

Citation for published version:

Bastante, F.G., Alonso, E., Araújo, M. et al. Analysis of the goodness of empirical approaches in predicting explosive detonation parameters. *Stoch Environ Res Risk Assess* 32, 2605–2618 (2018). <https://doi.org/10.1007/s00477-018-1589-y>

### **Peer reviewed version**

This version of the article has been accepted for publication, after peer review and is subject to Springer Nature's AM terms of use but is not the Version of Record and does not reflect post-acceptance improvements, or any corrections. The Version of Record is available online at <https://doi.org/10.1007/s00477-018-1589-y>

General rights:

*Copyright © 2018, Springer-Verlag GmbH Germany, part of Springer Nature*

# Stochastic Environmental Research and Risk Assessment

## Analysis of the goodness of empirical approaches in predicting explosive detonation parameters

<b>Manuscript Number:</b>	SERR-D-17-00397R1	
<b>Full Title:</b>	Analysis of the goodness of empirical approaches in predicting explosive detonation parameters	
<b>Article Type:</b>	Original research	
<b>Keywords:</b>	Explosive; Detonation parameters; Predictive models; Uncertainty	
<b>Corresponding Author:</b>	Fernando García Bastante, Ph.D. Universidade de Vigo SPAIN	
<b>Corresponding Author Secondary Information:</b>		
<b>Corresponding Author's Institution:</b>	Universidade de Vigo	
<b>Corresponding Author's Secondary Institution:</b>		
<b>First Author:</b>	Fernando García Bastante, Ph.D.	
<b>First Author Secondary Information:</b>		
<b>Order of Authors:</b>	Fernando García Bastante, Ph.D.	
	Elena Alonso, Ph.D	
	María Araújo, Ph.D	
	Julio García Menéndez, Ph.D	
<b>Order of Authors Secondary Information:</b>		
<b>Funding Information:</b>	Consellería de Cultura, Educación e Ordenación Universitaria, Xunta de Galicia (CN2011/025)	Not applicable
<b>Abstract:</b>	<p>Goodness of empirical models for predicting explosive detonation velocity and pressure was analysed using 3 databases consisting of experimental velocity and pressure measurements for different explosives. The first database was used to estimate experimental errors for detonation velocity and pressure measurements. The second database was used to compare residuals obtained by the experimental models and by various thermochemical codes. Finally, the third database, consisting of some 600 data on 130 explosive substances, was used to estimate residual bias and dispersion resulting from the application of the experimental models. Also analysed was model coherence with the ideal detonation theory. Our main conclusion is that all the models introduce bias in their predictions depending on the density and oxygen balance values of the explosive. Of those analysed, the Xiong model was notable for its good results, with residual dispersion comparable to that obtained from application of the best thermochemical codes. Our results would indicate that the Xiong model is the only model that may be compatible with the ideal detonation theory. The pressure equation derived from the ideal detonation theory and calibrated with experimental data had excellent predictive capacity.</p>	
	DOI: <a href="https://doi.org/10.1007/s00477-018-1589-y">https://doi.org/10.1007/s00477-018-1589-y</a>	

# Analysis of the goodness of empirical approaches in predicting explosive detonation parameters

Fernando G. Bastante,<sup>1</sup> · Elena Alonso,<sup>1</sup> · María Araújo,<sup>1</sup> · Julio García Menéndez<sup>1</sup>

<sup>1</sup>Department of Natural Resources and Environmental Engineering, University of Vigo, Spain

Corresponding author: Fernando G. Bastante

Address: School of Mining and Energy Engineering, University of Vigo, Campus Lagoas-Marcosende s/n, 36310 Vigo, Spain

Tel.: +34 986813794

E-mail address: bastante@uvigo.es

## Abstract

Goodness of empirical models for predicting explosive detonation velocity and pressure was analysed using 3 databases consisting of experimental velocity and pressure measurements for different explosives. The first database was used to estimate experimental errors for detonation velocity and pressure measurements. The second database was used to compare residuals obtained by the experimental models and by various thermochemical codes. Finally, the third database, consisting of some 600 data on 130 explosive substances, was used to estimate residual bias and dispersion resulting from the application of the experimental models. Also analysed was model coherence with the ideal detonation theory. Our main conclusion is that all the models introduce bias in their predictions depending on the density and oxygen balance values of the explosive. Of those analysed, the Xiong model was notable for its good results, with residual dispersion comparable to that obtained from application of the best thermochemical codes. Our results would indicate that the Xiong model is the only model that may be compatible with the ideal detonation theory. The pressure equation derived from the ideal detonation theory and calibrated with experimental data had excellent predictive capacity.

**Keywords** Explosive · Detonation parameters · Predictive models · Uncertainty

## 1 Introduction

Predicting detonation parameters is a task of paramount importance for the research and development of new explosive molecules and for the development of new enhanced-performance explosive formulations for use in engineering scenarios. Detonation velocity ( $D$ ), detonation pressure ( $P$ ) and detonation heat ( $Q$ ) are considered to be the key performance measures for explosives (Hardesty and Kennedy 1977). Different thermochemical codes exist for determining values for these parameters through the solution of equations derived from the ideal detonation theory. One of the underlying assumptions is that, in the Chapman-Jouguet (CJ) state, detonation products are in chemical equilibrium when the minimum  $D$  satisfies conservation laws.

Determining the equilibrium state for detonation products requires equations of state (EoS) to model their behaviour. Although different EoS have been proposed for gaseous products, there is no consensus regarding the suitability of one over another. The Panda (Kerley 1994) and EOSPro (Kerley 2010) codes use hard-sphere perturbation theory and the ideal mixing model to obtain the EoS for detonation products. In these codes, and leaving aside formic acid, detonation product parameters are not adjusted to fit explosive data. The BKW code (Mader 2008) uses the Becker-Kistiakowsky-Wilson EoS, which depends on a set of parameters calibrated by several authors to fit model application results to experimental measurements for the detonation properties of various explosives, giving rise to different reparameterizations of the BKW EoS — e.g. BKWR, BKWS and BKWC (Hobbs et al. 1999). The Jacobs-Cowperthwaite-Zwisler-Sandia (JCZS) EoS (Hobbs et al. 1999) uses a Mie-Grüneisen-type equation, in which the Grüneisen function and the internal pressure function are determined using an exponential 6 intermolecular potential function. The potential function parameters are calibrated using isentropes calculated from the BKWS EoS, and the radius of the minimum pair potential energy is optimized to fit the results of applying the model to experimental  $D$  measurements.

A number of authors — each using their own explosives database or sample — have proposed equations to relate  $D$  and  $P$  (typically calculated after first establishing a hierarchy for detonation product formation) to other parameters, calibrated using least squares regression to fit either ideal values of  $D$  and

$P$  — as obtained using the BKW EoS (Kamlet and Jacobs 1968) — or experimental measurements (Jeremić and Bogdanov 2012; Keshavarz et al. 2009; Xiong 1985).

The usefulness of each of these experimental predictive models (XPM), which lack any theoretical foundation, relies entirely on their best or worst predictions. This situation is typical in the modelling of all kinds of processes involving uncertainty (Tian et al. 2014; Salloum and Gharagozloo 2014; Liu et al. 2018). Goodness of fit and calibration for the models are obtained from calculations and analyses of different error indicators (Cheng et al. 2018; Liang et al. 2012). Thus, XPM developers typically justify the validity of their proposed model by including statistics on application errors, such as the mean of the relative residual (MRR), the mean of the absolute residual (MAR), the root mean squared residual (RMSR) and the coefficient of determination ( $R^2$ ) for the predicted and experimental values. However, since different explosive databases and different statistics are used to characterize error, it is difficult to analyse the goodness of the different models and to compare their results.

While some publications do address this issue, it is still not possible to draw any definitive conclusions, whether because sample sizes are small or because statistical analyses are not exhaustive. Shekhar (2012) analysed, in exclusively qualitative terms, predictions for detonation velocity for 5 XPMs, using a small sample, whereas Pepekin and Gubin (2003) included RMSR values for detonation velocity obtained from predictions made by different models. However, the results are not comparable as sample sizes are different (they vary from  $n=10$  to  $n=43$ ). Politzer and Murray (2014) analysed 4 XPMs, calculating residuals for detonation velocity and pressure for each model, using, however, samples of only  $n=14$  and  $n=8$ , respectively.

