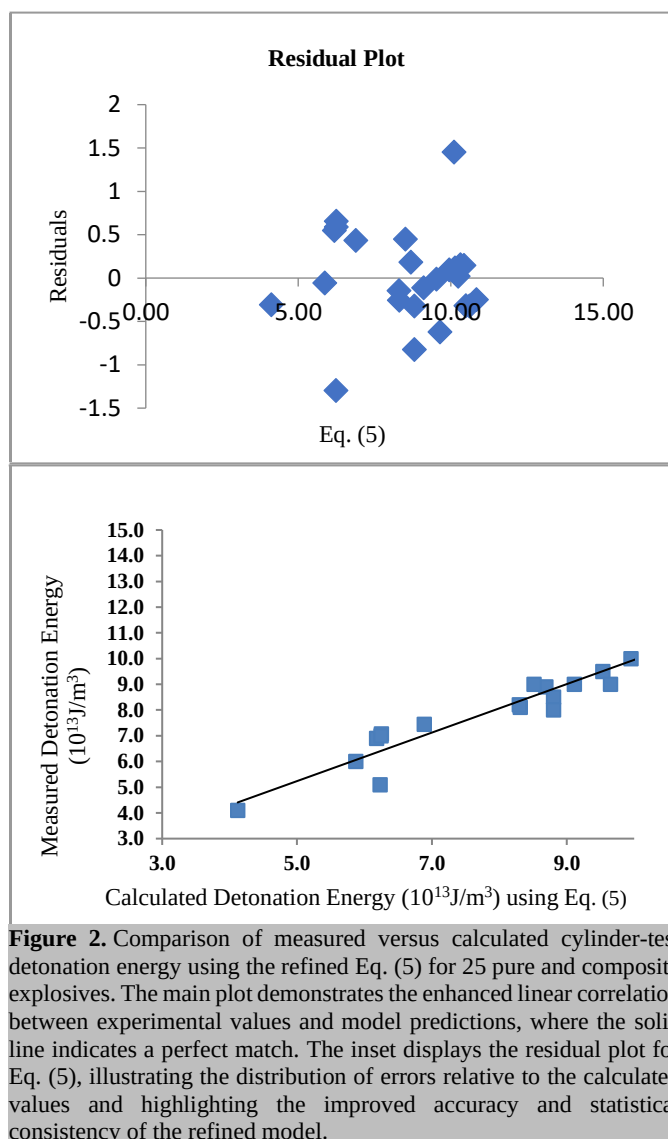
These results are visually confirmed in Figure 2, where the new model's predictions show a much tighter alignment with experimental data across all 25 training and test samples compared to the initial model in Figure 1. A major advantage of this approach

Table 3. Statistical summary of regression coefficients, standard errors, *t*-statistics, P-values, and 95% confidence intervals for the predictors of cylinder-test detonation energy in the training set (*n* = 18) according to Eq. (5).

Descriptor Term	Descriptor Name	Units of Coefficient	Coefficients	Standard error	t-statistic	P-value	Lower bound (95% confidence interval)	Upper bound 95% confidence interval
Intercept	Constant term	10^{13} J/m ³	-14.7	4.4	-3.4	0.004	-24.07	-5.36
$\log_{10}(AMWGP)$	Detonation energy structural parameter	Dimensionless (as the coefficient converts it to 10^{13} J/m ³)	8.90	3.30	2.71	0.016	1.89	15.92
$10^2 Q^{0.5}(\rho_0 \times NMGP)^{0.7}$	Logarithm of average molecular weight of gases	10^{13} J/m ³	0.355	0.031	11.4	8.49E-09	0.289	0.421

Table 4. Internal and external validation metrics for Eq. (5)

Internal validation parameters	
Q^2_{LOO}	0.8644
$RMSE_{CV}$	0.7044
MAE_{CV}	0.4770
CCC_{CV}	0.9293
$Q^2_{LMO, 25\%}$ (2000 iterations)	0.8210
R^2_{YS}	0.1095
Q^2_{YS}	-0.3113
$R^2-Q^2_{LOO}$	0.0521
External validation parameters	
R^2_{ext}	0.9482
R^2_m (test)	0.7454
ΔR^2_m (test)	0.0910
CCC_{ext}	0.9509
Q^2_{F1}	0.8843
Q^2_{F2}	0.8773
Q^2_{F3}	0.9293
$RMSE_{ext}$	0.5086
MAE_{ext}	0.4349



is its inherent simplicity; it provides high-level accuracy without requiring specialized technical expertise or resource-heavy software. Ultimately, this streamlined model provides a practical and reliable tool for predicting cylinder-test detonation energy, offering a simple alternative to complex thermochemical codes such as CHEETAH. To evaluate the robustness of the refined model (Eq. 5), a sensitivity analysis was performed by individually varying the input parameters (Q , ρ_0 , $NMGP$, and $AMWGP$) by $\pm 10\%$. The results indicate that cylinder-test detonation energy is most sensitive to variations in ρ_0 and Q , which account for the majority of the variance in work-performing capability. While the calculated descriptors ($NMGP$ and $AMWGP$) introduce a small degree of uncertainty due to the assumed decomposition pathways, their influence on the final DE is secondary to the physical density and chemical energy. The close agreement between the training and test sets further suggests that the model is resilient to minor experimental uncertainties in the input variables.