Although it is relatively easy nowadays to obtain access to thermochemical codes, there continues to be great interest in using XPMs. Some reasons are their application simplicity and their capacity for showing (at least approximately) the dependence between  $D$  and  $P$  through a series of easily calculated parameters that can be used to conduct initial searches for new substances. The main reason, however, is that the predictions of some XPMs have accuracy and precision values close to those obtained by complex and computationally costly thermochemical codes.

With the aim of ascertaining their usefulness in predicting  $D$  and  $P$ , experimental data were used to analyse a number of XPMs for CHNO explosives (the composition common to all the studied methodologies). In this article, first described is an analysis of uncertainty regarding  $D$  and  $P$  in the experimental data and the compilation of a number of goodness-of-fit indicators for thermochemical code and experimental data results so as to have a reference against which to compare XPM results. Next, briefly described are several XPMs for which a statistical analysis was performed aimed at comparing their results with experimental values extracted from various sources and for which purpose 3 different databases were created. The coherence of equations for predicting  $D$  and  $P$  with the ideal detonation theory was then analysed (as proposed in various studies). Since, according to this theory,  $D$  and  $P$  are functionally related, it can be established whether these equations, as well as being good predictors, accord with the ideal detonation theory. Finally, a new model is described that produced excellent results in terms of predicting both  $D$  and  $P$ .

## 2 Uncertainty in experimental measurements

Analysis of any prediction model requires an assessment of the uncertainty existing in experimental data, given the different possible sources of this uncertainty. With respect to experimental uncertainty, Mader (2008) indicated that detonation velocity  $D$  can be measured “easily to within 1%”. Kerley and Christian-Frear (1993), in comparing some 30 experimental values with those predicted by the Panda model, obtained a standard deviation of 1.4% for  $D$ , indicating that this value was “comparable to the scatter observed in the experimental measurements”. Hobbs et al. (1999) indicated that “detonation velocity measurements are probably good to within a few percent” and that “detonation pressure measurements are probably good to within 10% to 18%”. Fried and Souers (1996) estimated errors of 1% and 10% for  $D$  and  $P$ , respectively, and, finally, Hardesty and Kennedy (1997) considered accuracy of  $\pm 10\%$  in experimental measures of  $P$ .

As mentioned, several different sources of uncertainty exist in experimental data. Besides those due to the use of different measurement techniques for  $D$  and  $P$ , test conditions (e.g., load confinement and diameter), explosive charge preparation conditions and even human error will influence results dispersion. In order to better clarify and delimit uncertainty regarding  $D$  and  $P$ , a sample composed of representatives of each of the three main families of single explosives — namely, TNT (trinitrotoluene), PETN (pentaerythritol tetranitrate) and RDX (cyclotrimethylene trinitramine) — was statistically analysed.

To estimate uncertainty in measuring  $D$ , expressions were used that related experimental  $D$  with explosive density ( $\rho_o$ ). For TNT the expression used was that proposed by Urizar et al. (1961), whereby  $D$

is measured with different load diameters and the results are extrapolated to an infinite diameter ( $D_{\infty c}$ ). Used for PETN and RDX were expressions obtained from Dobratz and Crawford (1985) — although note that the detonation velocity  $D_c$  does not correspond to an infinite diameter. Assuming the above expressions to be true, the values of  $D_{\infty c}$  and  $D_c$  were statistically compared with experimental  $D$  as cited by other authors.

To quantify uncertainty, relative residual (RR) statistics were used, defined as  $RR_j = \left(\frac{T_j - E_j}{E_j}\right)$ , where  $T_j$  corresponds to the calculated values of  $D_{\infty c}$  and  $D_c$  and where  $E_j$  corresponds to the measured experimental values  $D$ . The statistics were the bias, or the mean of the relative residual, that is,  $MRR = (1/N) \sum_{j=1}^N RR_j$ , and, as a measure of dispersion, the root mean square residual,  $RMSR = \sqrt{(1/N) \sum_{j=1}^N RR_j^2}$ .

The choice of these RR statistics as indicators of uncertainty allowed a comparison of experimental errors, not only with residuals obtained applying the XPMs, but also with residuals obtained using thermochemical codes, for which RMSR is typically used to evaluate the goodness of predictions.

Figure 1 (left) shows  $D$  versus  $D_{\infty c}$  and  $D_c$  values for densities from 1 g/cm<sup>3</sup> and Table 1 shows the calculated statistics. We attribute the fact that the RMSR values for the different explosives vary greatly to factors external to the measurement technique used — for instance, for TNT, less than ideal behaviour and, for RDX, variations in the purity of the product tested. The MRR for the three explosives was 0.1% and the RMSR was around 1%. The range of residuals, at [-2.1% +4.1%], was slightly higher than indicated in any of the cited references. Given these results, we suggest the relative residual range for  $D$  in explosives with near-ideal behaviour to be around  $\pm 4\%$ .

Figure 1 (right) and Table 1 show the data and statistics for  $P$ . Highlighted is a TNT outlier as an indication that the data were non-exhaustively processed a priori in order to discard any such clearly anomalous values (as recognizable by mere visual inspection). The inclusion of outliers had little impact on the calculated statistics, although they did alter the range of residuals indicated in Table 1. In the absence of any expressions linking  $P$  and  $\rho_o$ , experimental data for each explosive were fitted to a polytropic function,  $P_R = k_1 \rho_o^{k_2}$ , where  $P_R$  is detonation pressure and where  $(k_1, k_2)$  are constants obtained by regression. Although, for the different explosives, the RMSR values for  $P$  showed less variability than the RMSR values for  $D$ , the former were about 3-7 times greater. For the data overall, the MRR was 0.1%% and the RMSR was around 4%. As for the range of relative residuals, [-10.3%, +12.5%], this was coherent with those reported in the cited references. Given these results, we considered  $\pm 12\%$  to be the range of uncertainty for experimental measurements of  $P$ .

It is also important to know the goodness-of-fit obtained on comparing experimental data results with thermochemical codes calibrated with experimental measurements. Table 2 lists literature references for RMSR values obtained from the implementation of different EoS, showing details of the data for which the authors calculated the statistics. The statistics were obtained from databases different to those used for model calibration, with the exception of those corresponding to the BKWS model (McGee et al. 1998) and, possibly, the BKWRR model (Gubin et al. 1987). Logically a smaller RMSR was to be expected for an analysis performed using the same sample as that used to calibrate the EoS. In Table 2 it can be observed that the RMSR values obtained using thermochemical codes were much greater than those obtained using experimental data: about 2-4 times greater for  $D$  and 2-3 times greater for  $P$ . The MRR values are not included as they were not reported in most of the cited references.

### 3 Experimental predictive models

The analysed XPMs used different hierarchies to approximate the composition of the detonation products. When this composition was known it was possible to calculate a number of parameters that could subsequently be used as explanatory variables in fitting models to experimental data by regression.

Hierarchies prioritize the inclusion of certain products over others on the basis of the values of a number of functions,  $F_i = F_i(c, h, o, mw)$ , dependent on oxygen ( $o$ ), carbon ( $c$ ) and hydrogen ( $h$ ) content in a given explosive with composition  $C_c H_h N_n O_o$  and molecular weight  $mw$ . The oxygen balance (OB) function, for instance, is defined as  $OB = 1600 (o - 2c - 0.5h) / mw$  and the oxygen coefficient (OC) function is defined as  $OC = 100 [o / (2c - 0.5h)]$ .

In their seminal work, Kamlet and Jacobs (1968) described a methodology to predict  $D$  and  $P$  for CHNO explosives, as a follow-up to the BKW EOS implemented in the STRETCH and RUBY thermochemical codes in the late 1960s. Code calculations showed that  $N_2$ ,  $H_2O$ ,  $CO_2$ ,  $CO$  and  $H_2$  accounted for most of the gaseous detonation products, and also that, when initial explosive density was intense, the ratios  $H_2O/H_2$  and  $CO_2/CO$  were sufficiently high to rule out the formation of  $H_2$  and  $CO$ . Kamlet and Jacobs proposed an arbitrary hierarchy ( $J_{KJ}$ ) for product formation, according to which oxidation of hydrogen to  $H_2O$  was prioritized over oxidation of carbon to  $CO_2$ . If the explosive was

deficient in oxygen (OB<0), part of the carbon remained unoxidized, and if the explosive had a surplus of oxygen (OB>0), this surplus remained as free oxygen. Using this hierarchy, [H<sub>2</sub>O - CO<sub>2</sub>], the authors, using lognormal regression, fitted the thermochemical code results to the following model (parameters are expressed using the international system of units, i.e.,  $\rho_o$  in kg/m<sup>3</sup>,  $P$  in Pa and  $D$  in m/s):

$$D = \varphi^{1/2}(A + B\rho_o) \text{ with } \varphi = NM^{1/2}Q^{1/2}, A = 22.331 \text{ and } B = 29.03 \times 10^{-3} \quad \text{Eq. 1}$$

$$P = K\rho_o^2\varphi \text{ with } K = 761.7 \times 10^{-3} \quad \text{Eq. 2}$$

where  $N$  is the number of moles of gaseous product per kg of explosive (mol/kg),  $M$  is the average molecular weight of the gaseous products (kg/mol) and  $Q$  is the detonation heat (J/kg), all calculated according to the J<sub>KJ</sub> hierarchy.

Kamlet and Jacobs (1968) reported that their model fitted surprisingly well to thermochemical code results for density values as small as 1 g/cm<sup>3</sup>, attributing this to the fact that the  $\varphi$  parameter in the equations was insensitive to detonation product composition. This circumstance opened the door to using other hierarchies in the XPMs that included this parameter.

Keshavarz et al. (2009) proposed equations in which the  $\varphi$  parameter was determined using the Kistiakowsky-Wilson hierarchy (J<sub>KW</sub>). In this hierarchy, [CO - H<sub>2</sub>O - CO<sub>2</sub>], the formation of CO was prioritized over H<sub>2</sub>O and, if oxygen remained after total hydrogen oxidation, then CO<sub>2</sub> was introduced. The equations obtained by these authors after data fitting with experimental measurements were as follows (the same notation and system of units as above are used):

$$D = A\varphi^{1/2}\rho_o + B \text{ with } A = 31.04 \times 10^{-3} \text{ and } B = 1970 \quad \text{Eq. 3}$$

$$P = K\rho_o^2\varphi - k \text{ with } K = 776.3 \times 10^{-3} \text{ and } k = 1.12 \times 10^9 \quad \text{Eq. 4}$$

In a later work, Keshavarz and Zamani (2015) slightly modified the value of the  $A$  and  $B$  constants and extended the hierarchy to the case where explosive composition included Cl, F and Al.

Other hierarchies similar to the J<sub>KW</sub> hierarchy used to estimate detonation products were the modified Kistiakowsky-Wilson hierarchy (J<sub>KWM</sub>) and the Springall-Roberts hierarchy (J<sub>SR</sub>) (Akhavan 2004). The J<sub>KWM</sub>, where the prioritization was [H<sub>2</sub>O - CO - CO<sub>2</sub>], was applied when explosive OB was very negative (OB < -40%). In the J<sub>SR</sub>, used in the first instance was the J<sub>KW</sub>, after which parts of CO and H<sub>2</sub> were transformed to C, CO and H<sub>2</sub>O.

Xiong (1985) proposed 5 different functions (F<sub>i</sub>) for his hierarchy (J<sub>XI</sub>). For example, when OB>0 he used J<sub>KJ</sub>, as OB decreased he introduced CO, C and CH<sub>4</sub>, and when OB was very negative he used J<sub>KW</sub> [CO - H<sub>2</sub>O]. Xiong's prediction equations are very different from the above equations:

$$D = (AQ^{\frac{1}{2}} + Bw\rho_o) \text{ with } A = 1.045 \text{ and } B = 243.2 \times 10^{-3} \quad \text{Eq. 5}$$

$$P = 10 \frac{\rho_o D^2}{\gamma + 1} \text{ with } \gamma = \left( \frac{\partial P}{\partial v} \right)_s \text{ in the Chapman - Jouguet state} \quad \text{Eq. 6}$$

where  $v$  is specific volume and  $w$  is the sum of the detonation product co-volumes per gramme of explosive whose values, for each of the products in the hierarchy, were defined in Xiong (1985). The value of the isentropic expansion coefficient  $\gamma$  was estimated by a function (also defined in Xiong article) that depended on explosive density and on detonation product composition.

Equation 5 is empirical whereas Eq. 6 is derived from the ideal detonation theory. It can be observed that  $D$  sensitivity to  $Q$  in this model was greater than in the other models. Xiong also made some clarifications regarding the use of his model for mixed explosives.

Jeremić and Bogdanov (2012) used a hierarchy (J<sub>JB</sub>) in which the possible products were the same as those of the J<sub>KW</sub> hierarchy. However, to calculate composition they used a function that depended on the OC. Obtained as a result were amounts of H<sub>2</sub>O/H<sub>2</sub> and CO<sub>2</sub>/CO that increased with the OC value. The equations proposed after fitting to experimental data by regression are as follows:

$$D = A\rho_o(NQ_e)^{\frac{1}{2}} + B \text{ with } A = 243.7 \times 10^{-6} \text{ and } B = 2264 \quad \text{Eq. 7}$$

$$P = K\rho_o^2NQ_e \text{ with } K = 48 \times 10^{-6} \quad \text{Eq. 8}$$

where  $Q_e$  is the explosion heat (J/kg).

Note that the only common point in all the models is the linear dependence of  $D$  on explosive density, and also that  $P$  is a function of the square of  $\rho_o$  in all the models except Xiong's.

Despite the differences between hierarchies and expressions proposed to predict  $D$  and  $P$ , the numerical values obtained from their application were generally quite similar.

Shown in Table 3, for illustrative purposes, are the detonation product compositions and the  $D$  and  $P$  values resulting from applying the different models to PETN (density 1.76 g/cm<sup>3</sup>). The maximum percentage differences between the values for the models were 3% and 11.5% for  $D$  and  $P$ , respectively.

All the models gave a greater value for  $D$  than the experimental data ( $\approx 8260$  m/s) and a value for  $P$  within the range of the experimental values consulted in the cited references ( $\approx 31$ - $34$  GPa).

When these calculations were extended to other explosives, the variation in results for the different models was small in percentage terms. No model was better than any other model in its fit to the experimental data for each explosive. However, it is reasonable to argue that some of them would better model the  $D$  and  $P$  behaviour of the explosives.

Among the objectives of our research was to determine which model(s) yielded the best fit(s) and to quantify deviations between model results and experimental measurements.

## 4 Methodology

In our twofold approach, first analysed were deviations between model results and experimental measurements for  $D$  and  $P$ , as compiled from different literature sources, and then analysed was the coherence between the equations proposed by the authors and the ideal detonation theory.

To analyse the predictive capacity of a given model, the residuals generated by the experimental data need to be analysed in terms of their relationship with the explanatory variables. Global statistics — such as the residual mean, residual variance or coefficient of determination for predicted and experimental values — do not yield sufficient information to interpret the goodness of a model. Furthermore, in order to have a baseline for a comparison of results, it is necessary to have some benchmark regarding experimental uncertainty or to obtain a benchmark using other models. Accordingly, the methodology used is described in what follows.

For the analysis of the deviations, 3 different databases of explosives with density values of  $\rho_0 > 1$  g/cm<sup>3</sup> were created. The first database, denominated PRT (the database used above to estimate experimental error), was used to compare error with the residuals obtained from application of the models. This database included the explosives PETN, TNT and RDX, given that a relatively large number of experimental  $D$  and  $P$  data are available for these explosives. The second database, based on McGee et al. (1998) and denominated MHB, included experimental data for  $D$  and  $P$  for different explosives as well as predicted values from the application of different EoS (BKWS, BKWC and JCZS). Following McGee et al. (1998), for the purpose of this research CHNO explosives were used to compare fits for the XPM results with thermochemical code results. Finally, the third database, called TW, included data from the above databases plus new experimental data for  $D$  and  $P$  obtained after a search in the literature. It was endeavoured to make this database as large as possible, given that the aim, ultimately, was to reconsider some of the conclusions drawn in previous studies so as to better estimate the uncertainty associated with the XPMs.