3.3. Evaluating model applicability domain with William plot analysis

The Williams Plot serves as a robust diagnostic tool for defining the applicability domain (AD) of a model, helping researchers distinguish between well-predicted compounds and potential outliers or overly influential data points. In Figure 3, the Williams Plot displays leverage values ($HAT\ i/i$) on the X-axis against standardized residuals. The warning leverage threshold (h^*) is established at 0.500 for this study.

Analysis of the plot reveals that all pure and composite explosives evaluated possess leverage values significantly below this 0.500 threshold. For instance, 23 of the explosives fall within the 0.059 to 0.272 range, indicating that their descriptor values are well-aligned with the data used to train the model. This confirms that these compounds do not exert disproportionate influence on the model's parameters and fall safely within its reliable predictive space.

The AD of the developed model was assessed by analyzing the leverage values and standardized residuals via a Williams plot ($HAT\ i/i$ vs. Standardized Residuals). This analysis identifies the reliable prediction space and highlights influential points or outliers. In the provided plot, all training (yellow circles) and prediction (blue circles) samples fall below the critical leverage warning limit ($h^* = 0.500$), indicating that all compounds in the dataset are within the model's structural domain. Furthermore, the vast majority of points exhibit standardized residuals within the acceptable range of ± 2.0 . However, specific points warrant detailed discussion regarding their influence on model performance:

Influential Training Points (High Leverage/High Residual): Two training samples exceed the ± 2.0 residual threshold. One sample (approx. $HAT\ i/i = 0.221$, Std. Residual = 2.10) shows a high positive residual, while another (approx. $HAT\ i/i = 0.187$, Std. Residual = -2.57) shows a significant negative residual, indicating they are more difficult for the model to predict accurately despite being within the leverage limits.

High Leverage Samples: Several training samples exhibit relatively high leverage compared to the main cluster (e.g., at $HAT\ i/i = 0.354$ and 0.485). Although their residuals are low (within ± 1.7), these points represent compounds with unique structural features or descriptors that strongly define the model's boundaries.

Prediction Set Reliability: All prediction samples (blue circles) fall within the ± 2.0 standardized residual range, with the highest leverage prediction point located at $HAT\ i/i = 0.217$. This confirms that the model generalizes well to new data within the defined AD. These outliers do not appear to belong to a distinct chemical class or a specific group of formulations (e.g., solely high-density compounds or halogenated binders) but rather represent individual

cases where the current model's predictive accuracy is slightly reduced. Their inclusion in the training set, however, contributes to the overall robustness and breadth of the model's applicability.

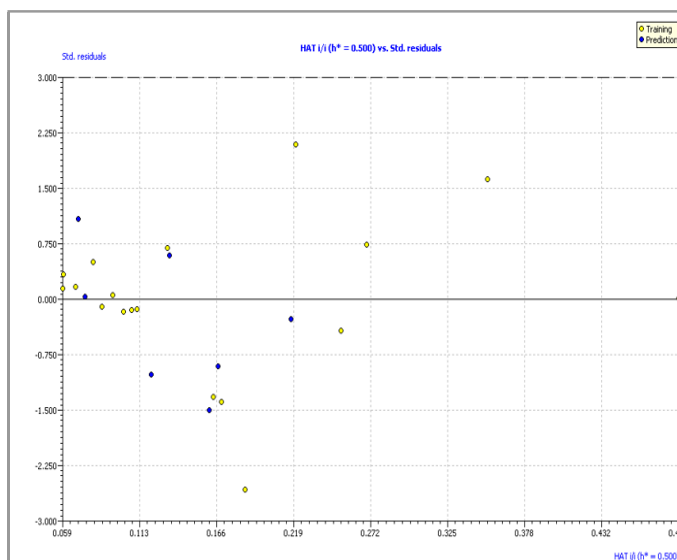


Figure 3. Williams plot for Eq. (5) illustrating the model's applicability domain; training and test sets are identified by yellow and blue circles, respectively, to visualize the distribution of data within the reliable predictive range.

4. Conclusion

The present study proposes a statistically robust correlation for estimating cylinder-test detonation energy based on thermochemical and gas-phase descriptors. The model demonstrates strong agreement with experimental cylinder-test data for the energetic materials included in the present dataset. However, the predictive capability of the correlation should be interpreted within its defined applicability domain. The model was developed using a relatively small set of chemically related high-explosive formulations, and therefore its reliability is expected to be highest for compounds with similar composition ranges and descriptor values (Q , ρ_0 , $NMGP$, and $AMWGP$). The Williams plot analysis further confirms that all analyzed samples fall within the acceptable leverage limit ($h^* = 0.500$), indicating that the regression is statistically valid for this domain. Accordingly, the proposed equation should be regarded as a predictive correlation applicable to energetic materials within the descriptor ranges represented in the current dataset, rather than a universally general model for all explosive systems. Future work incorporating larger and more chemically diverse datasets would help extend and further validate the applicability of the model.

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