The fact that the ideal detonation theory establishes a functional relationship between  $D$  and  $P$  would indicate that these parameters are related. For this reason, analysed was the coherence of equations to determine  $D$ , as proposed in the literature, with the ideal detonation theory and also the predictive capacity of the resulting models.

## 5 Results and analysis

### 5.1 Analysis of the predictive capacities of the models

#### 5.1.1 PRT database

Table 4 summarizes the statistics resulting from applying the different models to the PRT database. In bold are values that fell within or near the previously estimated experimental error.

Some disparity can be observed in the statistics, depending on the explosive. For example, the  $J_{KJ}$  and  $J_{XI}$  models gave results for  $D$  for RDX and TNT that were within the experimental error, but overestimated  $D$  for PETN. In fact, all the models overestimated  $D$  for PETN and, with the exception of  $J_{JB}$ , also tended to overestimate  $P$  for the three explosives. It can be concluded, consequently, that a good predictor of  $D$  for a particular explosive may be not such a good predictor of  $P$  for the same explosive.

Comparing the RMSR values obtained for the PRT database (the 2 rightmost columns in Table 4) with the results given in Table 2, no significant differences were evident. Based solely on these overall statistics, it might be inferred that the predictive capacity of the  $J_{JB}$  model is as good as that of the best thermochemical models. In reality, however, this statement would be exaggerated, as, not only were just 3 explosives analysed, 2 global statistics calculated for aggregated data are not sufficient to characterize the residual distribution functions for each of the explosives, which, ultimately, is what determines the goodness of the models.

Defined as a good predictor of a given parameter ( $P$ ,  $D$ ) of a set of explosives  $\{explosives\}$  within a given density range  $[\rho_{om}, \rho_{oM}]$  is a model in which, if, for each and every density, the MRR approaches zero and the RMSR (or any other statistical indicator of residual dispersion) is reasonably small. In our exploration of uncertainty in experimental measurements (Section 2), we tried to quantify the meaning of the term “reasonably”.

For example, according to the first condition in the above definition, a good model should at least satisfy:

$$E\{RR_p | (\rho_{oi}, explosive_j)\} \approx 0, \forall \rho_{oi} \in [\rho_{om}, \rho_{oM}] \text{ and } \forall explosive_j \in \{explosives\}$$

where  $E$  represents the mathematical expectation operator and the subscript  $p$  represents the analysed  $D$  or  $P$  parameter. Note that this condition is more stringent than the simple requirement that the model satisfies  $E\{RR_p\} \approx 0$ , in other words, that it does not introduce bias.

Evaluating the goodness-of-fit of a particular model according to the above definition would require a large quantity of experimental data that we do not have. However, using the MHB database we could implement a more profound analysis than that based on global statistics.

### 5.1.2 MHB database

This database (generated from McGee et al. 1998) includes 99 and 63 measurements of  $D$  and  $P$ , respectively, reflecting 45 different explosive compositions. Also considered from the same reference (McGee et al. 1998) were the results reported for application of the BKWS, BKWC and JCSZ EoS to each of the explosives, so as to enable a comparison of the results of the empirical models and the results obtained with the EoS. Table 5 shows the statistics obtained from application of the different hierarchy models (the  $J_{SR}$  model is excluded as its results were virtually identical to those for the  $J_{KW}$  model). Table 5 also shows the percentage of results whose absolute residual value  $|RR_j|$  was inside the previously estimated experimental uncertainty range.

In view of the results it can be concluded that different databases produce significantly different values for the statistics. For instance, regarding overall predictive capability, the  $J_{JB}$  model performed best with the PRT database but worst with the MHB database. This is explained by the fact that the distribution function for the residuals obtained for each model depended on both the explosive and its density and, therefore, on the database used in the analysis.

It can also be observed in Table 5 that some experimental models yielded results that were comparable or even better than those obtained by the thermochemical codes. This raises the question as to whether these results may depend on the database used. The answer to this question would require an analysis of the behaviour of residuals with respect to the pairs formed by the variables  $(\rho_o, explosive)$ . However, as this would require a large amount of experimental data that we do not have, we performed this analysis by projecting the residuals independently on the  $\rho_o$  and explosive axes.

The question now arises as to how to characterize the explosive variable. The empirical models used different predictor variables to characterize the explosive, namely  $\varphi$ ,  $NQ$  and  $Q$ . However, it would seem more logical to use the same variable as the basis for comparing different models. For the sake of convenience, we used the OB function as holding a certain correlation with the above predictor variables.

Figure 2 shows scatter plots mapping residuals for  $D$  against density and OB for the different models. To facilitate interpretation, trend lines reflecting the relative residual values are shown.

Regarding density, the  $J_{KJ}$  and  $J_{XI}$  models — which showed less bias overall — reflected a slightly positive bias for lower densities. The BKWC and JCSZ models showed a small positive bias for higher densities and the  $J_{KW}$  model performed well from 1.6 g/cm<sup>3</sup>. Noteworthy was the heteroskedasticity of the residuals: the RMRS decreased with density in the  $J_{KJ}$ ,  $J_{XI}$  and BKWC models, whereas the reverse happened with the JCSZ model.

Regarding OB, the JCSZ model performed best, followed by BKWC, which showed a slight tendency to underestimate or overestimate values depending on the OB. The  $J_{KJ}$  and  $J_{XI}$  models showed good behaviour up to higher OB values, when a positive bias was observed; the  $J_{KW}$  model also performed better for higher OB values than the other models.

For the MHB database, BKWS was the model with the widest range of residuals, at -14% to +9%, compared to the  $J_{XI}$  and  $J_{KJ}$  models, with the narrowest ranges, at -5% to +8% and -8% to +8%, respectively. Considering the 2 scatter plots in Fig. 2, the best performing models overall were  $J_{XI}$  and  $J_{KJ}$ . Furthermore, assuming that the OB was sufficient to characterize the explosive, for the MHB database and for OB values below (approximately) -15% both these models could predict  $D$  at least as well as the BKWC and JCSZ models.

Figure 3 shows scatter plots mapping residuals for  $P$  against density and OB for the different models. It can be observed that residuals tended towards negative values as density increased, except in the JCSZ



model, which showed a slight opposite trend. In terms of the MRR and RMRS, the best models were  $J_{KW}$  and  $J_{XI}$  for densities above  $1.6 \text{ g/cm}^3$  and  $J_{KW}$  for lower densities.

As for OB, a trend for the experimental model residuals to increase towards the extremes can be observed. For values above  $-60\%$ , the  $J_{KW}$  model, followed by  $J_{KJ}$  and  $J_{XI}$ , were those with the lowest MRR and RMRS values, whereas the  $J_{XI}$  model behaved best for lower OB values. The JCSZ model, meanwhile, consistently underestimated  $P$  throughout the entire OB range.

For the MHB database, BKWS was the model with the greatest range of residual  $P$  values, at  $-28\%$  to  $+24\%$ , contrasting with the  $J_{KW}$  and  $J_{XI}$  models, with the narrowest ranges, at  $-10\%$  to  $+17\%$  and  $-10\%$  to  $+20\%$ , respectively.

It can be concluded that the model that performed best regarding  $P$  was  $J_{KW}$ , followed by  $J_{XI}$  and  $J_{KJ}$ . Note, however, that the residuals of all the models show certain trends regarding both density and OB. From the above analysis for this database, it cannot be concluded that the  $J_{KW}$ ,  $J_{XI}$  and  $J_{KJ}$  models are worse predictors of  $P$  than the BKWS and JCSZ.

### 5.1.3 TW database

This third database, as the largest of the 3 databases used for this research, allowed us to make a comparison of results and to estimate the uncertainty associated with the experimental models.

This database, compiled from various references (Cooper 1996; Dobratz and Crawford 1985; Džingalašević et al. 2004; Green and Lee 2006; Jeremić and Bogdanov 2012; Kozyrev 2015; Mader 2008; McGee et al. 1998; Pepekin et al. 2011; Pepekin and Gubin 2003; Victorov et al. 2010; Xiong 1985), includes 375 and 250 experimental measurements of  $D$  and  $P$ , respectively, reflecting 65 single explosives and 65 composite explosive mixtures with densities from  $1 \text{ g/cm}^3$ . Table 6 summarizes the general characteristics of the explosives in the database; excluded were explosives with ammonium nitrate in their composition, and included were a number of compositions with a small percentage (up to 6% by weight) of elements (Cl, F and P) different from CHNO. In our calculations, these elements were only taken into account in the Xiong model. Note that the overall statistics were not found to be affected by the inclusion of these explosives.

Global statistics are summarized in Table 7. Results for the  $J_{JB}$  model, as the poorest performer regarding residuals, are excluded and included instead are the results for a variant of the Xiong model called  $J_{XB}$ , discussed further below.

As would be expected, the statistics were somewhat different from those obtained for the MHB database, in part because of the different structure of the TW database in terms of the density distribution function and OB values for the explosives: this database includes a higher percentage of explosives with extreme OB values (see Fig. 4). Nonetheless, in global terms the results in comparison with those for the MHB database (Table 5) were similar.

Figure 4, which shows the residuals corresponding to  $D$  for the TW database, largely corroborates the results obtained for the MHB database. The best performing model was Xiong's. Even so, the residual average showed a slight trend to change with both density and OB values.

As for the residuals corresponding to  $P$  for the TW database, shown in Fig. 5, the results further validate the statement for the MHB database: the residuals showed trends to change with both density and OB values. In fact, the  $J_{KW}$ ,  $J_{XI}$  and  $J_{KJ}$  models showed a high level of bias for explosives with low density and high OB:  $E\{RR_P | \rho_{oi} < 1.6 \text{ g/cm}^3; OB > -20\% \} \approx 10\%$ .

Given the above observations, for the ( $D$ ,  $P$ ) pair, the Xiong model would appear to be the best predictor for the TW database.

## 5.2 Analysis from the functional perspective

As commented in the introduction, the calibration of models with experimental data is a task that has been implemented with most of the EoS that use thermochemical codes. Empirical approaches to predicting  $P$  and  $D$  for explosives use different equations, also calibrated from the data, to calculate those parameters. Although the strongly statistical nature of these XPMs is undeniable, some can be considered to have a certain theoretical and experimental grounding. For example, following a series of approximations of some of the parameters in the BKW EoS, Kazandjian and Danel (2006) obtained the analytical expression for  $P$  for the Kamlet and Jacobs model from the corresponding EoS. Another example is the expression for  $D$  in the Xiong model, which, when  $\rho_o \approx 0$ , was an approximation of the application of the ideal detonation theory to gases with polytropic behaviour. The Xiong model also reflected a behaviour of  $D$  in explosives that, within a certain range of densities, was approximately linear with density. Both these models would, however, be better grounded if the constraints imposed by the ideal detonation theory were introduced in the equations to predict  $D$  and  $P$ .

As mentioned previously, in accordance with the ideal detonation theory,  $D$  and  $P$  are functionally related. According to Davis (1981), an expression of the form  $D = D(\rho_o, Q_{cj})$ , where  $Q_{cj}$  is explosion heat in the CJ state, implies “an equation of state complete enough for hydrodynamic calculations”.

Referring to the equation derived from the CJ condition:

$$P = 10 \frac{\rho_o D^2}{\gamma + 1} \quad \text{with } \gamma = \left( \frac{\partial P}{\partial v} \right)_s \quad \text{in the Chapman – Jouguet state} \quad \text{Eq. 9}$$

given  $D = D(\rho_o, Q_{cj})$ , if the value of  $\gamma$  is known, then the value of  $P$  can be calculated. While there may be expressions that enable us to estimate  $\gamma$  according to explosive density (Bastante et al. 2012), this parameter is, in fact, fully defined by the function  $D(\rho_o, Q_{cj})$ . Indeed, according to Davis (1981):

$$\gamma = a + [(1 + a)^{1/2} + b]^{1/2} \quad \text{with } a = \rho_o / D(\partial D / \partial \rho_o) \quad \text{and } b = D(\partial D / \partial Q_{cj}) \quad \text{Eq. 10}$$

Hence, from the expression  $D = D(\rho_o, Q)$  as proposed in each methodology, and assuming that  $Q \approx Q_{cj}$ , values for  $a$ ,  $b$  and the corresponding value for  $\gamma$  can be calculated, which, once introduced in Eq. 9, gives the desired  $P$ . Note that none of the methodologies followed this procedure for calculating  $P$  but instead operated in reverse: the value of  $\gamma$  was calculated from  $D$  and  $P$  using Eq. 9.

In view of Eqs. 9 and 10, the question that now arises is how to measure the coherence of each model with the CJ condition. Davis (1981) compared the  $P$  calculated from Eqs. 9 and 10 to the  $P$  obtained from direct application of the Kamlet and Jacobs equation (Eq. 2), using a wide range of values of  $Q$  and  $NM^{1/2}$  in the density range 1 g/cm<sup>3</sup> to 1.8 g/cm<sup>3</sup>, obtaining a maximum difference of a few percentage points between the 2 approaches.

However, it may be more interesting to implement the analysis by adopting a more conceptual perspective. If the expression  $D = D(\rho_o, Q)$  proposed by any given model is coherent with the CJ condition, then there must be an intersection between the 2 solution spaces (or confidence regions) for the adjustable parameters, obtained when regression is performed on  $D$  and on  $P$ , and using, for this purpose, the functional relationship reflected in Eqs. 9 and 10. We clarify this issue by applying this approach to the Kamlet and Jacobs and the Xiong models.

Eqs. 1 and 5 are the functional relationships  $D = D(\rho_o, Q)$ , for which the constants  $A$  and  $B$  for each model are considered to be adjustable parameters to be determined by regression. Eq. 10 was used to calculate the expression for  $\gamma$  for each model as follows:

$$\gamma_{KJ} = \frac{AB\rho_o}{D} \sqrt{\varphi} + \left[ \left( 1 + \frac{AB\rho_o}{D} \sqrt{\varphi} \right)^2 + \frac{D^2}{4Q} \right]^{1/2} \quad \text{Eq. 11}$$

$$\gamma_{XB} = \frac{Bw\rho_o}{D} + \left[ \left( 1 + \frac{Bw\rho_o}{D} \right)^2 + \frac{AD}{2Q^{1/2}} \right]^{1/2} \quad \text{Eq. 12}$$

The optimal parameters ( $A_D, B_D$ ) — in the sense of minimum RMSR values — and the corresponding confidence region  $\{A, B\}_D$  are determined — using Eq. 1 for the Kamlet and Jacobs model and Eq. 5 for the Xiong model — by regression of the experimental measurements of  $D$ . Furthermore, using Eqs. 1, 11 and 10 for the Kamlet and Jacobs model and Eqs. 5, 12 and 10 for the Xiong model, the regression is implemented with the experimental measurements of  $P$ , resulting in the optimums ( $A_P, B_P$ ) and the corresponding confidence region  $\{A, B\}_P$ . For each model, the detonation velocity equation is compatible with the CJ condition when there is intersection between the confidence regions,  $\{A, B\}_D$  and  $\{A, B\}_P$ , calculated in the corresponding regressions. The closer the value of  $A_D$  to  $A_P$  and of  $B_D$  to  $B_P$ , the greater the compatibility between the expression for  $D$  and the CJ condition.

Applying this methodology to the TW database, estimated using the F-test (Newville et al. 2014) was the 95% confidence regions for the adjustable parameters in each model. Figure 6 shows the results for the Kamlet and Jacobs and the Xiong models, along with the statistics resulting from the application of the respective optimum parameters to the database. It can be observed that the confidence regions obtained with the Kamlet and Jacobs model do not intersect and that the optimal solutions, in percentage terms, are far apart, indicating that this model is not compatible with the CJ condition. Even so, the results of the statistics for  $P$  obtained with the optimal values ( $A_P, B_P$ ) were significantly better than those obtained with Eq. 2 (see Table 7, referring to the TW database).

Regarding the Xiong model, Fig. 6 shows that there was less dispersion in the parameter values, as the 95% confidence regions are very close, although, strictly speaking, they do not intersect. It can be observed that ( $A_D, B_D$ ) and ( $A_P, B_P$ ), as the optimal solutions, are very close together (to three significant figures, in fact,  $B_D = B_P$ ), and also that the statistics resulting from application of these solutions, for both  $D$  and  $P$ , were very satisfactory (compare these values with those in Table 7).

The optimal joint solution is indicated in Fig. 6 as ( $A, B$ )<sub>o</sub> for the  $D$  and  $P$  data. The solution obtained, **(0.944, 0.250)**, was used to perform the calculations corresponding to the model previously referred to as J<sub>XB</sub>. It can be observed in Table 7 that, with this solution, the global statistics hardly changed with respect

to the local optimums of  $D$  and  $P$  as shown in Fig. 6. It can also be observed in Figures 4 and 5 that bias for both  $D$  and  $P$  was practically zero throughout most of the density and OB ranges considered.

Figure 7 shows the cumulative distribution function for the absolute values of the relative residuals for the  $J_{XB}$  model and, for comparative purposes, for the JCZS model (for the MHB database). It can be observed that the  $J_{XB}$  distribution function for  $P$  was a better predictor than that of the JCZS model. All the residuals were in the range  $\pm 16\%$ . This outcome is rather puzzling, given the relative simplicity of the  $J_{XB}$  model. As for  $D$ , the  $J_{XB}$  results were similar to those for the JCZS, although the value for the range of residuals was slightly higher. This was only to be expected, as the TW database is much larger than the MHB database.

In brief, for explosives with behaviour close to the ideal, with compositions and OB values as indicated in Table 7 and with densities greater than  $1 \text{ g/cm}^3$ , the Xiong hierarchy and expression for  $D$  (Eq. 5) — with a small modification in the values of the constants  $A$  and  $B$  — was an excellent predictor that showed almost no bias in the analysed density and OB ranges. The same conclusion applies to  $P$ , but, in this case, our calculation methodology was used, that is, using values for  $\gamma_{XB}$  and  $P$  calculated using Eq. 12 and Eq. 9, respectively.

The above results also suggest that Eq. 12 could be a good predictor of  $\gamma$ , as, unlike other similar equations, it establishes a dependency of  $\gamma$  not only on density but also on detonation heat, that is,  $\gamma = \gamma(\rho_o, Q)$ . The question thus arises as to whether  $\gamma = \gamma(\rho_o)$  can be derived from Eq. 12. Cooper (1996), after analysing 230 experimental data, established an expression for density in the CJ state as  $\rho_{CJ} = 1.386\rho_o^{0.96}$ . The detonation theory dictates that  $\rho_{CJ} = (1 + \gamma)\rho_o/\gamma$ , then it follows that  $\gamma = \gamma(\rho_o)$ .

To demonstrate this approach,  $\rho_{CJ}$  was calculated from  $\gamma$ , as defined by Eq. 12, and was regressed against  $\rho_o$  using the TW database, for a result of  $\rho_{CJ} = 1.388\rho_o^{0.95}$  — virtually the same as that reported by Cooper. Note that the Cooper database included a significant proportion of data with densities of below  $1 \text{ g/cm}^3$ , that is, outside the range used in this research.

## 6 Conclusions

We analysed different experimental predictive models for detonation parameters, both from the statistical perspective and from the perspective of coherence with detonation theory. In order to have a results comparison benchmark, we first estimated error for the experimental measurements. Using database data, we then compared experimental model results with thermochemical code results. Finally, using a much larger database we were able to better characterize residuals for each model. The main contribution of this research is, therefore, an exhaustive analysis of the predictive capacity of models that includes both global statistics and residual plots for each model.

We found experimental error dispersion for detonation velocity and detonation pressure of  $1\% \pm 0.5\%$  and  $4.2\% \pm 1.2\%$ , respectively, and error range of  $\pm 4\%$  and  $\pm 12\%$ , respectively. The analysed experimental predictive models had mean residual dispersions of around 3% and 7.5% for detonation velocity and detonation pressure, respectively, and 80%-90% of residuals fell within the experimental error range. Of the models analysed in this research, the best results were obtained by the Xiong model, which had significantly lower detonation velocity dispersion (2.3%); broadly speaking, the dispersions for this model were about twice those of the experimental error dispersion.

While these results can be considered to be very satisfactory (especially in comparison with results for the much more elaborate thermochemical codes), this analysis reveals that the residuals of all the models show a tendency to change depending on the explosive density and oxygen balance variables. This would suggest that predictive ability varies significantly according to the explosive in question, with real values over- or under-estimated in accordance with the value of the density and oxygen balance variables.

Regarding model coherence with the ideal detonation theory, when applied to the Xiong model, the equation relating detonation pressure and detonation velocity as derived from this theory had good predictive ability. This implies that there is no need, a priori, for an equation to predict detonation pressure, as this can be derived from the detonation velocity equation. In fact, once the 2 constants in the predictive equations were calibrated, we obtained surprisingly good prediction results: mean dispersion values for the velocity and pressure residuals of 2.1% and 5.5%, respectively, and around 96% of residuals within the experimental error range.

A second contribution of this research is the demonstration that a good experimental can and should be able to yield relatively accurate predictions of detonation pressure from the velocity equation. We would suggest that this methodology for analysing different predictive models — based on the equation for detonation velocity and detonation pressure (as derived from the equation for detonation velocity) and taking into account not only model predictive capacity but also model coherence with the ideal theory of detonation — is a useful approach to analysing and seeking out new models to predict explosive detonation parameters. A direct consequence of application of this methodology is the new  $J_{XB}$  model

proposed here, whose predictive capacity has been shown to be better than that of the other experimental models described.

From the analysis of the solution spaces for the adjustable parameters in model regression, it is concluded that only the Xiong model is coherent with the ideal theory of detonation. Using the Xiong model and an experimental database of some 600 velocity and pressure values, we obtained confidence regions that were very close and that had well defined values in very narrow regions. The non-intersection of the regions would suggest that the coherence of the Xiong model with the ideal theory of detonation could be improved by modifying the detonation velocity equation as proposed by Xiong. That equation includes the term corresponding to the sum of detonation product co-volumes. The Xiong values were obtained from Mader (2008); however, in reality, product co-volume values depend very much on how they are calculated. The consequence is reparameterizations of the BKW EoS and proposals for different product co-volumes based on the best fit between predictions and experimental data. This raises the question as to whether Xiong co-volume values should be adjusted on the basis of experimental data rather than be established a priori, and also whether the predictive capacity of the model could be improved by including new explanatory variables. Future research will focus on trying to answer these questions.

**Acknowledgements** This work was supported by the Consellería de Educación y Ordenación Universitaria de Galicia. Ailish M.J. Maher provided assistance with English usage in a version of this manuscript.

## References

- Akhavan J (2004) The chemistry of explosives. Second Edition, Royal Society of Chemistry, Cambridge, UK
- Bastante FG, Alejano L, González-Cao J (2012) Predicting the extent of blast-induced damage in rock masses. *Int J Rock Mech Min Sci* 56:44–53
- Cheng QB, Chen X, Xu CY, Zhang ZC, Reinhardt-Imjela C, Schulte A (2018) Using maximum likelihood to derive various distance-based goodness-of-fit indicators for hydrologic modeling assessment. *Stoch Environ Res Risk Assess* 32(4):949–66
- Cooper P (1996) Explosives engineering. Wiley-VCH, NY, USA
- Davis WC (1981) Equation of state from detonation velocity measurements. *Combustion and Flame* 41:171–178
- Dobratz BM, Crawford PC (1985) LLNL Explosives handbook properties of chemical explosives and explosive simulants. Lawrence Livermore National Laboratory, California
- Džingalašević V, Antić G, Mladenović D (2004) Ratio of detonation pressure and critical pressure of high explosives with different compounds. *Scientific Technical Review, LIV(3-4):72–76*
- Fried LE, Souers PC (1996) BKWC: An empirical BKW parametrization based on cylinder test data. *Propellants, Explosives, Pyrotechnics* 21:215–223
- Green LG, Lee EL (2006) Detonation pressure measurements on PETN. 13th International Detonation Symposium, Norfolk, VA, United States, Jul 23 - Jul 28, pp 1144–1150
- Gubin SA, Odintsov VV, Pepekin VI (1987) Thermodynamic calculation of ideal and nonideal detonation. *Combust Explos Shock Waves* 23(4):446–454
- Hardesty DR, Kennedy JE (1977) Thermochemical estimation of explosive energy output. *Combustion and Flame* 28: 45–59
- Hobbs ML, Baer MR, McGee BC (1999) JCZS: An intermolecular potential database for performing accurate detonation and expansion calculations. *Propellants, Explosives, Pyrotechnics* 24:269–279
- Jeremić R, Bogdanov J (2012) Development of a new model for the calculation of the detonation parameters of high explosives. *J Serb Chem Soc* 77(3):371–380
- Kamlet MJ, Jacobs SJ (1968) Chemistry of detonations I. A simple method for calculating detonation properties of C-H-N-O explosives. *J Chem Phys* 48(1):23–35
- Kazandjian L, Danel JF (2006) A discussion of the Kamlet-Jacobs formula for the detonation pressure. *Propellants, Explosives, Pyrotechnics* 31(1):20–24
- Kerley GI (1994) Equations of state for explosive detonation products: the Panda model. Sandia National Laboratories. Joint USA-Russia Energetic Material Technology Symposium Livermore, California, May 18–25
- Kerley GI (2010) EOSPro code: An Interim Report, Version. 3.00. Kerley Technical Services
- Kerley GI, Christian-Frear TL (1993) Prediction of explosive cylinder tests using equations of state from the PANDA code. Sandia National Laboratories Report No. SAND93-2131
- Keshavarz MH (2009) Prediction of detonation performance of CHNO and CHNOAl explosives through molecular structure. *J Hazard Mater* 166:1296–1301
- Keshavarz MH, Motamedshariati H, Moghayadnia R, Nazari HR, Azarniamehraban J (2009) A new computer code to evaluate detonation performance of high explosives and their thermochemical properties, part I. *J Hazard Mater* 172(2–3):1218–1228
- Keshavarz MH, Zamani A (2015) A simple and reliable method for predicting the detonation velocity of CHNOFCl and aluminized explosives. *Cent Eur J Energ Mater* 12(1):13–33
- Kozyrev NV (2015) Reparametrization of the BKW equation of state for CHNO explosives which release no condensed carbon upon detonation. *Cent Eur J Energ Mater* 12(4):651–669
- Liang Z, Chang W, Li B (2012) Bayesian flood frequency analysis in the light of model and parameter uncertainties. *Stoch Environ Res Risk Assess* 26(5):721–30
- Liu D, Guo S, Wang Z, Liu P, Yu X, Zhao Q, Zou H (2018) Statistics for sample splitting for the calibration and validation of hydrological models. *Stoch Environ Res Risk Assess*. <https://doi.org/10.1007/s00477-018-1539-8>
- Mader CL (2008) Numerical modeling of explosives and propellants. Third Edition, CRC Press

- McGee BC, Hobbs ML, Baer MR (1998) Exponential 6 parameterization for the JCZ3-EOS. Sandia National Laboratories, Albuquerque, New Mexico, SANDIA REPORT SAND98-1191
- Newville M, Stensitzki T, Allen DB, Ingargiola A (2014) LMFIT: Non-linear least-square minimization and curve-fitting for Python [Data set]. Zenodo. <http://doi.org/10.5281/zenodo.11813/>. Accessed 12/01/2015
- Pepekin VI, Gubin SA (2003) Methods of calculating the detonation parameters of explosives. *Khimicheskaya fizika*, 22(9):72–97 [in Russian]
- Pepekin VI, Matyushin Yu N, Gubina TV (2011) Enthalpy of formation and explosive properties of 5,6-(3,4-Furazano)-1,2,3,4-Tetrazine-1,3-Dioxide. *Russ J Phys Chem B* 5(1):97–100
- Politzer P, Murray JS (2014) The role of product composition in determining detonation velocity and detonation pressure. *Cent Eur J Energ Mater* 11(4):459-474
- Salloum M, Gharagozloo PE (2014) Empirical and physics-based mathematical models of uranium hydride decomposition kinetics with quantified uncertainty. *Chemical Engineering Science*, 116:452–464
- Shekhar H (2012) Studies on empirical approaches for estimation of detonation velocity of high explosives. *Cent Eur J Energ Mater* 9(1):39-48
- Tian Y, Booij MJ, Xu YP (2014) Uncertainty in high and low flows due to model structure and parameter errors. *Stoch Environ Res Risk Assess* 28(2):319-32
- Urizar MJ, James E Jr, Smith LC (1961) Detonation velocity of pressed TNT. *Phys Fluids* 4(2):262-274
- Victorov SB, El-Rabii H, Gubin SA, Maklashova IV, Bogdanova YA (2010) An accurate equation of state model for thermodynamic calculation of chemically reactive carbon-containing systems. *J Energ Mater* 28:35–49
- Xiong W (1985) A simple method for calculating detonation parameters of explosives. *J Energ Mater* 3(4):263-277

Acknowledgement is given to: Stochastic Environmental Research and Risk Assessment, **Springer**,

<https://link.springer.com/article/10.1007/s00477-018-1589-y#citeas>

*Bastante, F.G., Alonso, E., Araújo, M. et al. Analysis of the goodness of empirical approaches in predicting explosive detonation parameters. Stoch Environ Res Risk Assess 32, 2605–2618 (2018). <https://doi.org/10.1007/s00477-018-1589-y>*

## TABLES

**Table 1** Indicators of experimental uncertainty in detonation velocity and pressure ( $\rho_o > 1 \text{ g/cm}^3$ )

Detonation Velocity, $D$		MRR	RMSR
TNT [42 data]	$D$ vs $D_{\text{oe}}$	0.1 %	0.8 %
PETN [45 data]	$D$ vs $D_e$	-0.2 %	0.5 %
RDX [31 data]	$D$ vs $D_e$	0.6 %	1.4 %
RR RANGE [ $\Sigma$ data]		[-2.1 % +4.1 %]	
Detonation Pressure, $P$		MRR	RMSR
TNT [27 data]	$P$ vs $P_R$	0.1 %	5.4 %
PETN [44 data]	$P$ vs $P_R$	0.0 %	2.9 %
RDX [29 data]	$P$ vs $P_R$	0.1 %	3.7 %
RR RANGE [ $\Sigma$ data]		[-10.3 % +12.5%]	

**Table 2** RMSR for detonation velocity and pressure obtained from applying different EoS

[ $D$ ] [ $P$ ] Reference / ( $D$ - $P$ ) Sample size	BKWC		BKWR		BKWS		JCZS		BKW		BKWRR
	$D\%$	$P\%$	$D\%$	$P\%$	$D\%$	$P\%$	$D\%$	$P\%$	$D\%$	$P\%$	$D\%$
[ <sup>a</sup> ] [ <sup>b</sup> ] / (68 - 61)	2.6	-	3.7	11.3	4.2	7.8	-	-	-	-	-
[ <sup>c</sup> ] [ <sup>c</sup> ] / (111-67)	3.0	7.6	-	-	5.1	10.5	2.3	8.2	-	-	-
[ <sup>d</sup> ] [ <sup>d</sup> ] / (74 - 74)	-	-	-	-	-	-	-	-	2.9*	8.6*	-
[ <sup>e</sup> ] / (60 <sup>f</sup> -)	-	-	3*/2.4**	-	-	-	-	-	-	-	0.1*/1.6**

<sup>a</sup> Fried and Souers (1996); <sup>b</sup> Keshavarz (2009); <sup>c</sup> McGee et al. (1998); <sup>d</sup> Jeremić and Bogdanov (2012); <sup>e</sup> Gubin et al. (1987); <sup>f</sup> 60 individual CHNO explosives with densities close to maximum values; \* MRR \*\*Standard deviation

**Table 3** Detonation products, pressure and velocity for PETN for different models ( $\rho_o = 1.76 \text{ g/cm}^3$ )

Hierarchy	mol/mol <sub>PETN</sub>								$P$ (GPa)	$D$ (m/s)
	H <sub>2</sub> O	CO <sub>2</sub>	CO	CH <sub>4</sub>	H <sub>2</sub>	C	O <sub>2</sub>	N <sub>2</sub>		
J <sub>KJ</sub>	4.00	4.00	0.00	0.00	0.00	1.00	0.00	2	32.8	8659
J <sub>KW</sub>	4.00	3.00	2.00	0.00	0.00	0.00	0.00	2	<sup>a</sup> 33.1	<sup>a</sup> 8485
J <sub>SR</sub>	4.00	3.33	1.33	0.00	0.00	0.33	0.00	2	<sup>a</sup> 32.9	<sup>a</sup> 8464
J <sub>XI</sub>	3.44	4.00	0.56	0.28	0.00	0.16	0.00	2	34.0	8544
J <sub>JB</sub>	3.73	3.22	1.78	0.00	0.27	0.00	0.03	2	30.5	8407

<sup>a</sup>from Eqs. 3-4

**Table 4** Statistics resulting from applying the different models to the PRT database

Hierarchy	$D$ (MRR%/RMSR%)			$P$ (MRR%/RMSR%)			MRR%/RMSR% [ $\Sigma$ data]	
	PETN	RDX	TNT	PETN	RDX	TNT	$D$	$P$
J <sub>KJ</sub>	5.3/5.5	<b>0.8/1.6</b>	<b>-0.2/0.9</b>	7.6/12	3.6/6.1	7.3/11.8	2.3/3.6	6.5/10.7
J <sub>KW</sub>	2.2/2.4	-2.3/2.8	2.3/2.6	5.3/8.1	2.5/5.2	5.4/8.8	1.2/2.5	4.6/7.6
J <sub>SR</sub>	2.0/2.1	-2.5/2.9	3.6/3.8	4.5/7.6	1.9/4.9	9.4/12.0	1.4/3.0	5.1/8.4
J <sub>XI</sub>	3.9/4.1	<b>0.0/1.3</b>	<b>-0.2/0.9</b>	10.5/14.1	4.4/6.3	7.0/12.1	1.5/2.7	8.0/11.9
J <sub>JB</sub>	1.8/2.0	-1.3/1.8	<b>0.0/0.9</b>	0.0/8.6	<b>0.5/4.8</b>	-4.8/9.4	<b>0.4/1.6</b>	-1.1/8.0

**Table 5** Statistics resulting from applying the different models to the MHB database

<b>Hierarchy</b>	<b>D</b>		<b>P</b>	
	<b>MRR%/RMSR%</b>	<b>% ( RR &lt;4%)</b>	<b>MRR%/RMSR%</b>	<b>% ( RR &lt;12%)</b>
J <sub>KJ</sub>	<b>0.2/2.6</b>	86	<b>0.7/6.6</b>	<b>91</b>
J <sub>KW</sub>	-0.1/3.3	83	<b>1.2/5.9</b>	<b>94</b>
J <sub>XI</sub>	<b>0.4/2.1</b>	<b>94</b>	<b>2.1/6.6</b>	<b>92</b>
J <sub>JB</sub>	-1.5/3.3	84	-7.2/10.3	77
BKWS	1.2/3.7	78	-2.3/8.3	<b>91</b>
BKWC	<b>-0.1/2.3</b>	<b>92</b>	-/-	-
JCZS	<b>-0.3/2.3</b>	<b>92</b>	<b>-4.2/7.6</b>	88

**Table 6** Composition and oxygen balance for explosives in the TW database

<b>Composition</b>	<b>Range (weight %)</b>
[C]	6 / 46
[H]	0 / 7
[N]	13 / 59
[O]	24 / 65
[Cl+F+P]	0/6
Oxygen balance	-100 /+49

**Table 7** Statistics resulting from applying the different models to the TW database

<b>Hierarchy</b>	<b>D</b>		<b>P</b>	
	<b>MRR%/RMSR%</b>	<b>% ( RR &lt;4%)</b>	<b>MRR%/RMSR%</b>	<b>% ( RR &lt;12%)</b>
J <sub>KJ</sub>	1.1/3.0	81	2.0/7.5	88
J <sub>KW</sub>	0.4/3.0	86	2.3/7.5	88
J <sub>XI</sub>	0.9/2.3	92	3.7/7.3	89
J <sub>XB</sub>	-0.2/2.1	95	0.8/5.4	97

## Figure captions

**Fig. 1** Detonation velocity and pressure vs explosive density

**Fig. 2** Detonation velocity: residuals vs density (left) and residuals vs oxygen balance (right) [MHB database]

**Fig. 3** Detonation pressure: residuals vs density (left) and residuals vs oxygen balance (right) [MHB database]

**Fig. 4** Detonation velocity: residuals vs density (left) and residuals vs oxygen balance (right) [TW database]

**Fig. 5** Detonation pressure: residuals vs density (left) and residuals vs oxygen balance (right) [TW database]

**Fig. 6** Confidence regions for the adjustable parameters A, B [TW database]

**Fig. 7** Cumulative distribution functions for the absolute value of the velocity ( $D$ ) and pressure ( $P$ ) residuals



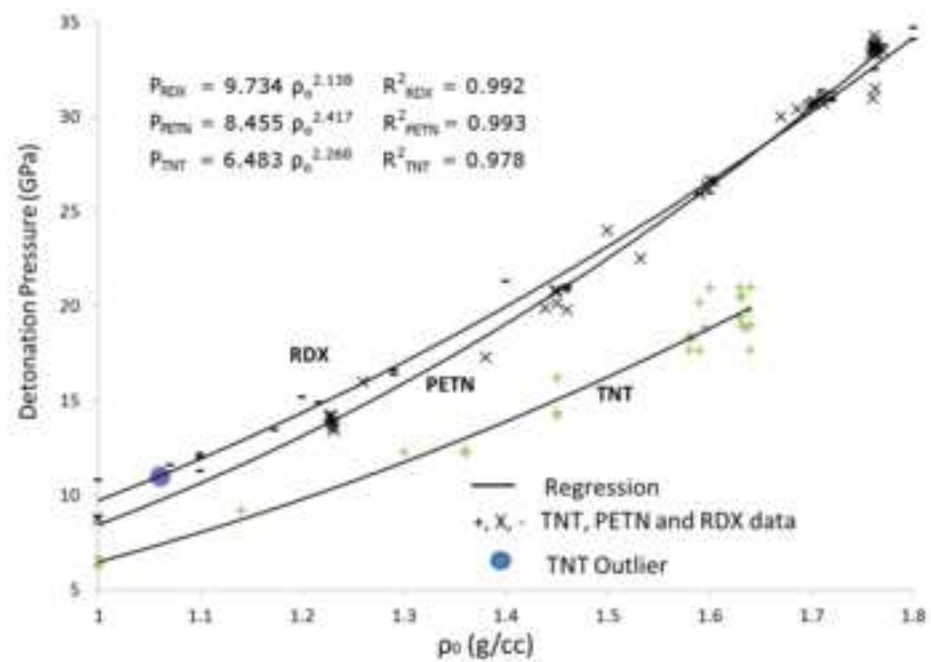
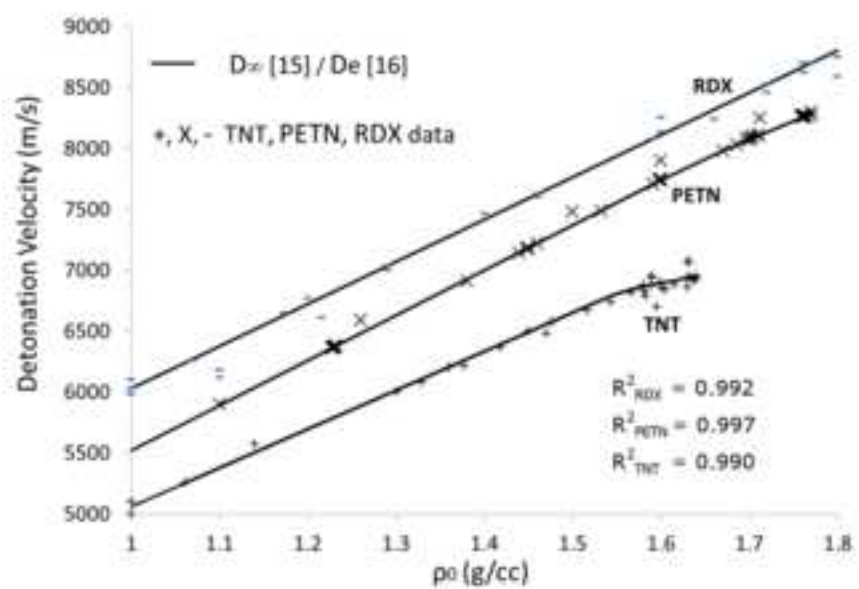


figure 2

